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## Liquid Crystals

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# Synthesis and mesomorphic properties of some bisegmented compounds derived from 4,4'-disubstituted biphenyl

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New unsymmetrical disubstituted biphenyls have been synthesized. Two different chains (one hydrocarbon and the other fluorinated) are linked through an acetamide bond to 4-methoxy-4'-hydroxybiphenyl. Their mesomorphic properties have been characterized by light microscopy and by differential thermal analysis showing the peculiar contribution of the hydrocarbon chain and the fluorinated tail. The enhancement of the hydrocarbon moiety from one to twelve methylene groups leads to a decrease of the clearing temperatures; furthermore the enantiotropic behaviour is changed to monotropic. The variation of the fluorinated moiety generates strong effects on the transition temperatures. These mesomorphic properties are compared to those of their monocatenar perfluorinated analogues incorporating a connector of the ester or monosubstituted amide type.

## 1. Introduction

Liquid crystal materials containing two or several chains on an aromatic ring have been described in the past [1, 2]. The study of polycatenar compounds, within the hydrocarbon series, has led, in particular, to showing clearly the relation between molecular structure and mesomorphic behaviour [3, 4]. All such compounds studied generally have, within the branched moiety, hydrocarbon chains with the same length. On the other hand, liquid crystal materials within the fluorinated series have been the subject of many publications [5]. However, little work has been done on the study of mixed systems, i.e. incorporating in the same structure chains with a hydrocarbon part and a perfluorinated moiety. Nevertheless, the production of amphiphilic structures which include two groups of a different chemical nature linked through a covalent bond has led to the formation of microphasic domains resulting in mesophase appearance. This peculiar behaviour, well known in the domain of surfactants, has been shown clearly by the study of the liquid crystalline phases of di- [6] or tri-block [7] semi-fluorinated alkanes. Tournilhac *et al.*, have synthesized and studied a series of polyphilic compounds containing a succession of two moieties (fluorinated/hydrocarbon) derived from biphenyl (4,4'-disubstituted) which have led to systems with the properties of

ferroelectric materials [8] and which are of very particular interest [9].

The structures studied in this work can be represented generally by the structure at the top of figure 2. Of the two aliphatic chains, one is perfluorinated at its extremity and the other is hydrocarbon. In this study, the mesogenic group is constant, and derived from a 4,4'-disubstituted biphenyl. The fact that there is no chemical function between the rings to generate potentially undesirable properties on the mesomorphic behaviour (irreversibility, thermal or chemical instability [10, 11]) makes the structure of great interest. In fact, it is well known that 4,4'-disubstituted biphenyls of different types usually form liquid crystalline mesophases [12]. In the case of unsymmetrical compounds, substituted with simple substituents, low melting points are especially to be expected.

Previously, we have investigated the mesomorphic properties of monocatenar homologous structures which differ in the nature of the connector. In this study, we report the influence of two mixed chains on the mesomorphic properties. The behaviour of all the compounds has been studied by differential thermal analysis and light microscopy.

## 2. Results and discussion

Initially, we were interested in structures **A** and **B** (see again figure 2). These monocatenar compounds both incorporate a perfluorinated chain. Perfluoroalkylated groups, which are stable in chemical reactions and are

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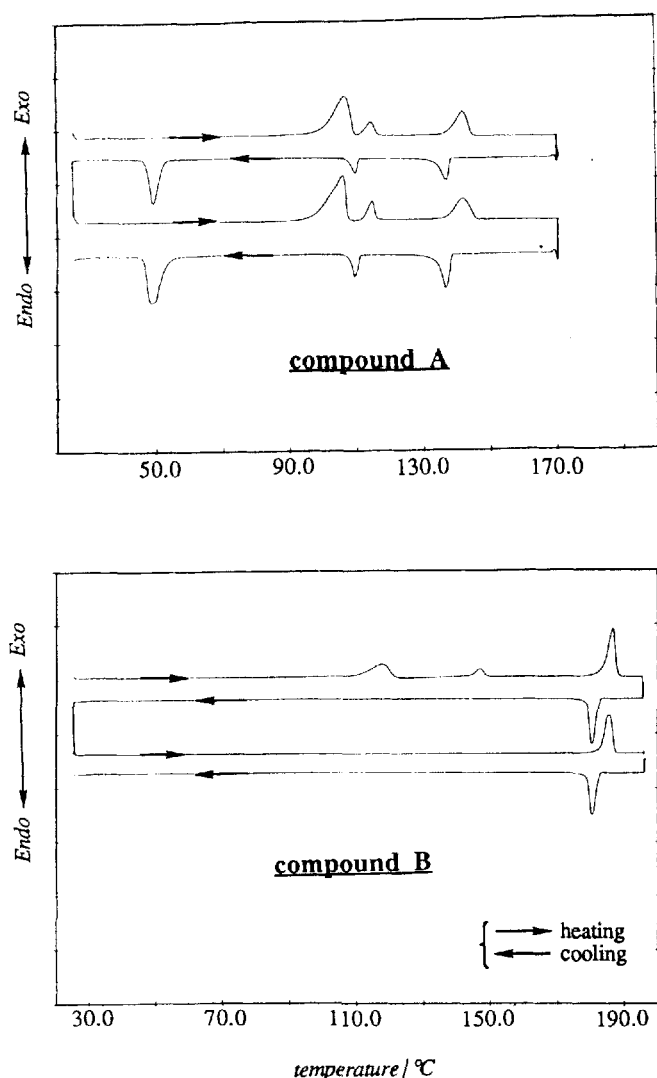


