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Influence of different spacers on the mesomorphic properties of 4-biphenyl derivatives within the F-alkylated series

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In order to determine the influence of modification of the shape of the connector, within the fluorinated series, on the formation of mesophases in low molecular mass compounds, we decided to examine the mesomorphic behaviour of molecules which consist of a 4-biphenyl unit linked to a fluorinated tail via different spacers. The synthesis and the physical properties of these new materials are reported. The mesomorphic properties were characterized by polarized light microscopy and by differential thermal analysis, thereby showing the peculiar contribution of each of the spacers. The data collected from the 4-biphenyl derivatives synthesized allow us not only to confirm the enhancement of the smectic properties owing to the fluorinated alkyl chains, but also to display the impact of the spacer on these properties. Actually, some spacers like the amide or thioether type, as well as that of the hemithioacetal derivatives give suppression of the smectic character. Some others like that in the esters with an OC(O) spacer lead to mesophase or a short range SmA phase, and others give rise to broad enantiotropic behaviour like that of the esters with a C(O)O spacer, and of the ether or thioester types. These last mentioned give mesomorphic behaviour over a wide temperature range.

1. Introduction

In the literature, within the hydrocarbon series, the 4-biphenyl derivatives generally show no liquid crystalline behaviour, whatever the spacer used to link the hydrocarbon moiety to the biphenyl unit [1]. However, in previous work in this laboratory, we observed interesting smectic behaviour for *N*-(2-F-alkyl)-1-(4-biphenyl)-methanimines [2, 3]. Actually, these compounds show a polymorphic behaviour over a wide temperature range, whereas their hydrocarbon homologous are not liquid crystalline. These results allowed us to think that the perfluorinated chain strongly promotes liquid crystalline character and more particularly the enhancement of smectic phases. Furthermore, the fact that there is no chemical function between the rings to generate potentially undesirable effects on the mesomorphic behaviour (irreversibility, thermal or chemical instability [4, 5]) makes the 4-substituted biphenyl derivatives of great interest.

As part of our interest in studying the effect of a semiperfluorinated tail on the mesomorphic properties of low molecular mass liquid crystal materials, and in order to determine the influence of the spacer on the stability of the smectic behaviour, some 4-biphenyl derivatives were prepared and their mesomorphic properties determined. The structures studied in this work can be represented generally by that at the top of figure 1. In this study, the mesogenic group is constant and derived from 4-substituted biphenyl. The substances synthesized differ only in the spacer linking the fluorinated tail to the rigid core. The mesomorphic behaviour of all the compounds has been studied by differential thermal analysis and polarized light microscopy. The influence of the perfluoroalkylated tail and the impact of the spacer linking this chain to the biphenyl unit on these properties will be discussed.

2. Discussion of syntheses

The compounds synthesized could be described as four families according to the nature of the spacer linking the 2-F-alkylethyl chain to the mesogenic core.

The amide derivatives will be denoted **AI-*n*** for the monosubstituted amides and **AII-*np*** for the disubstituted amides (where ***n*** represents the number of carbons in the perfluorinated tail and ***p*** the number of carbons in the hydrocarbon chain). These amide compounds were synthesized from 4-biphenyl carbonyl chloride and the corresponding amines using pyridine, in dry chloroform, at room temperature. The **AI-*n*** amides were obtained from F-alkylated primary amines [6] and the **AII-*n,p*** from secondary bisegmented amines, i.e. having both a

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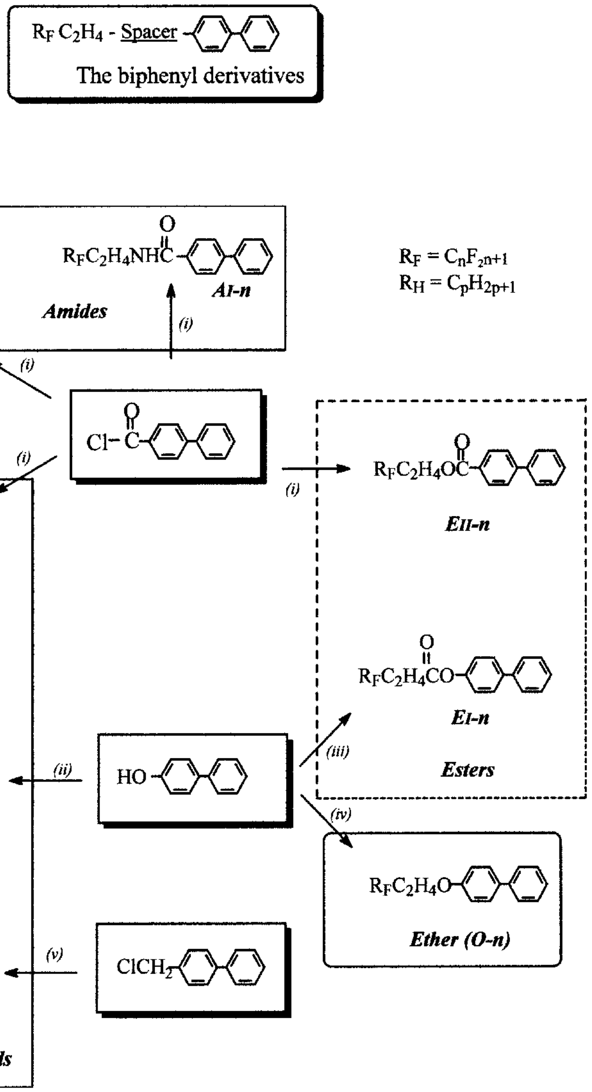


