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# Synthesis and mesomorphic properties of perfluorinated rod-like liquid crystals with sulphur-containing spacers

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In order to determine the influence of 'sulphur-containing' spacers on the formation of mesophases in low molecular mass compounds, we have examined the mesomorphic behaviour of molecules which consists of a 4-biphenyl unit linked to an unbranched fluorinated chain via a short spacer including at least a sulphur atom. The synthesis of these compounds has been carried out from 2-F-butylethyl iodide or from the 2-F-alkylethyl mercaptans in the case of the F-hexyl and F-octyl tails. The mesomorphic properties have been characterized by polarized light microscopy and by differential thermal analysis showing the peculiar contribution of each of the spacers. The influence of the fluorinated chain and the shape of the connector on the stability of the mesophases has been investigated. The compounds with a thioether or a hemithioacetal spacer showed no mesomorphic properties, whereas the structures with a thioester spacer showed a very interesting enantiotropic behaviour of the smectic A type over a wide temperature range. Furthermore from the series exhibiting liquid crystalline behaviour, increasing the number of fluoromethylene units simultaneously increases both the melting and the clearing temperature. These mesomorphic properties within the fluorinated series are compared with those of their monocatenar hydrocarbon homologues.

## 1. Introduction

Low molecular mass mesogens generally consist of a succession of three basic moieties: an aliphatic chain, a linking group (spacer) and a rigid core unit. Concerning the rigid core which represents the mesogenic moiety, polycyclic [1] and more particularly polyaromatic [2] systems are the most often used because they promote liquid crystalline mesophases. Among the polycyclic compounds, biphenyl derivatives have been extensively studied [3] because the omission from the mesogenic system of a central linking group between the rings prevents potentially undesirable chemical or photochemical stability [4]. Our interest in this work lay with the 4-biphenyl derivatives with the chemical structures shown in figure 1.

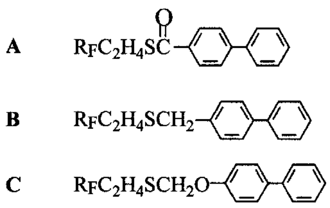

Figure 1. The three polyphilic compounds investigated.

Within the analogues hydrocarbon series, the 4-biphenyl derivatives generally showed no liquid crystalline behaviour whatever the spacer used to link the hydrocarbon moiety to the biphenyl unit [5], only one case, curiously, being reported to show nematic character [6]. On the other hand, little work has been done on the study of 4-biphenyl derivatives within the fluorinated series. The 4-perfluoroalkylbiphenyls have not shown any mesomorphic properties [7], but Guittard *et al.* observed the formation of interesting smectic phases for *N*-(2-F-alkylethyl)-1-(4-biphenyl)methanimines [8, 9]. It is worth noting that the introduction of a methyl group on the imine function suppresses the enantiotropic properties observed for the F-hexylethyl compound, leading to a monotropic behaviour in which the appearance of the mesophase is related to the scanning rate on cooling from the isotropic liquid. These results allowed us to conclude that:

(i) the perfluorinated chain can induce mesomorphic behaviour;
(ii) the chemical function linking this perfluoroalkylethyl moiety to the rigid core seems to have a great influence on the liquid crystalline properties.

The purpose of this work was to establish the effect of 'sulphur-containing' spacers on the mesomorphic

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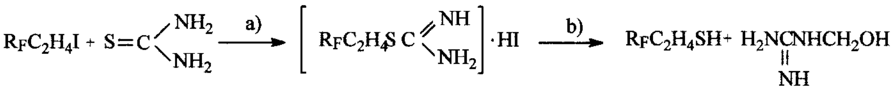


Figure 2. Procedure for the synthesis of 2-F-alkylethyl thiols.