Figure 1. DSC diagrams for the ester (a) and the monosubstituted amide (B)—both with  $n = 6$  at a scanning rate of  $10^{\circ}\text{C min}^{-1}$ .

strongly electron withdrawing, can lead to unusual liquid crystal behaviour. However, the presence of fluorinated chains, notably perfluorinated, has often led to controversy in the past concerning the influence on the mesophase. The replacement of the hydrocarbon chain by a fluorinated analogue can directly affect the mesomorphic characteristics. For example, the presence of fluorinated chains can totally eliminate the liquid crystal properties compared to their hydrocarbon analogues [13, 14] or enhance the smectic character [15] to the detriment of the nematic phase [16].

The DSC spectra, for the compounds A and B, recorded during two consecutive thermal cycles are illustrated in figure 1. We observe two different thermal behaviours for the ester derivative (A) and the monosubstituted amide (B). Compound A gives two thermal cycles in which the transitions can be perfectly reproduced. Both give three

peaks on heating and on cooling. With light microscopy, the ester derivative (A) shows liquid crystal behaviour: the peak at the lowest temperature corresponds to the crystal to liquid crystal transition and the highest temperature peak to the liquid crystal to isotropic transition. In agreement with the enantiotropic character, it exhibits two thermotropic smectic polymorphic phases (see photographs a and b in figure 7) over a temperature domain of  $36^{\circ}\text{C}$  on heating.

In contrast, the monosubstituted amide (compound B) does not exhibit liquid crystal behaviour. During the DSC studies, the transitions that were observed before the isotropization temperature occurred only during the first thermal cycle, showing that they are probably related to solid–solid transitions. In fact, a second thermal cycle carried out on the same capsule decreases greatly the enthalpies of the previous transitions and shows clearly only the peak corresponding to melting and isotropization ( $178^{\circ}\text{C}$ ). Nevertheless, it seemed interesting to us to have synthesized this compound which can potentially form hydrogen bonds. Actually, other results have shown a favourable effect on liquid crystal behaviour as a consequence of these types of interactions [17–19]. In our case, it seems that they increase the crystal stability of the system, giving a high melting point ( $178^{\circ}\text{C}$ ) in comparison with their ester analogues ( $145^{\circ}\text{C}$ ), and contribute to masking the liquid crystal character. This must also, of course, be related to the molecular structure. The mesogenic potential of this material could be shown clearly by the transformation of a monosubstituted amide into a disubstituted amide.

These preliminary studies of the influence of the nature of the connector (spacer located between the perfluoroalkylated chain and the mesogenic group derived from biphenyl) therefore allowed us to consider the synthesis and the mesomorphic properties of new bisegmented compounds (structure C in figure 2) characterized by two chains of different nature, connected to the nitrogen atom and forming a disubstituted amide function. The synthetic scheme for this series of compounds is illustrated in figures 2 and 3.

Figures 4 and 5 represent the phase transformations obtained on heating these new materials from the crystalline state and on cooling from the isotropic state, respectively. These diagrams have been obtained by studying samples using differential thermal analysis as well as a polarizing optical microscopy. Data so obtained concerning the temperature ranges of the mesophases are collected in the table. Firstly, it is observed that when a monosubstituted amide is transformed into a disubstituted amide, a decrease in the transition temperatures is clearly observed, and a liquid crystal phase appears. In the phase diagrams that we have obtained, the magnitude of the even–odd effect for  $p$  seems strongly attenuated and

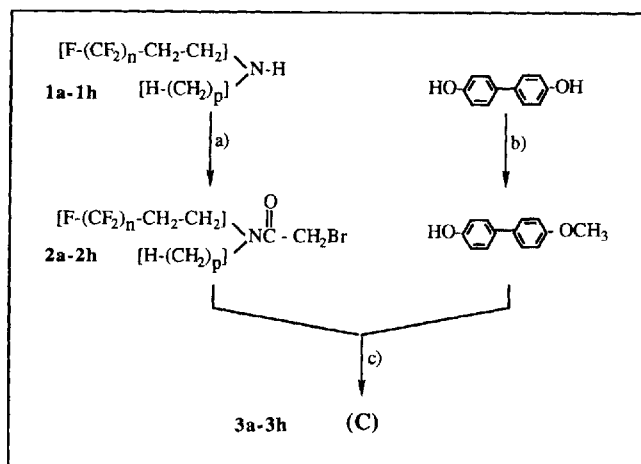
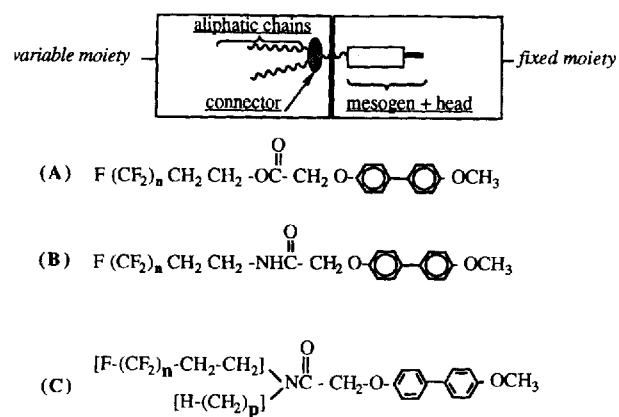