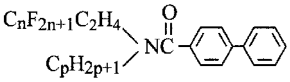
Reagents and conditions: (i) 2-F-alkylethyl compounds with a labile hydrogen, $CHCl_3$, py., room temp. (ii) $R_FC_2H_4SCH_2Br$, K_2CO_3, acetone, reflux (iii) $R_FC_2H_4C(O)Cl$, THF, py., reflux (iv) $R_FC_2H_4OH$, DEAD, TPP, THF, room temp. (v) $R_FC_2H_4SH$, EtONa, EtOH, 70°C.

Figure 1. Synthetic routes to the biphenyl derivatives.

perfluoroalkylated moiety and a hydrocarbon tail [7]. The physical properties and the phase behaviour of compounds **AI-*n*** and **AII-*n*,*p*** are listed in table 1.

The ether derivatives will be denoted **O-*n***. The Williamson reaction [8], which involves a nucleophilic substitution of a halide by an alcohol in a basic media, is still the best general method for the preparation of unsymmetrical ethers. Unfortunately, this method could not be used with the 2-F-alkylethyl iodides due to the formation of the by-product, i.e. the 2-F-alkylethene ($R_F CH{=}CH_2$) obtained in the case where the nucleophilic agents are strong bases [9, 10]. This behaviour seems to be due to the inductive effect of the perfluorinated tail, because increasing the number of methylene units leads to an increasing rate of substitution while the percentage of the elimination by-product decreases [11]. The reaction used to obtain the ethers was the Mitsunobu reaction [12], which involves reaction between an alcohol and an acidic component, by the use of diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP). Generally, speaking the condensation of alcohols with acids by the use of organic reagents such as cardodiimides involves initial activation of the latter components. Thus relatively strong acids such as phosphoric or carboxylic acids only can be utilized as the acidic components. On the other hand, with the diethyl azodicarboxylate/triphenylphosphine system, alcohols are initially activated by the formation of alkoxyphosphonium salts which subsequently alkylate acidic components. This reaction proceeds under mild

Table 1. Physical data for the amide derivatives (**AI-*n*** and **AII-*n*,*p***).



Compound	*n*	*p*	Yield/%	B.p/°C/mb	Transition temperatures/°C				
					Cr		SmA		I
AI-4.0	4	0	77%	—	•	153	—		•
AI-6.0	6	0	75%	—	•	175	—		•
AI-8.0	8	0	78%	—	•	205	—		•
AII-4.4	4	4	72%	$140/8.10^{-3}$			—		•
AII-6.1	6	1	65%	—	•	87	•	90	•
AII-6.2	6	2	67%	—	•	88	—		•
AII-6.3	6	3	63%	—	•	82	—		•
AII-6.12	6	12	68%	—	•	19	—		•

neutral conditions (room temperature or below) and exhibits stereospecificity, functional selectivity, and regioselectivity. Bittner and Assaf [13] and Manhas *et al.* [14] have independently reported the formation of alkyl aryl ethers from phenols and alcohols using the diethyl azodicarboxylate/triphenylphosphine reaction.

Thus, the preparation of the required ethers was based on the alkylation of the 4-phenylphenol by the 2-F-alkylethanols using the diethyl azodicarboxylate/triphenylphosphine system. The reaction proceeds in 12 hours at room temperature in dry tetrahydrofurane. The yields obtained were relatively low but this reaction allowed us to isolate and characterize the F-butyl (**O-4**) and the F-hexyl (**O-6**) derivatives. Yields and transition temperatures of these ethers are given in table 2.

The synthesis and mesomorphic properties of the sulphur-containing compounds have been reported previously [15]. They will be denoted **SI-*n*** for the compounds with a thioester spacer [SC(O)], **SII-*n*** for the hemithioacetal derivatives [SCH_2O] and **SIII-*n*** for the thioether compounds [SCH_2], where ***n*** represents the number of fluoromethylene units. The transition temperatures on heating are summarized in figure 2.