*(a)* EtOH / $N_2$, 80°C; *(b)* $NH_2CH_2OH$, NaOH / $H_2O$

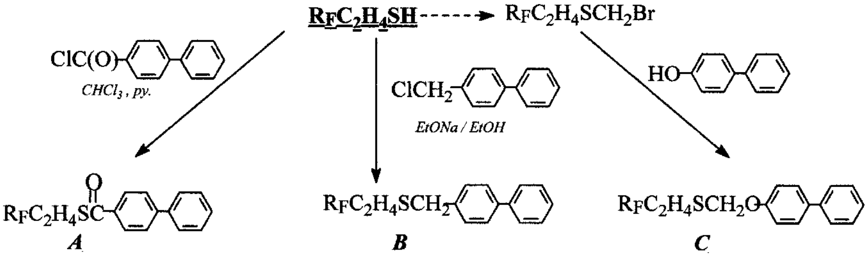


Figure 3. Reaction pathway for synthesis of derivatives **A**, **B** and **C**.

properties of low molecular mass compounds within the fluorinated series. Previous work has shown that the introduction of a sulphur atom in the form of a thioester link between the rings of the mesogenic core of certain compounds can lead to interesting mesomorphic behaviour within chiral structures [10, 11]. The spacers described in this work are of the thioester (structure **A**), thioether (structure **B**) and hemithioacetal (structure **C**) types according to figure 1. For the molecular structures showing an efficient liquid crystal behaviour, we planned to synthesize the hydrocarbon analogues and so determine the impact of the fluorinated tails on the evolution of thermotropic mesomorphism.

## 2. Discussion and syntheses

All the compounds were prepared from 2-F-alkylethanthiols [12] which were synthesized as shown in figure 2.

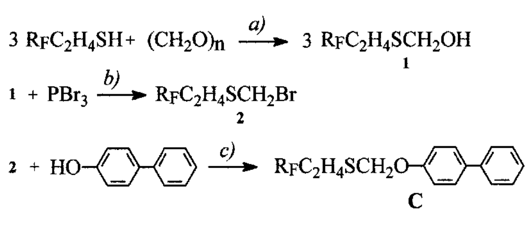
The first step involved the reaction of 2-F-alkylethyl iodides with thiourea. The thiouronium salt was then hydrolysed to give the appropriate thiol in very good yield (80 to 88%). The thiols are very good nucleophiles and enable the synthesis of different families of sulphur-containing compounds. The synthesis of the type **A** compounds involved the alkylation of 4-biphenyl carbonyl chloride with 2-F-alkylethanthiols using pyridine in dry chloroform. The reaction proceeds at room temperature and the products were obtained in good yield after purification on a silica-gel column. Preparation of the type **B** substances was realized according to the pathway shown in figure 3.

The F-alkylated thiolate ions are very good nucleophilic agents [13]; they were prepared from the corresponding 2-F-alkylethanethiols using EtONa/EtOH, under a nitrogen atmosphere. The preparation of the required mesogens involved nucleophilic attack of the thiolate ions on 4-chloromethylbiphenyl. This reaction is analogous to a Williamson-type *S*-alkylation. The synthesis of the type **C** compounds was carried out in three steps according to figure 4: the first step consisted in the formation of the hemithioacetals obtained from 2-F-alkylethanethiols by the action of polyoxymethylene with triethylamine. The addition of phosphorous tribromide gave the corresponding bromide [14] in yields of 80 to 90%.

In order to avoid the simultaneous formation of the by-product dithioacetal $(R_F C_2H_4S)_2CH_2$, the reaction was carried out at 0°C, under an inert atmosphere and in diethyl ether freshly distilled over sodium. The formation of the hemithioacetal derivatives (**C**) through reaction of the 2-F-alkylethylthiomethyl bromide with the 4-phenylphenol in the presence of potassium carbonate gave very good yields of 88 to 91%. All the compounds are colourless and chemically stable. They were purified by column chromatography and checked for purity by thin layer chromatography, mass spectrometry and elemental analysis.

## 3. Mesomorphic behaviour

The phase behaviour of these new fluorinated materials was studied by optical polarizing microscopy in combination with differential scanning calorimetry (DSC). The phase transition temperatures of compounds



(a) $NEt_3$, $N_2$, 0°C; (b) Anhydrous $Et_2O$, 0°C, $N_2$; (c) $K_2CO_3$ acetone

Figure 4. Synthetic route to the hemithioacetal derivatives.

**A**, **B** and **C** are shown in the table. The transition enthalpies (in kJ g$^{-1}$) are also listed in brackets beside the transition temperatures.