Figure 2. General structures and synthetic scheme for **C** (**3a-3h** see also table); (a)  $BrCH_2COOH/DCC, CHCl_3, 1-1.5\text{ h RT}$ ; (b) [28]; (c)  $K_2CO_3/acetone, 6-12\text{ h reflux}$ .

indeed reversed. In fact, our structures have a connector which permits the linkage of the hydrocarbon/fluorinated chains to a rigid core in the structure. As a result, the influence of the variation of the lateral chains on the mesomorphic properties of the compound is screened by this acetamide unit. Furthermore, the existence of two chains, which are chemically different, but are connected to the same atom, may generate intramolecular interactions having an influence on the total anisotropy of the system. By comparing these diagrams, the following points can clearly be concluded.

The general aspect of the lines joining the points display

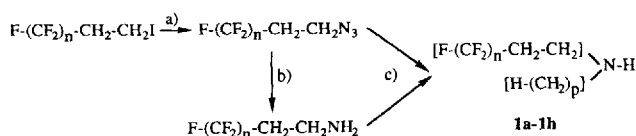


Figure 3. Synthetic routes to *N*-2-perfluoroalkylethyl-*N*-alkylamines (**1a-1h**); (a) see [29]; (b) see [24, 25]; (c) see [30].

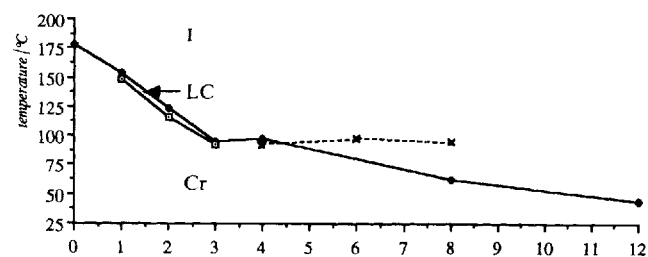


Figure 4. Transitions observed on heating the compounds (**C**). LC: liquid crystal phase.  $p$  ( $\bullet$ ,  $\square$ ) for  $n = 6$  or  $n$  ( $\times$ ) for  $p = 4$ .

two tendencies as a function of variation of the nature of the chains. The variation of the hydrocarbon group significantly influences the isotropization temperature, which ranges from 178 to 38°C for a value of the perfluorinated chain equal to F-hexyl. Furthermore, it has been noticed that the introduction of a low number of fluorine atoms on an aliphatic chain induces generally a variation of the physico-chemical properties such as melting point, clearing temperatures, viscosity... [20]. It is worth noting that variation of the perfluorinated chain length for these structures, when  $p$  is constant and equal to 4, seems weakly related to the transition temperatures. The occurrence of two different sets of lines, one exhibiting a liquid crystal domain only for the low values of  $p$  on heating, and the other displaying mesomorphic behaviour for all of the compounds studied on cooling, allows us to define the monotropic and enantiotropic members of the series.

Those compounds with values of  $p$  higher than 3 give a monotropic mesophase, seen only on cooling. The term monotropic is used here to indicate that the compounds show their liquid crystal character only on cooling, without any implication of metastability or thermal instability [21, 22] which has not been observed during variation of the temperature scanning rates.

The compounds with  $p < 4$  (but not  $p = 0$ ) are enantiotropic in character. The structure for  $p = 3$  and  $n = 6$  is the last member of the series showing enantiotropic character. The DSC spectrum recorded on three thermal

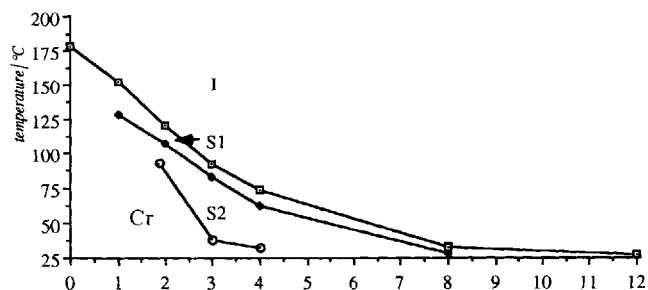


Figure 5. Transitions observed on cooling the isotropic liquids of the compounds (**C**).  $p$  for  $n = 6$ .

Yields and thermodynamic data for the compounds **A**, **B**, and **C**.