The synthesis and mesomorphic properties of the **EI-*n*** ester derivatives [with the spacer C(O)O] are described elsewhere [16]; their transition temperatures on heating are collected in figure 2. The preparation of the **EII-*n*** ester compounds [with the spacer OC(O)] involved the alkylation of 4-biphenyl carbonyl chloride with 2-F-alkylethanols using pyridine in dry chloroform at room temperature. The yields obtained and the mesomorphic behaviour of these last esters are summarized in table 3.

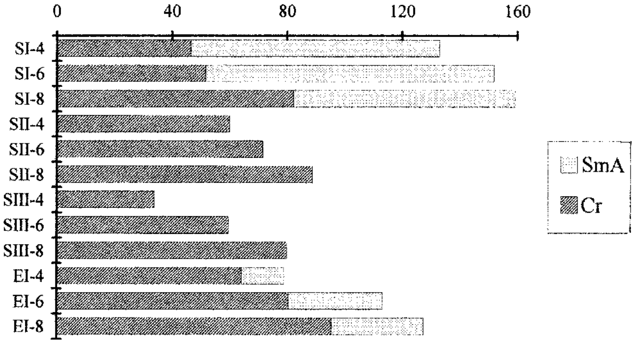
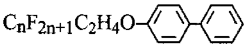


Figure 2. Transition temperatures observed on heating for the sulphur-containing compounds **SI-*n***, **SII-*n***, **SIII-*n*** and the ester derivatives **EI-*n***.

3. Mesomorphic properties

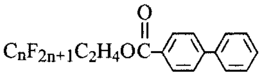
Within the amide series, the monosubstituted amides (**AI-*n***) showed no liquid crystalline behaviour. During the DSC studies, the transitions that were observed before the isotropization temperature occurred only

Table 2. Physical data for the ether derivatives (**O-*n***).

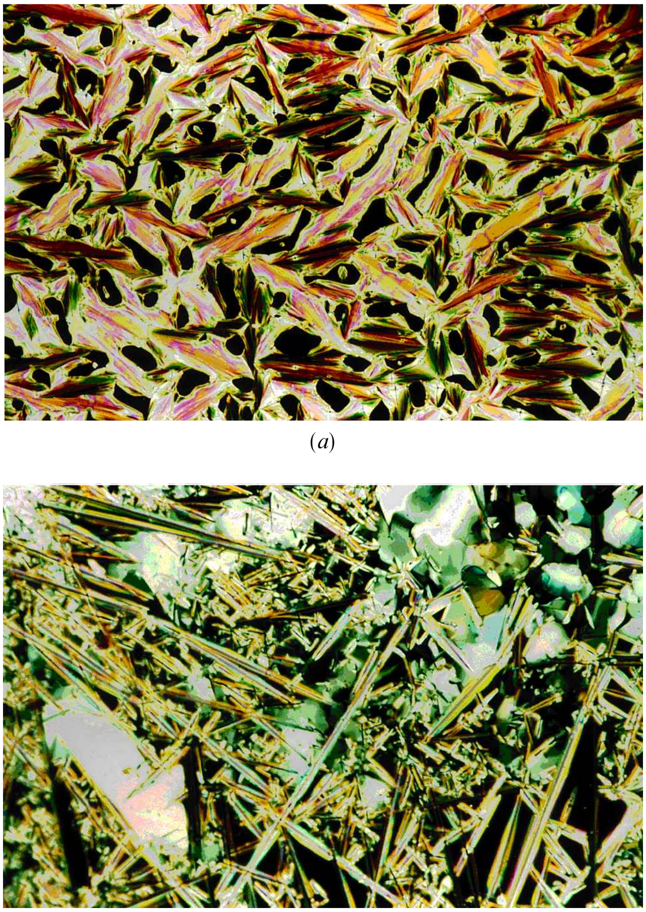


Compound	R_F	Yield/%	Transition temperatures/°C						
			Cr		E		SmA		I
O-4	C_4F_9	10	•	61.1	•		—	76.6	•
O-6	C_6F_{13}	10	•	81.4	•	96.1	•	105.5	•

Table 3. Yields and transition temperatures for the ester derivatives (**EII-*n***).