It follows from the table that only the type **A** substances (with a thioester group as spacer) were mesomorphic over a wide temperature range. Structures of type **B** and **C**, e.g. with a thioether or a hemithioacetal group as spacer, 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 supression of the liquid crystalline properties. The same behaviour has been seen when an oxygen atom was introduced close to the rigid core to give the hemithioacetal structures. It is clear from this result that the nature of the chemical function linking the perfluoroalkylethyl moiety to the rigid core, dramatically influences the thermotropic mesomorphism. The stabilization and the appearance of the mesophase are more sensitive to the nature of the connector than to the nature of the linear tail. From preceding work [15] on unsymmetrical disubstituted biphenyls incorporating two different tails (one hydrocarbon and the other fluorinated) linked through an acetamide junction, we have observed that the nature of the tail (branched or not) can in the same manner destabilize the mesomorphic liquid crystal character, but more weakly when the stuctural change is far from the mesogenic unit [16].

In figure 5 the phase diagram of the thioester series is shown where the transition temperatures on heating are plotted against the carbon number *n* of the terminal perfluoroalkylated moieties. No significant change occurs in the transition temperatures after prolonged heating above the isotropic transition. It follows from figure 5 that increasing the fluorinated chain length increases the melting temperatures as well as the clearing temperatures.

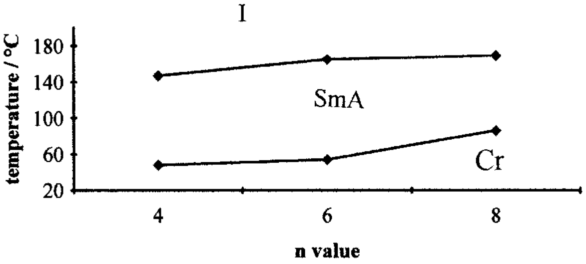


Figure 5. Phase diagram for thioesters.

Compound **A4**, which corresponds to the compound **A** with an F-butyl tail, melts at 46°C forming a smectic phase with a clearing temperature of 133°C, whereas compound **A6** melts at 52°C and the smectic phase obtained has a clearing temperature of 152°C. The F-hexyl chain increases the smectic range despite increasing both the melting and the clearing temperatures, as compared with **A4**: the mesophase exists in a range over 100°C for **A6**, whereas the range is recorded over 87°C for **A4**. With the structure incorporating a perfluoro-octyl chain, both melting and clearing temperatures increase, but the temperature range of the mesophase is smaller (77°C) in this case. By optical microscopic observation, the mesophases of all members of this series appear as bâtonnets on cooling from the isotropic melt and these 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 using standard materials [9] showed that the phases described are of the smectic A type. The characteristic textures of phases observed are illustrated in figure 6.

Non-fluorinated reference substances were synthesized to compare the influence of the fluorinated tails on the mesomorphic properties. Figure 7 illustrates the thermograms obtained from differential thermal analysis.

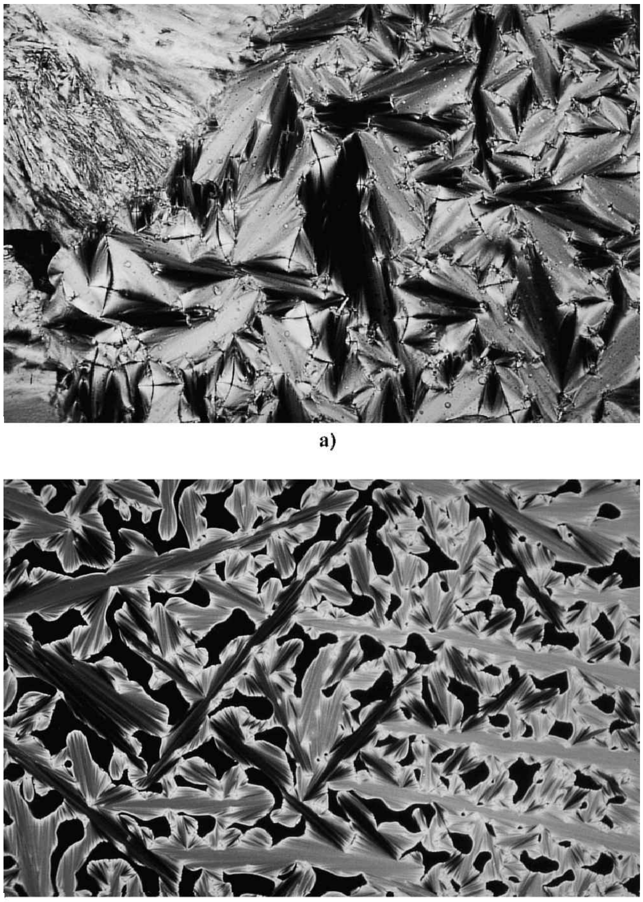
Within the hydrocarbon series, the thioester type of structure does not generate liquid crystalline behaviour. This result is not surprising when compared with many