Compound	$R_T/R_H$ value	Yield <sup>†</sup> per cent	Thermal transition <sup>‡</sup> °C	
			Heating	Cooling
( <b>A</b> )	C <sub>6</sub> F <sub>13</sub>	56	Cr 106 S <sub>2</sub> 116 S <sub>1</sub> 142 I	I 136 S <sub>1</sub> 111 S <sub>1</sub> 49 Cr
( <b>B</b> )	C <sub>6</sub> F <sub>13</sub>	41	Cr 178 I	I 176 Cr
( <b>C</b> ) <b>3a</b>	C <sub>6</sub> F <sub>13</sub> /CH <sub>3</sub>	36	Cr 144 S <sub>1</sub> 151 I	I 152 S <sub>1</sub> 128 Cr
( <b>C</b> ) <b>3b</b>	C <sub>6</sub> F <sub>13</sub> /C <sub>2</sub> H <sub>5</sub>	36	Cr 116 S <sub>1</sub> 123 I	I 121 S <sub>1</sub> 107 S <sub>2</sub> 99 Cr
( <b>C</b> ) <b>3c</b>	C <sub>6</sub> F <sub>13</sub> /C <sub>3</sub> H <sub>7</sub>	38	Cr 92 S <sub>1</sub> 95 I	I 93 S <sub>1</sub> 83 S <sub>2</sub> 25 Cr
( <b>C</b> ) <b>3d</b>	C <sub>6</sub> F <sub>13</sub> /C <sub>4</sub> H <sub>9</sub>	39	Cr 95 I	I 74 S <sub>1</sub> 71 S <sub>2</sub> 38 Cr
( <b>C</b> ) <b>3e</b>	C <sub>6</sub> F <sub>13</sub> /C <sub>8</sub> H <sub>17</sub>	39	Cr 58 I	I 41 S <sub>1</sub> 28 Cr
( <b>C</b> ) <b>3f</b>	C <sub>6</sub> F <sub>13</sub> /C <sub>12</sub> H <sub>25</sub>	36	Cr 48 I	I 29 S <sub>1</sub> 25 Cr
( <b>C</b> ) <b>3g</b>	C <sub>4</sub> F <sub>9</sub> /C <sub>4</sub> H <sub>9</sub>	32	Cr 88 I	I 69 S <sub>1</sub> 43 Cr
( <b>C</b> ) <b>3h</b>	C <sub>8</sub> F <sub>17</sub> /C <sub>4</sub> H <sub>9</sub>	33	Cr 91 I	I 71 S <sub>1</sub> 42 Cr

<sup>†</sup> Yield from 2-F-alkylethanol (**A**) and from 2-F-alkylethyl iodide (**B**, **C**); <sup>‡</sup> Cr: crystal; S<sub>1</sub>, S<sub>2</sub>: smectic phase; I: isotropic.

cycles starting from a temperature of 25°C is represented in figure 6. When two thermal cycles are undertaken with a time interval below two hours, it can be seen, as optical microscopy confirms, that the system did not entirely crystallize. Also, the spectra recorded on the second heating cycle show the same transitions that are obtained on the first cooling cycle. A third cycle undertaken using the same conditions and on the same sample, after waiting for over two hours at room temperature, displays again a succession of phase transitions identical with the first cycle. This establishes the stability and the reversibility of the thermal phenomena and the occurrence of polymorphism on cooling from the isotropic state with the last transition occurring only at room temperature (25°C) and kinetically regulated. A schematic description of the phase reversibility is illustrated in figure 6(b). By light microscopy, the mesophases appear as rods on cooling from the isotropic melt; they coalesce to give a well developed fan shaped texture with focal conic domains. Rods and a fan shaped textures are characteristic of the layer structures of smectic mesophases [23] (figure 7(a) (e)). For the monotropic phases, a similar fan shaped texture is observed with focal conic domains.

### 3. Experimental

#### 3.1. Techniques

The liquid crystalline textures were observed with an Olympus BH-2 polarizing microscope equipped with crossed polarizers and using a Mettler model FP-52 hot stage. The phase transition temperatures (clearing temperatures and smectic transitions) were determined with a Perkin-Elmer differential scanning calorimeter DSC7 equipped with a thermal analysis controller TAC 7/DX and also by polarizing microscopy as described above. The heating and cooling curves were obtained at rates of 2 and 10°C min<sup>-1</sup>, in a nitrogen atmosphere. IR spectra

were recorded with a Bruker IFS-45 spectrometer at room temperature. <sup>1</sup>H NMR (chemical shifts measured in deuteriated solvents are given in ppm from TMS) and <sup>19</sup>F NMR (CFCl<sub>3</sub> as internal reference) spectra were recorded with a Bruker AC 200 MHz spectrometer, using CDCl<sub>3</sub> and CD<sub>3</sub>COCD<sub>3</sub> solutions (5–10 wt%). Mass spectra were obtained using a Finnigan Mat INCOS 500 E mass spectrometer coupled with a gas chromatograph (Varian 3400). Distillations were performed using a Kugelrohr Aldrich with an Alcatel pump 2004 A.

#### 3.2. Materials

The syntheses of perfluoroalkylated compounds such as *N*-(2-perfluoroalkylethyl)-*N*-alkylamines [24, 25, 30] and 2-perfluoroalkylethyl-bromoacetamides and -bromoacetates [26, 27] are described elsewhere. The compounds **C** were made as shown in the synthetic scheme in figure 2. 4,4'-biphenol was purchased from Aldrich; solvents were reagent grade and were used without further purification.