Compound	R_F	Yield/%	Transition temperatures/°C				
			Cr		SmA		I
EII-4	C_4F_9	81	•	59.3			•
EII-6	C_6F_{13}	79	•	70.5	•	72.0	•
EII-8	C_8F_{17}	82	•	51.7			•



(*a*)

(*b*)

Figure 3. Optical polarizing micrograph (× 33) displayed on cooling from the isotropic melt by: (*a*) **AII-6,1**, $T = 73.2$°C (SmA); (*b*) **O-4**, $T = 81.8$°C (crystal E).

during the first thermal cycle, showing that they are probably related to solid–solid transitions. It is worth noting that the presence of hydrogen bonds is often good for the appearance of liquid crystalline phases [17–19]. In our case, however, it seems that the hydrogen bonds increase the crystal stability of the system, giving high melting temperatures (153°C for the F-butyl derivative to 205°C for the F-octyl compound), and contribute to masking the liquid crystal character. The introduction of a hydrocarbon chain for the hydrogen, to give the disubstituted amides **AII-*n*,*p*** leads to decreases in the melting temperatures (melting point of 175°C for the compound **AI-6** compared with 87°C for the **AII-6.1** derivative). Within the disubstituted series **AII-*n*,*p***, we observe that lengthening of the hydrocarbon tail leads to decrease in the melting temperatures which range from 90 to 19°C for a value of the perfluorinated chain equal to F-hexyl.

On cooling from the isotropic phase, birefringence of **AII-6.1** was detected at 78°C by the growth of bâtonnets; on further cooling, the characteristic focal-conic texture was recognized, see figure 3(*a*). Rods and fan-shaped textures are characteristic of the layer structures of smectic mesophases [20]. Miscibility studies carried out with standard materials show that this phase is a smectic A phase. This smectic phase can be supercooled to about 67°C. On the other hand, for the other mixed amides of the series (**AII-6.2**, **AII-6.3**, …, **AII-6.12**) the melting temperatures decrease with lengthening of the hydrocarbon chain, but we observe total suppression of the smectogenic character. These results have something in common with those observed for homologous structures in our previous work [21].

Within the ether series, the optical microscopic observations and DSC measurements clearly showed smectic character for the two compounds involved. Slow cooling of the **O-4** derivative results in the growth of birefringent lancet-like domains observed below 90°C see figure 3(*b*). This texture characterizes a smectic E phase growing directly from the isotropic liquid, and this was confirmed by miscibility studies. The lancet texture is stable down to room temperature whereupon recrystallization takes place.

On the DSC thermogram of compound **O-6** [figure 4(*a*), see also table 2], the polymorphism (Cr–E–SmA–I) was evidenced on heating by a broad endotherm between 76.3 and 90.4°C corresponding to a crystal–liquid crystal transition, and a second liquid crystalline mesophase is evidenced by a well-defined transition at 96.1°C. Finally, the liquid crystal–isotropic transition occurs at 105.5°C. On cooling, these transitions were detected by three exotherms at 104.3, 92.1 and 55.5°C.

Within the group of sulphur-containing compounds, previous work led us to observe a smectic A behaviour for the thioester derivatives over about 100°C for each compound. On the other hand, the thioether as well as the hemithioacetal derivatives have only crystal–isotropic transitions with no evidence of mesomorphism. It seems that the potential reduction of the carbonyl group within the thioester series to give the homologous thioether induces a total suppression of the liquid