Table 1. Phase transition temperatures and enthalpies and the yields obtained for series **A**, **B** and **C** compounds.

| | | | | Transition temperatures/°C | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | Spacer | $R_F$ | Yield/%[a] | Cr | | SmA | | I |
| **A4** | $C_2H_4SC(O)$ | $C_4F_9$ | 78 | • | 46.5 [24.9][b] | • | 133.0 [15.7] | • |
| **A6** | $C_2H_4SC(O)$ | $C_6F_{13}$ | 73 | • | 51.6 [27.6] | • | 152.0 [14.7] | • |
| **A8** | $C_2H_4SC(O)$ | $C_8F_{17}$ | 71 | • | 82.3 [25.3] | • | 159.3 [9.2] | • |
| **B4** | $C_2H_4SCH_2$ | $C_4F_9$ | 78 | • | 33.9 [41.0] | | | • |
| **B6** | $C_2H_4SCH_2$ | $C_6F_{13}$ | 77 | • | 59.7 [53.1] | | | • |
| **B8** | $C_2H_4SCH_2$ | $C_8F_{17}$ | 71 | • | 80.0 [58.3] | | | • |
| **C4** | $C_2H_4SCH_2O$ | $C_4F_9$ | 75 | • | 60.1 [43.1] | | | • |
| **C6** | $C_2H_4SCH_2O$ | $C_6F_{13}$ | 79 | • | 71.6 [40.4] | | | • |
| **C8** | $C_2H_4SCH_2O$ | $C_8F_{17}$ | 78 | • | 88.9 [47.4] | | | • |

[a] Yield from 2-F-alkylethanethiols.

[b] Figures in square brackets denote enthalpies of transition (kJ mol$^{-1}$).


a)

b)

Figure 6. Optical photomicrograph (×33) for typical thioesters on cooling from the isotropic melt: (*a*) $n=4$, $T=20.2$°C (SmA→Cr); (*b*) $n=6$, $T=158.5$°C (SmA).

other results published concerning 4-substituted biphenyls within the hydrocarbon series. Variation of the nature of the connector among the types ether [17], ester [18], thioether [19], ketone [20] and others [21], does not, according to the authors, give rise to thermotropic mesomorphism. The same behaviour has been found when the aliphatic hydrocarbon chain is directly connected to biphenyl in the 4-position [22]. It is worth noting that in most cases studied within different perfluorinated series, the introduction of fluorine atoms can directly affect the mesomorphic properties in different ways. For example, the presence of fluorinated chains can totally eliminate the liquid crystalline characteristics compared with their hydrocarbon analogues [23], can decrease the nematic or cholesteric character [24] or enhance the smectic character to the detriment of the nematic phase [25]. Conversely, a fluorinated tail with the same length as that in the hydrocarbon analogues can also generate liquid crystal behaviour when it does not occur in the hydrocarbon series [8]. In this work, within the thioester series, the hydrocarbon analogues are not mesomorphic whereas the F-alkylated series show enantiotropic smectic properties over a wide temperature range.