#### 3.3. Synthesis

##### 3.3.1. 4-Methoxy-4'-(2-perfluoroalkylethoxycarbonyl-methoxy)biphenyl (**A**)

2-Perfluorohexylethyl bromoacetate (1 mmol), previously prepared from the reaction of 2-perfluoroalkylethanol with bromoacetyl bromide, in acetone was added to 4-methoxy-4'-hydroxybiphenyl in a dilute suspension of potassium carbonate (2 mmol) in acetone. The mixture was heated under reflux for 6 h, then filtered at room temperature and the solid washed with acetone. The resulting acetone layer was evaporated under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 1:1 hexane/ethyl acetate mixture as eluent and recrystallized from acetonitrile to yield the pure compound **A** (yield 82 per cent); <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS), δppm, (*J*, Hz): 2.53 (m, 2 H), 3.83 (s,

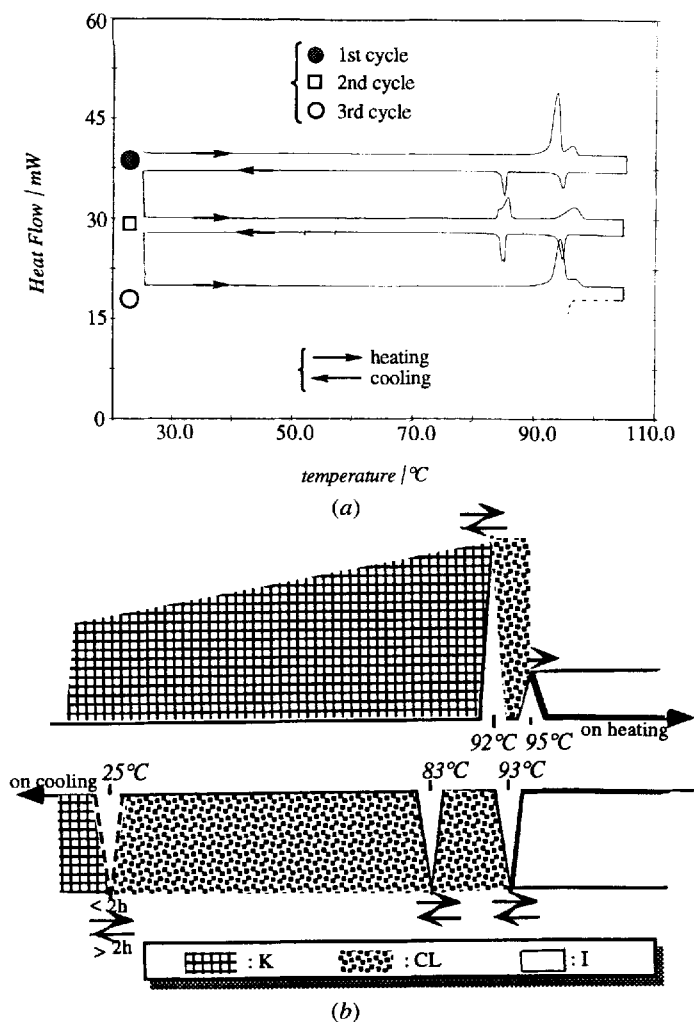


Figure 6. (a) DSC diagrams for (C) with  $n = 6$  and  $p = 3$ , scanning rate  $2^{\circ}\text{C min}^{-1}$  on heating and cooling; (b) schematic interpretation.

3 H,  $\text{CH}_3$ ), 4.52 (t, 2 H, 7.1,  $\text{CH}_2$ ), 4.69 (s, 2 H,  $\text{CH}_2$ ), 6.93–7.49 (4d, 8  $\text{H}_{\text{arom.}}$ , 8.7);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.4 (m,  $\text{CF}_3$ ), 114.5 (m,  $\text{CF}_2$ ), 122.3 (m,  $\text{CF}_2$ ), 123.3–124.0 (m, 4 F,  $\text{CF}_2$ ), 126.6 (m,  $\text{CF}_2$ ); SM  $m/z$ : 604 ( $\text{M}^+$ ).

### 3.3.2. 4-Methoxy-4'-[N-(2-perfluoroalkylethyl)amino-carbonylmethoxy]biphenyl (B)

2-Perfluorohexyl bromoacetamide (1.5 mmol), previously prepared from 2-perfluoroalkylethyl iodide according to [24, 26], in acetone (3 ml) was added to a mixture of 4-methoxy-4'-hydroxybiphenyl and potassium carbonate (3 mmol) in acetone (3 ml). The mixture was boiled for 12 h, then filtered at room temperature. The acetone layer was evaporated under slightly reduced pressure and the residue purified by column chromatography on silica gel using dichloromethane as eluent and recrystallized from

methanol to yield compound **B** (yield 80 per cent); SM  $m/z$ : 603,  $\text{M}^+$ .

### 3.3.3. 4-Methoxy-4'-[N-alkyl, N-(2-perfluoroalkylethyl)-aminocarbonylmethoxy]biphenyls

The precursor bromoacetamides (**2a–2h**) (1 mmol), previously prepared from 2-perfluoroalkylethyl iodide and the amines (**1a–1h**) according to [24, 30], in acetone (1 ml) were added to a mixture of 4-methoxy-4'-hydroxybiphenyl and potassium carbonate (3 mmol) in acetone (3 ml). The mixture was boiled for 9 h, then filtered at room temperature and the solid washed with acetone. The acetone layer was evaporated under slightly reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane as eluent and recrystallized from methanol or ether/hexane mixture to yield compound **C**.