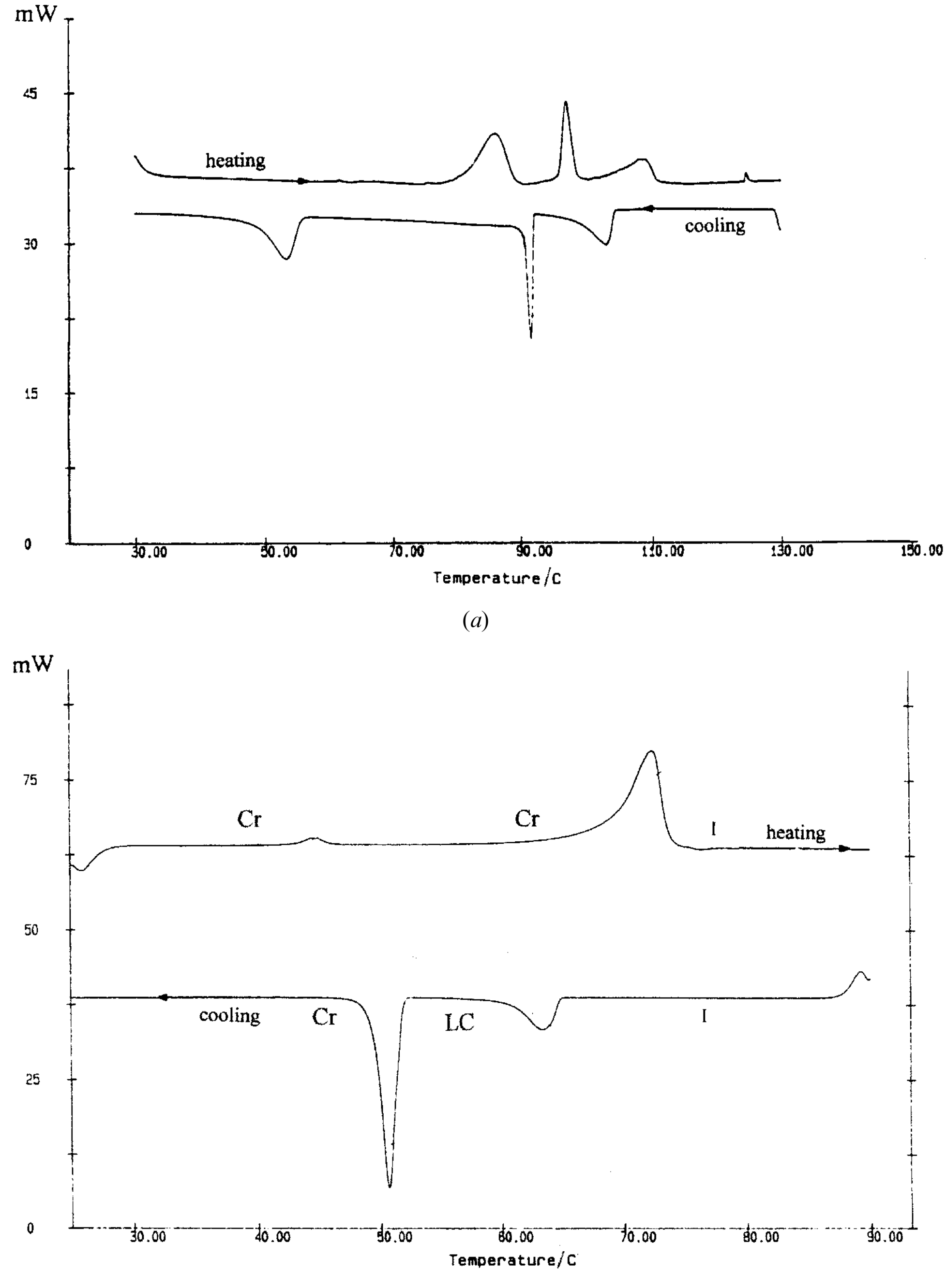


Figure 4. DSC curves for compounds (*a*) **O-6** and (*b*) **EII-6**.

crystalline properties. The same behaviour has been seen when an oxygen atom is 'introduced' close to the rigid core to give the hemithioacetal structure.

Within the ester series **EII-*n***, the studies carried out by polarized light microscopy, lead us to note that, on heating and only for the compound **EII-6**, an unstable liquid crystalline phase exists over a very short temperature range (about 2°C). Unfortunately, the DSC studies carried out at a heating rate of 10°C min^{-1} do not allow us to confirm these previous observations. However, at a lower scanning rate of 1°C min^{-1} we observe a splitting of the peak recorded at a scanning rate of 10°C min^{-1} and so confirm the presence of the SmA phase. Actually, the DSC thermogram of **EII-6** [see figure 4(*b*)] shows, on heating, a transition at 43.1°C and a broad endotherm between 61.0 and 75.3°C corresponding to the overall melting transition. On cooling, a liquid–liquid crystal transition was shown by an exotherm at 64.8°C and the liquid crystal–crystal transition was detected by an exotherm at 51.7°C. The transition occurring at 43.1°C on heating corresponds to a crystal–crystal transition and this has not been investigated in detail.

4. Comparison of the mesomorphic properties

The liquid crystal transition temperatures of a series of biphenyl derivatives differing only in the nature of the spacer linking the fluorinated moiety (equal to six fluoromethylene units) to the rigid core are collated in table 4. Inspection of the transition temperatures listed shows a direct correlation between the nature of the spacer linking the perfluorinated tail to the rigid core and mesophase range.

When we compare the esters **EI** and **EII** which differ only by the position of the carbonyl group, we see that the spacer can greatly alter the mesomorphic properties. Indeed, when the carbonyl group is next to the mesogenic core (i.e. ester of the **EII** type), we observe only a 2° phase range, whereas when it is on the other side of the oxygen we observe an enantiotropic behaviour over a wide range of temperature and to a much higher isotropization temperature. On the other hand, the total removal of the carbonyl group, to give the homologous ether derivatives, leads to enantiotropic polymorphism (a second smectic type phase is observed), and isotropization occurs at an intermediate value (see figure 5), but closer to that of **EII-6**.