## 4. Experimental

### 4.1. *Techniques*

The initial phase assignments and corresponding transition temperatures were determined using an Olympus BH-2 polarizing microscope equipped with crossed polarizers and a Mettler model FP-52 hot stage. Temperatures and enthalpies of transition were investigated by DSC using a Perkin-Elmer PC series DSC7 calorimeter. The heating and cooling curves were obtained at rates of 2 and 10°C min$^{-1}$, in a nitrogen atmosphere. In all cases, during heating and cooling cycles, transition temperatures were reported at the maxima and minima of the endothermic and exothermic peaks, respectively. Zn and In were used as calibration standards. 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 for solutions in $CDCl_3$ with $CFCl_3$ for $^{19}$F NMR and TMS as internal reference for $^{1}$H NMR. $^{19}$F NMR (188 MHz) spectra for compounds with the same perfluoroalkane chain lengths were identical. For this reason we only exemplify, in the synthesis part, the structural description for one compound of each series. The purity of the compounds was determined by thin layer chromatography (TLC), gas chromatography (GC) and DTA analysis.

### 4.2. *Materials*

4-Biphenyl carbonyl chloride, 4-chloromethylbiphenyl and 4-phenylphenol were purchased from Aldrich and used without further purification. The synthesis of 2-perfluoroalkylethylthiomethyl bromide and the procedure for the preparation of 2-F-butylethyl mercaptan are described elsewhere [12–14]. Unless specified as dry, the solvents were of unpurified reagent grade.

### 4.3. *Synthesis*

#### 4.3.1. *2-(Perfluoro-n-alkyl)ethyl 4-phenylthiobenzoate (**A**)*

A solution of 4-biphenyl carbonyl chloride ($5\times10^{-3}$ mol) in anhydrous chloroform was added dropwise to a mixture of 2-F-alkylethanthiol ($6\times10^{-3}$ mol), pyridine ($5\times10^{-3}$ mol) freshly distilled, and anhydrous chloroform (5 ml). The reaction mixture was boiled and monitored by thin layer chromatography until removal of the phenol was completed (18 h). The reaction mixture was filtered and then evaporated. The residue was