**3a.** (67 per cent recovered yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 2.40 (m,  $\text{CH}_2$ ), 3.15 (s,  $\text{CH}_3$ ), 3.68 (t,  $\text{CH}_2$ ,  $J = 7.3$ ), 3.84 (s,  $\text{CH}_3$ ), 4.71 (s,  $\text{CH}_2$ ), 6.93–7.49 (4d, 8  $\text{H}_{\text{arom.}}$ ,  $J = 8.7$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.3 (m,  $\text{CF}_3$ ), 114.6 (m,  $\text{CF}_2$ ), 122.4 (m,  $\text{CF}_2$ ), 123.3–124.0 (m, 4 F,  $\text{CF}_2$ ), 126.6 (m,  $\text{CF}_2$ ). Analysis: Calculated for  $\text{C}_{24}\text{H}_{20}\text{F}_{13}\text{NO}_3$  (617.4): C, 46.69; H, 3.26; F, 40.00; N, 2.27; Found: C, 46.96; H, 3.33; F, 40.29; N, 2.41 per cent.

**3b.** (71 per cent recovered yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 1.26 (t,  $\text{CH}_3$ ,  $J = 7.1$ ), 2.47 (m,  $\text{CH}_2$ ), 3.44 (q,  $\text{CH}_2$ ,  $J = 7.1$ ), 3.62 (t,  $\text{CH}_2$ ,  $J = 7.4$ ), 3.84 (s,  $\text{CH}_3$ ), 4.72 (s,  $\text{CH}_2$ ), 6.93–7.49 (4d, 8  $\text{H}_{\text{arom.}}$ ,  $J = 8.7$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.3 (m,  $\text{CF}_3$ ), 114.6 (m,  $\text{CF}_2$ ), 122.3 (m,  $\text{CF}_2$ ), 123.3–124.0 (m, 4 F,  $\text{CF}_2$ ), 126.6 (m,  $\text{CF}_2$ ). Analysis: Calculated for  $\text{C}_{25}\text{H}_{22}\text{F}_{13}\text{NO}_3$  (631.4): C, 47.56; H, 3.51; F, 39.11; N, 2.21; Found: C, 47.72; H, 3.59; F, 39.42; N, 2.36 per cent.

**3c.** (72 per cent recovered yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 0.97 (t,  $\text{CH}_3$ ,  $J = 7.3$ ), 1.69 (m,  $\text{CH}_2$ ), 2.46 (m,  $\text{CH}_2$ ), 3.33 (t,  $\text{CH}_2$ ,  $J = 7.6$ ), 3.62 (t,  $\text{CH}_2$ ,  $J = 7.4$ ), 3.84 (s,  $\text{CH}_3$ ), 4.72 (s,  $\text{CH}_2$ ), 6.93–7.49 (4d, 8  $\text{H}_{\text{arom.}}$ ,  $J = 8.7$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.4 (m,  $\text{CF}_3$ ), 114.6 (m,  $\text{CF}_2$ ), 122.4 (m,  $\text{CF}_2$ ), 123.4–124.0 (m, 4 F,  $\text{CF}_2$ ), 126.7 (m,  $\text{CF}_2$ ). Analysis: Calculated for  $\text{C}_{26}\text{H}_{24}\text{F}_{13}\text{NO}_3$  (645.5): C, 48.38; H, 3.75; F, 38.26; N, 2.17; Found: C, 48.54; H, 3.83; F, 38.41; N, 2.31 per cent.

**3d.** (68 per cent recovered yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 0.98 (t,  $\text{CH}_3$ ,  $J = 7.4$ ), 1.34–1.63 (m, 4 H), 2.43 (m,  $\text{CH}_2$ ), 3.34 (t,  $\text{CH}_2$ ,  $J = 7.6$ ), 3.60 (t,  $\text{CH}_2$ ,  $J = 7.4$ ), 3.83 (s,  $\text{CH}_3$ ), 4.72 (s,  $\text{CH}_2$ ), 6.93–7.49 (4d, 8  $\text{H}_{\text{arom.}}$ ,  $J = 8.7$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.4 (m,  $\text{CF}_3$ ), 114.6 (m,  $\text{CF}_2$ ), 122.4 (m,  $\text{CF}_2$ ), 123.3–124.0 (m, 4 F,  $\text{CF}_2$ ), 126.6 (m,  $\text{CF}_2$ ). Analysis: Calculated for  $\text{C}_{27}\text{H}_{26}\text{F}_{13}\text{NO}_3$  (659.5): C, 49.17; H, 3.97; F, 37.45; N, 2.12; Found: C, 49.51; H, 4.11; F, 37.72; N, 2.26 per cent.