In the same way, if we compare the properties of the compounds **AI-6** [amide spacer NHC(O)], **EII-6** [ester spacer OC(O)], and **SI-6** [thioester spacer SC(O)], we observe that the nitrogen atom causes total suppression of the liquid crystalline behaviour (probably due to hydrogen bonding which increases the melting temperature).

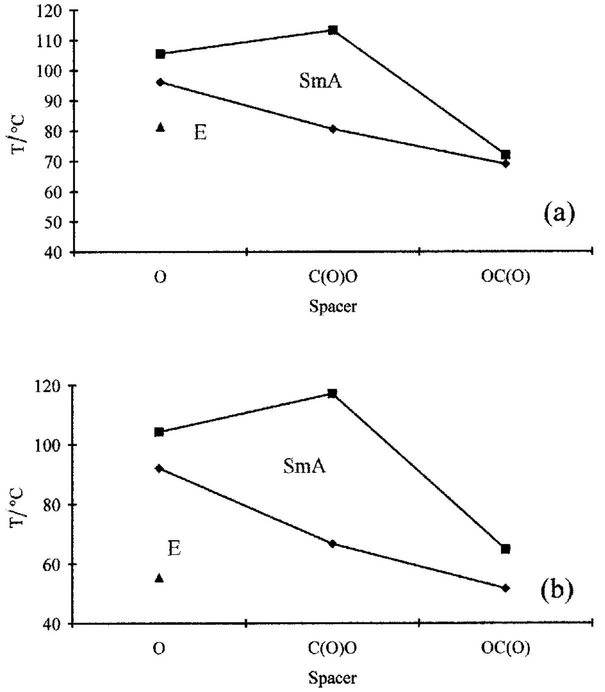


Figure 5. Comparison of the mesomorphic properties on heating (*a*) and on cooling (*b*) for the compounds **O-6** (ether), **EI-6** [ester C(O)O] and **EII-6** [ester OC(O)].

The ester derivative shows a smectic phase over only about 2°C whereas the thioester compound exhibits an enantiotropic behaviour over more than 100°C (see figure 6) with a much higher SmA–I transition at 152°C.

5. Experimental

5.1. *Techniques*

The initial phase assignments and corresponding transition temperatures were determined with an Olympus BH-2 polarizing microscope equipped with

Table 4. Transition temperatures observed for the F-hexyl derivatives in relation to the spacer shape: enthalpies of transition ($kJ\ mol^{-1}$) in square brackets.

$C_6F_{13}C_2H_4$ – *Spacer* –

Compound	Spacer	Transition temperatures/°C						
		Cr		E		SmA		I
A-6.0	NHC(O)	•	175					•
A-6.1[a]	N(CH_3)C(O)	•	87			•	90	•
EI-6	C(O)O	•	80.5 [32.6]			•	113.2 [11.8]	•
EII-6[a]	OC(O)	•	70.5			•	72.0	•
SI-6	SC(O)	•	51.6 [27.6]			•	152.0 [14.7]	•
SII-6	SCH_2O	•	71.6 [40.4]					•
SIII-6	SCH_2	•	59.7 [53.1]					•
O-6	O	•	81.4 [21.7]	•	96.1 [10.5]	•	105.5 [9.5]	•

[a] Transitions observed from optical microscopy.

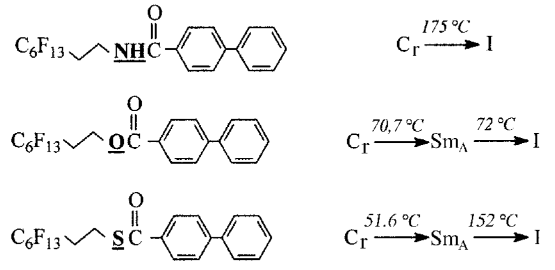


Figure 6. Comparison of the mesomorphic properties on heating and on cooling for the compounds **AI-6** (amide), **EII-6** [ester OC(O)] and **SI-6** (thioester).

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 Bruker AC 200 MHz spectrometer. All spectra were recorded using $CDCl_3$ as solvent with TMS as internal reference for ^1H NMR and $CFCl_3$ for ^{19}F NMR. The purity of the compounds was determined by thin layer chromatography (TLC), gas chromatography (GC) and DTA analysis.

5.2. *Materials*

4-Biphenylcarbonyl chloride, 4-phenylphenol, triphenylphosphine and diethyl azodicarboxylate were purchased from Aldrich and used without further purification. The syntheses of the perfluorinated compounds such as 2-F-alkylethylamine [6] and *N*-alkyl-*N*-2-F-alkylethylamine [7] are described elsewhere. Unless specified as dry, the solvents were of unpurified reagent grade.