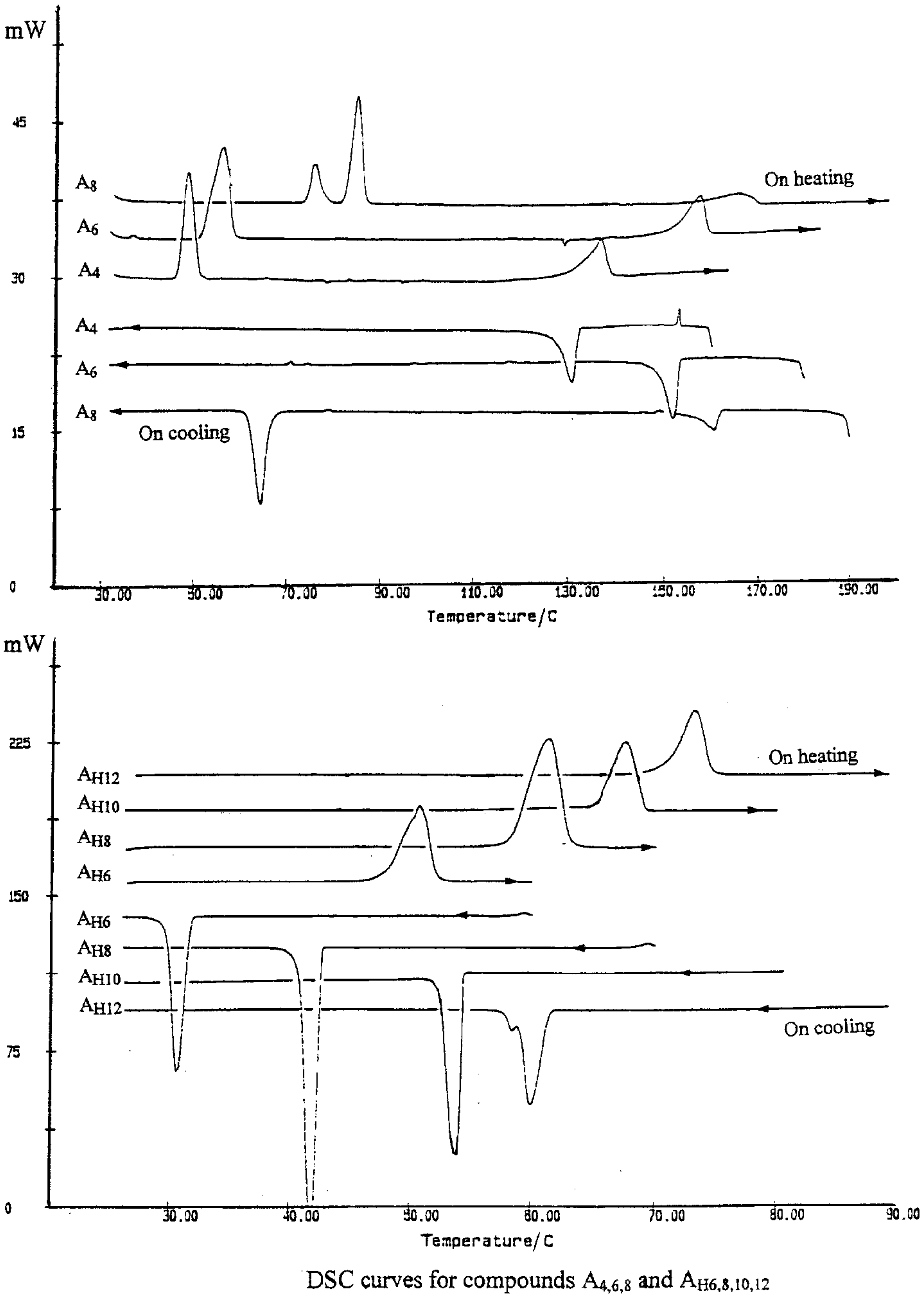


Figure 7. DSC curves for compounds **A**$_{4,6,8}$ (upper) and the hydrocarbon analogues **A**$_{H6,8,10,12}$ (lower).

recrystallized from acetonitrile to yield compound **A** (see the table).

**A**$_4$ (78% recovered yield). $^1$H NMR (CDCl$_3$/TMS) $\delta$ (ppm): 2.51 (m, 2H); 3.31 (t, 2H, $^3J = 7.8$ Hz); 7.37 to 7.52 (m, 3H); 7.59 to 7.78 (m, 4H); 8.08 (AA′BB′, 2H, $J = 8.5$ Hz). $^{19}$F NMR (CDCl$_3$): $-81.3$ ppm (m) [CF$_3$]; $-115.5$ ppm (m) [(CF$_2$)$_\alpha$]; $-124.8$ ppm (m) [(CF$_2$)$_\beta$]; $-126.4$ to $-126.6$ ppm (m) [(CF$_2$)$_\gamma$]. MS (70 eV): *m/z* 460 (0.8%) [M$^+$]; *m/z* 181 (100%); *m/z* 169 (0.7%); *m/z* 152 (33.4%); *m/z* 127 (2.8%); *m/z* 119 (1.3%) [C$_2$F$_5^+$]; *m/z* 69 (5.2%) [CF$_3^+$]. Elemental analysis: calc. for $C_{19}H_{13}F_9SO$ (460.36) C 49.57, H 2.85, F 37.14, S 6.96; found C 49.62, H 2.87, F 37.21, S 7.03%.

### 4.3.2. *2-(Perfluoro-n-alkyl)ethylthiomethyl biphenyl-4-yl ether (**B**)*

2-F-alkylethanthiol ($2 \times 10^{-3}$ mol) was added dropwise to a solution of sodium ethanolate ($2 \times 10^{-3}$ mol) in absolute ethanol (4 ml) at 0°C under an atmosphere of nitrogen. The mixture was stirred at room temperature for 10 min. Then 4-chloromethylbiphenyl ($2 \times 10^{-3}$ mol) was added in solid form to the solution and stirring continued at 70°C for 5–6 h. The product was extracted into diethyl ether and the solution washed several times with water before being dried over sodium sulphate, filtered and evaporated. The resulting colourless solid was recrystallized from acetonitrile (see the table).