**3e.** (72 per cent recovered yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 0.98 (t,  $\text{CH}_3$ ,  $J = 7.4$ ), 1.22–1.65 (m, 12 H), 2.42

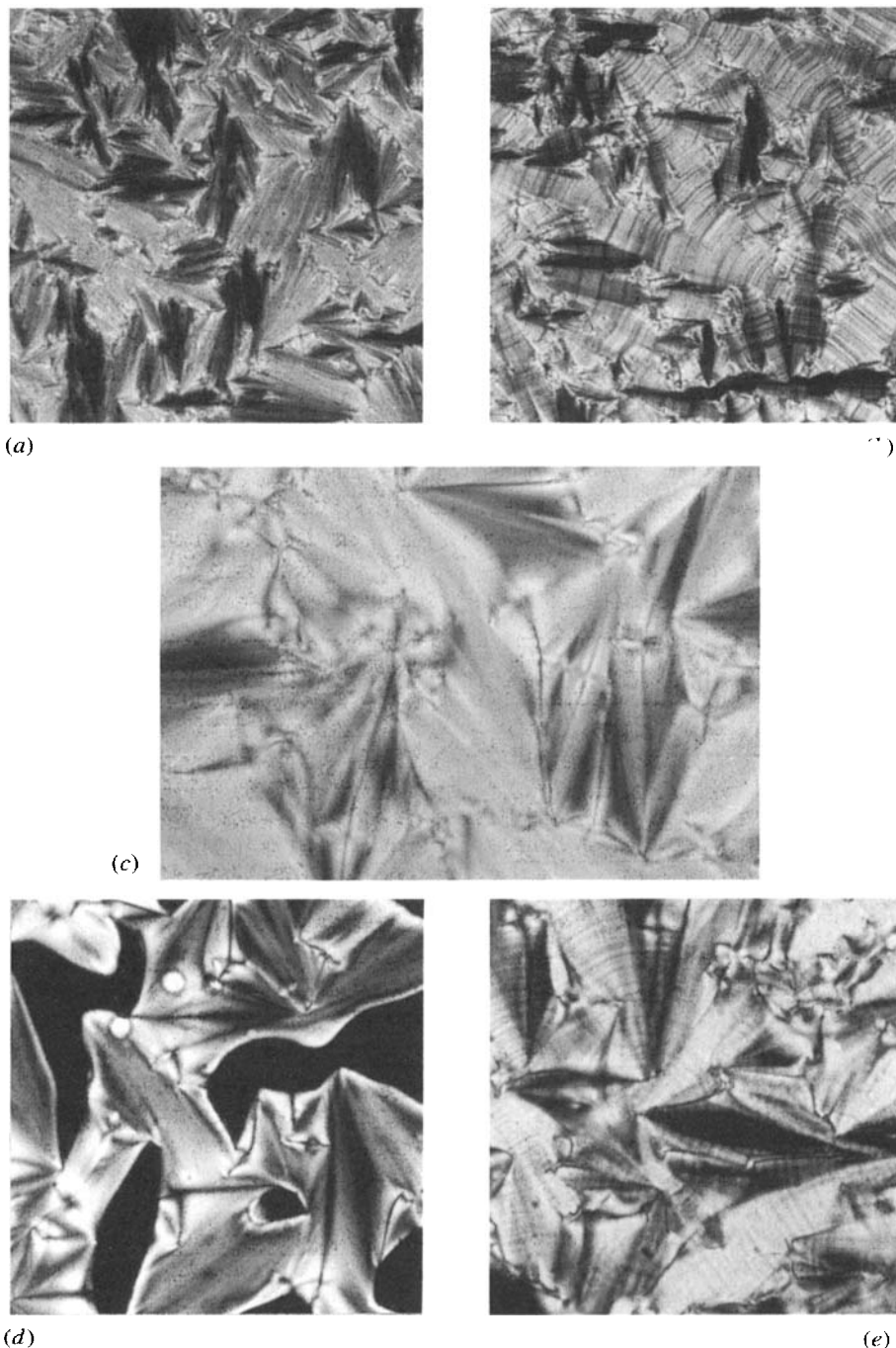


Figure 7. Optical polarizing photomicrographs of compound A,  $T = 142^\circ\text{C}$   $S_1$  (a),  $T = 116^\circ\text{C}$   $S_2$  (b), **C**, **3c**,  $T = 91^\circ\text{C}$   $S_1$  (c), **3d**,  $T = 74^\circ\text{C}$   $S_1$  (d), **3d**,  $T = 58^\circ\text{C}$   $S_2$  (e).

(m,  $\text{CH}_2$ ), 3.33 (t,  $\text{CH}_2$ ,  $J = 7.7$ ), 3.60 (t,  $\text{CH}_2$ ,  $J = 7.4$ ), 3.84 (s,  $\text{CH}_3$ ), 4.72 (s,  $\text{CH}_2$ ), 6.93–7.49 (4d,  $8\text{H}_{\text{arom.}}$ ,  $J = 8.78$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.3 (m,  $\text{CF}_3$ ), 114.6 (m,  $\text{CF}_2$ ), 122.3 (m,  $\text{CF}_2$ ), 123.3–124.0 (m, 4 F,  $\text{CF}_2$ ), 126.6 (m,  $\text{CF}_2$ ). Analysis: Calculated for  $\text{C}_{31}\text{H}_{34}\text{F}_{13}\text{NO}_3$  (715.6): C, 52.03; H, 4.79; F, 34.51; N, 1.96; Found: C, 52.33; H, 4.85; F, 34.78; N, 2.21 per cent.