5.3. *Synthesis*

5.3.1. *N-(2-F-alkylethyl)-4-(4-phenyl)phenylcarboxamide (**AI-n**) and N-(2-F-alkylethyl)-N-alkyl-4-(4-phenyl)phenylcarboxamide (**AII-n,p**)*

A solution of 5×10^{-3} mol of 4-biphenylcarbonyl chloride in anhydrous chloroform (5 ml) was added dropwise to a mixture of 6×10^{-3} mol of *N*-alkyl-*N*-2-F-alkylethylamine and 5×10^{-3} mol of freshly distilled pyridine in anhydrous chloroform (10 ml) under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature and monitored by thin layer chromatography until removal of the carbonyl chloride (2–12 h). The solvent was then removed in vacuum and the crude product diluted with diethyl ether, filtered to remove insoluble material which was washed several times with ether. The combined ethereal solutions were washed with acidic water (pH 5), dried (Na_2SO_4), filtered and evaporated. The crude product was purified by column chromatography on silica gel using chloroform as eluent.

A-6.0 (yield 75%). ^1H NMR ($CDCl_3$/TMS), δ (ppm), J (Hz); 2.62 (Tt, 2H, $C\underline{H}_2{-}R_F$, $^3J_{H\text{-}F} = 18.8$, $^3J_{H\text{-}H} = 6.6$), 3.79 (t, 2H, $R_F{-}CH_2{-}C\underline{H}_2$, $^3J_{H\text{-}H} = 6.6$), 7.42 (m, $3H_{arom.}$); 7.71 (m, $4H_{arom.}$); 7.97 (m, $2H_{arom.}$). ^{19}F NMR ($CDCl_3$/$CFCl_3$), δ (ppm); – 81.3 ($C\underline{F}_3$), – 115.2 ($C\underline{F}_2\ \alpha$), – 122.6 ($C\underline{F}_2\ \beta$), – 123.3 to – 123.8 (2 $C\underline{F}_2\ \gamma$), – 126.6 ($C\underline{F}_2\ \omega$). MS (70 eV), *m*/*z* (%): 543 (100), 210 (< 1), 181 (88.5), 169 (< 1), 153 (17.9), 131 (1), 119 (1.3), 69 (2.9).

A-4.4 (yield 72%). ^1H NMR ($CDCl_3$/TMS), δ (ppm), J (Hz); 0.87 (m, 3H, $C\underline{H}_3$), 1.21 (m, 2H $C\underline{H}_2$), 1.55 (m, 2H, $C\underline{H}_2$), 2.53 (m, 2H, $C\underline{H}_2{-}R_F$), 4.25 (m, 2H, $R_F{-}CH_2{-}C\underline{H}_2$), 3.76 (m, 2H, $R_H{-}C\underline{H}_2{-}N$), 7.42 (m, $5H_{arom.}$), 7.42 (m, $4H_{arom.}$). ^{19}F NMR ($CDCl_3$/$CFCl_3$), δ (ppm); – 81.6 ($C\underline{F}_3$), – 114.8 ($C\underline{F}_2\ \alpha$), – 124.9 ($C\underline{F}2\beta$), – 126.6 ($C\underline{F}2\omega$). MS (70 eV), *m*/*z* (%) 499 (39.2), 456 (39.1), 443 (12.7), 266 (1.4), 252 (2.4), 224 (< 1), 210 (17.9), 181 (100), 153 (24.3), 131 (< 1), 119 (< 1), 69 (1.7).

5.3.2. *2-(F-alkyl)ethyl biphenyl ether (**O-n**)*

A solution of triphenylphosphine (1×10^{-2} mol) and 2-F-alkylethanol (1×10^{-2} mol) in dry tetrahydrofuran (25 ml) was added dropwise to a stirred solution of 4-phenylphenol (1×10^{-2} mol) and diethyl azodicarboxylate (1×10^{-2} mol) in dry tetrahydrofuran (25 ml) at room temperature under a nitrogen atmosphere. The reaction mixture was then stirred for 18 h. The solvent was removed in vacuum and the crude product diluted with diethyl ether and filtered through a pad of 'Hyflosupercel'. The filtrate was then dried (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 (yield 10%).