**B6** (77% recovered yield). $^{1}$H NMR (CDCl$_3$/TMS) $\delta$ (ppm): 2.32 (m, 2H); 2.68 (t, 2H, $^{3}J = 8.0$ Hz); 3.79 (s, 2H); 7.32 to 7.61 (m, 9H). $^{19}$F NMR (CDCl$_3$): – 81.3 ppm (m) [CF$_3$]; – 115.2 ppm (m) [(CF$_2$)$_\alpha$]; – 122.6 ppm (m) [(CF$_2$)$_\beta$]; – 123.3 to – 123.8 ppm (m) [2(CF$_2$)$_\gamma$], – 126.6 ppm (m) [(CF$_2$)$_\omega$]. MS (70 eV): *m/z* 546 (1.9%) [M$^+$]; *m/z* 199 (1.5%); *m/z* 167 (100%); *m/z* 152 (27.8%); *m/z* 119 (0.9%) [C$_2$F$_5^+$]; *m/z* 77 (5.3%); *m/z* 69 (2.0%) [CF$_3^+$]. Elemental analysis: calc. for $C_{21}H_{15}F_{13}S$ (546.07) C 46.15, H 2.77, F 45.23, S 5.85; found C 46.32, H 2.95, F 45.47, S 5.99%.

### 4.3.3. *2-(Perfluoro-n-alkyl)ethylthiomethyl biphenyl-4-yl ether (**C**)*

A solution of 2-F-alkylethylthiomethyl bromide ($2 \times 10^{-3}$ mol), previously prepared from 2-F-alkylethanthiol [14], in acetone (6 ml) was added to a mixture of 4-phenylphenol ($2 \times 10^{-3}$ mol) and potassium carbonate ($4 \times 10^{-3}$ mol) in acetone (6 ml). The reaction mixture was boiled for 12 h, then filtered at room temperature, 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 **C** as a white solid (see the table).

**C6** (88% recovered yield). $^{1}$H NMR (CDCl$_3$/TMS) $\delta$ (ppm): 2.50 (m, 2H); 2.99 (t, 2H, $^{3}J = 7.4$ Hz); 5.26 (s, 2H); 6.99 (AA′BB′, 2H, $J = 8.7$ Hz); 7.25 to 7.57 (m, 7H). $^{19}$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* 562 (14%) [M$^+$]; *m/z* 393 (100%); *m/z* 183 (20.7%); *m/z* 169 (21.6%); *m/z* 152 (40.4%); *m/z* 119 (5.8%) [C$_2$F$_5^+$]; *m/z* 77 (14.7%); *m/z* 69 (18.0%) [CF$_3^+$]; *m/z* 51 (13.6%). Elemental analysis: calc. for $C_{21}H_{15}F_{13}SO$ (562.06) C 44.83, H 2.69, F 43.94, S 5.69; found C 45.01, H 2.87, F 44.21, S 5.69%.

## 5. Conclusion

The synthesis of a series of partially fluorinated liquid crystal materials has been reported. We describe in this work the large effect of the introduction of 2-(perfluoro-*n*-alkyl)ethyl chains into the 4-position of biphenyl via a thioester connector. Even though the hydrocarbon analogues are not mesomorphic, the compounds of the F-alkylated series show an enantiotropic smectic A phase over a wide temperature range. Increasing the number of fluoromethylene units (4, 6, 8) led to an increase of both melting and clearing temperatures.

Some examples have shown in the past that the formal substitution of hydrogen by fluorine in the alkyl chains of hydrocarbon liquid crystal compounds can lead to the suppression of the liquid crystalline character. It is worth noting that this suppression of the liquid crystal behaviour is not due to the introduction of fluorine, but rather to the nature of the spacer (shape and chemical nature) linking the mesomorphic core to the fluorinated tail. In fact, we have observed, in this work, that the formal 'reduction' of the thioester derivatives, leading to the thioether compounds, suppresses the liquid crystalline behaviour. The same observation was made when we 'added' an oxygen atom near the mesogenic core to give the hemithioacetal structures. Compared to previous work, we find that the impact of the connector governs the stability of the mesophase. The chemical and thermal stability of fluoroalkyl groups and of the mesophases obtained for the thioester derivatives allow us to consider the 2-(perfluoro-*n*-alkyl)ethyl group as a good precursor for the enhancement of smectic thermotropic behaviour.

The authors thank Atochem for the gift of 2-(F-alkyl)ethyl iodides, 2-(F-hexyl)ethyl thiol and 2-(F-octyl)ethyl thiol.

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