**3f**. (72 per cent recovered yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3/$

TMS): 0.98 (t,  $\text{CH}_3$ ,  $J = 7.4$ ), 1.21–1.68 (m, 20 H), 2.42 (m,  $\text{CH}_2$ ), 3.32 (t,  $\text{CH}_2$ ,  $J = 7.7$ ), 3.60 (t,  $\text{CH}_2$ ,  $J = 7.4$ ), 3.84 (s,  $\text{CH}_3$ ), 4.72 (s,  $\text{CH}_2$ ), 6.93–7.49 (4d,  $8\text{H}_{\text{arom.}}$ ,  $J = 8.7$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.3 (m,  $\text{CF}_3$ ), 114.5 (m,  $\text{CF}_2$ ), 122.3 (m,  $\text{CF}_2$ ), 123.3–124.0 (m, 4 F,  $\text{CF}_2$ ), 126.6 (m,  $\text{CF}_2$ ). Analysis: Calculated for  $\text{C}_{35}\text{H}_{42}\text{F}_{13}\text{NO}_3$  (771.7): C, 54.48; H, 5.49; F, 32.00; N, 1.81; Found: C, 54.69; H, 5.56; F, 32.31; N, 1.98 per cent.

**3g.** (58 per cent recovered yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 0.98 (t,  $\text{CH}_3$ ,  $J = 7.2$ ), 1.35 (m,  $\text{CH}_2$ ), 1.64 (m,  $\text{CH}_2$ ), 2.42 (m,  $\text{CH}_2$ ), 3.34 (t,  $\text{CH}_2$ ,  $J = 7.6$ ), 3.60 (t,  $\text{CH}_2$ ,  $J = 7.4$ ), 3.84 (s,  $\text{CH}_3$ ), 4.72 (s,  $\text{CH}_2$ ), 6.93–7.49 (4d, 8  $\text{H}_{\text{arom.}}$ ,  $J = 8.7$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.6 (m,  $\text{CF}_3$ ), 114.8 (m,  $\text{CF}_2$ ), 124.9 (m,  $\text{CF}_2$ ), 126.6 (m,  $\text{CF}_2$ ). Analysis: Calculated for  $\text{C}_{25}\text{H}_{26}\text{F}_9\text{NO}_3$  (559.5): C, 53.67; H, 4.68; F, 30.56; N, 2.50; Found: C, 53.81; H, 4.72; F, 30.77; N, 2.69 per cent.

**3h.** (74 per cent recovered yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 0.98 (t,  $\text{CH}_3$ ,  $J = 7.4$ ), 1.35 (m,  $\text{CH}_2$ ), 1.64 (m,  $\text{CH}_2$ ), 2.42 (m,  $\text{CH}_2$ ), 3.34 (t,  $\text{CH}_2$ ,  $J = 7.6$ ), 3.60 (t,  $\text{CH}_2$ ,  $J = 7.4$ ), 3.84 (s,  $\text{CH}_3$ ), 4.72 (s,  $\text{CH}_2$ ), 6.93–7.49 (4d, 8  $\text{H}_{\text{arom.}}$ ,  $J = 8.7$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{CFCl}_3$ ): 81.3 (m,  $\text{CF}_3$ ), 114.6 (m,  $\text{CF}_2$ ), 122.4 (m, 6F,  $\text{CF}_2$ ), 123.2–123.9 (m, 4F,  $\text{CF}_2$ ), 126.6 (m,  $\text{CF}_2$ ). Analysis: Calculated for  $\text{C}_{29}\text{H}_{26}\text{F}_{17}\text{NO}_3$  (759.5): C, 45.86; H, 3.45; F, 42.52; N, 1.84; Found: C, 46.21; H, 3.54; F, 42.82; N, 2.09 per cent.

#### 4. Conclusions

Two kinds of material have been prepared in this work. The monocatenar compounds (**A** and **B**) demonstrated the influence of the spacer. The ester function generating an enantiotropic mesomorphism, and the monosubstituted amide function leading to no liquid crystal behaviour. Using these results we have investigated, for the first time, mixed bicatenar structures, i.e. incorporating a fluorinated tail and a hydrocarbon chain linked to the same atom of the connector. The study of these disubstituted amides has allowed us to show clearly two phenomena. Increase in length of the fluorinated moiety weakly influences the melting temperatures (when  $p = 4$ ), while increase in the number of methylene groups,  $p$ , in the hydrocarbon moiety (1–12) strongly decreases the melting point (178–38°C). Furthermore, it is clear that the size of the hydrocarbon tail is important, leading to either enantiotropic ( $p \leq 3$ ) or monotropic ( $p \geq 4$ ) behaviour. Finally, smectic thermotropic polymorphism has been observed notably when  $p = 3$  and when the perfluorinated chain is equal to perfluorohexyl. With the aim of extending the temperature ranges and bearing electro-optical applications in mind, the large variety of structures obtained gives us the possibility of their use in eutectic mixtures.

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