^1H NMR ($CDCl_3$/TMS), δ (ppm), J (Hz); **O-4**, **O-6**: 2.61 (Tt, 2H, $C(C\underline{H}_2{-}R_F$, $^3J_{H\text{-}F} = 18.8$, $^3J_{H\text{-}H} = 7.4$), 4.25 (t, 2H, $C\underline{H}_2{-}O$, $^3J_{H\text{-}H} = 7.4$), 6.97 (AA′BB′, $2H_{arom.}$), 7.32 (m, $7H_{arom.}$). ^{19}F NMR ($CDCl_3$/$CFCl_3$), δ (ppm); **O-4**: – 81.6 ($C\underline{F}_3$), – 114.8 ($C\underline{F}_2\ \alpha$), – 124.9 ($C\underline{F}_2\ \beta$), – 126.6 ($C\underline{F}_{2\ \omega}$); **O-6**: – 81.3 ($C\underline{F}_3$), – 115.2 ($C\underline{F}_2\ \alpha$), – 122.6 ($C\underline{F}_2\ \beta$), – 123.3 to – 123.8 (2 $C\underline{F}_2\ \gamma$), – 126.6 ($C\underline{F}_2\ \omega$). MS (70 eV), *m*/*z* (%) exemplified for **O-6**: 516 (100), 183 (7.5), 170 (72.8), 169 (2.1), 154 (3.2), 119 (3.0), 69 (1.2).

5.3.3. *2-(F-alkyl)ethyl 4-phenylbenzoate (**EII-n**)*

A solution 5×10^{-3} mol of 4-biphenylcarbonyl chloride in anhydrous chloroform (5 ml) was added dropwise to a mixture of 6×10^{-3} mol of 2-F-alkylethanol and 5×10^{-3} mol of freshly distilled pyridine in anhydrous chloroform (10 ml) under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature and monitored by thin layer chromatography until removal of the carbonyl chloride (12 h). The solvent was then removed in vacuum and the crude product diluted with diethyl ether, filtered and the residue washed several times with ether. The combined ethereal solutions were washed with acidic water (pH 5), dried (Na_2SO_4), filtered and evaporated. The crude product was purified by column chromatography on silica gel using chloroform as eluent.

^{1}H NMR ($CDCl_3$/TMS), δ (ppm), J (Hz); **EII-4**, **EII-6**, **EII-8**: 2.61 (Tt, 2H, $CH_2–R_F$, $^3J_{H\text{-}F} = 18.8$, $^3J_{H\text{-}H} = 7.2$), 4.62 (t, 2H, CH_2–O, $^3J_{H\text{-}H} = 7.2$), 7.47 (m, $3H_{arom.}$), 7.65 (m, $4H_{arom.}$), 8.13 (m, $2H_{arom.}$). ^{19}F NMR ($CDCl_3$/$CFCl_3$), δ (ppm); **EII-4**: – 81.6 (CF_3), – 114.8 ($CF_2\,\alpha$), – 124.9 ($CF_2\,\beta$), – 126.6 ($CF_2\,\omega$); **EII-6**: – 81.3 (CF_3), – 115.2 ($CF_2\,\alpha$), – 122.6 ($CF_2\,\beta$), – 123.3 to – 123.8 (2 $CF_2\,\gamma$), – 126.6 ($CF_2\,\omega$); **EII-8**: – 81.2 (CF_3), – 114.5 ($CF_2\,\alpha$), – 122.1 ($CF_2\,\beta$), – 123.5 to – 123.9 (4 $CF_2\,\gamma$), – 126.5 ($CF_2\,\omega$). MS (70 eV), m/z (%) exemplified for **EII-8**: 644 (100), 219 (2.8), 211 (0.3), 198 (5.3), 181 (36.1), 169 (1.5), 153 (7.6), 131 (2.7), 119 (3.0), 69 (1.2).

6. Conclusion

The evaluation of the mesomorphic behaviour of these new 4-biphenyl derivatives, incorporating different spacers bonding the mesogenic core to the fluorinated tail, using polarized light microscopy and differential scanning calorimetry, allows us to point out some interesting properties and to highlight some peculiar properties for the overall structures.

Actually, some spacers like the amide or thioether types, as well as that in the hemithioacetal derivatives give total suppression of the smectic character. Some others like the OC(O) spacers in the esters **EII-*n***, lead to very short range smectic behaviour; or for the best of the esters **EI-*n*** with a C(O)O spacer, the ethers or the thioester compounds to a broad range enantiotropic SmA behaviour, in one case with an additional E phase.

The data collected from the biphenyl derivatives synthesized lead us first to confirm the enhancement of the smectic properties owing to the perfluorinated tail, but also to display the impact of the spacer on these properties. It is clear, from the above results, that the 2-F-alkylethyl chain contributes to generating the smectic phase, but equally that the nature of the unit linking this fluorinated tail to the rigid core strongly influences the occurrence and the stability of the liquid crystalline behaviour.

The chemical and thermal stability of the fluoroalkyl groups and their ability to form mesophases with different spacers give us short term prospects for the synthesis of mesogenic polymers or chiral compounds in order to obtain new liquid crystalline materials for potential applications in display devices.

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