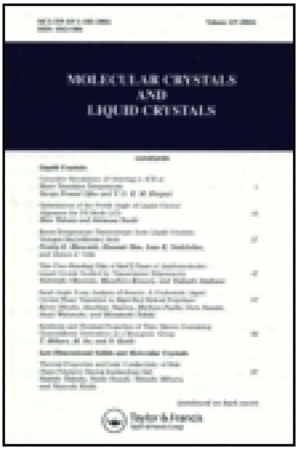

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Synthesis and Thermotropic Liquid Crystal Partially Fluorinated Materials Derived from Biphenyl Incorporating an Ester Connector

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We have developed new molecules which consist of a 4,4'-biphenyl unit linked at the 4 position to a linear fluorinated chain via a short spacer of ester type. The 4′ position of the biphenyl group can be an hydrogen, or a bromine atom, a methoxy or a cyano group. The mesomorphic properties have been characterized by light microscopy and by differential thermal analysis. The influence of the fluorinated chain and the nature of the 4′ substituent on the stability of the mesophases has been investigated. All the compounds showed a very interesting smectic enantiotropic behavior over a wide temperature range. The increase of the number of fluoromethylene units simultaneous increase both the melting and the clearing temperatures. The introduction of methoxy unit lead to a dimorphic behavior and the presence of the bromine atom dramatically affect the span of the mesophase as compared to the other 4' substituents.

Keywords: 2-*F*-alkylethyl; smectic phase; ester connector; biphenyl

INTRODUCTION

It is known that linearity, rigidity, and polarizability are the most important factors for a molecule to display liquid crystalline properties. Addition of polar group in terminal position has led to subgroups of the conventional smectic phases[1-3]. Another way of enhancing a smectic behavior involves the partial

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substitution of hydrogen atoms by fluorine atoms in the terminal alkyl moiety[4-6].

Recently, numerous compounds containing perfluoroalkyl groups have been synthesized[7-10]. The ester connector are the object of numerous studies within hydrocarbon series; they are among the extensive studied compounds in the thermotropic short molecule field, mainly for the obtaining of chiral liquid crystals[11-13]. We are interested in this work to the description of the synthesis including the main molecular structural moiety : a linear perfluorinated tail, an ester connector and a biphenyl core. We are also carried out the reaction from the 4,4'-biphenyl parasubstituted in 4' position by "H", OMe, CN or Br (Z) in order to evaluate the impact of these substitutions on the mesomorphic behavior.

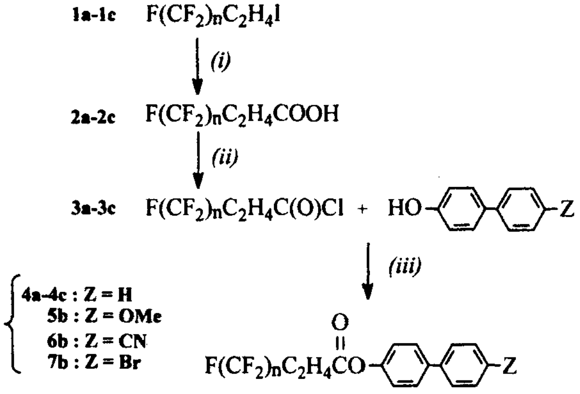
EXPERIMENTAL

Measurements

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.

Synthesis

4'-substituted-4-phenylphenol were purchased from Aldrich and were used without further purification. The 2-*F*-alkylpropanoic chloride [14] (3a-3c) have been prepared from 2-*F*-alkylethyl iodides (1a -1c) via the corresponding 2-*F*-alkylpropanoic acid (2a - 2c).



(i) Mg / CO_2 / H_2O; Et_2O, 20-35°C (ii) PCl_5 (iii) THF / py. / reflux.

FIGURE 1 Synthetic route to the compounds 4a-4c, 5b, 6b and 7b.

Compounds 4a-4c, 5b, 6b and 7b have been synthesized according to the standard procedures and illustrated by Figure 1. 2-*F*-alkylpropanoic chloride ($5.5\ 10^{-3}$ mol) was added dropwise to a solution of 4'-substitued-4-phenylphenol (5.10^{-3} mol), freshly distilled pyridine (5.10^{-3} mol) and dry tetrahydrofuran (15 ml). After complete addition, the resulting mixture was left to reflux and followed by thin layer chromatography until removal of the phenol (24h). The reaction mixture was then filtered and evaporated. The residue was purified by column chromatography on silica gel using chloroform as eluent.

^{1}H NMR ($CDCl_3$ / TMS) δ (ppm): **4a-4c**: 2.57 (Tt, 2H, $^3J_{H-H}$=6.3Hz, $^3J_{H-F}$=18.6Hz); 2. 95 (t, 2H, ^3J=6.3 Hz); 7.10-7.69 (m, 9H arom); **5b**: 2.59 (Tt, 2H, $^3J_{H-H}$=6.3Hz, $^3J_{H-F}$=18.6Hz); 2.95 (t, 2H, ^3J=6.3 Hz); 3.90 (s, 3H); 6.73-7.78 (3d, 8H arom); **6b**: 2.57 (Tt, 2H, $^3J_{H-H}$=6.3Hz, $^3J_{H-F}$=18.6Hz); 2. 95 (t, 2H, ^3J=6.3 Hz); 7.59-7.78 (m, 8H arom); **7b**: 2.60 (Tt, 2H, $^3J_{H-H}$=6.3Hz, $^3J_{H-F}$=18.6Hz); 2.94 (t, 2H, ^3J=6.3 Hz); 7.14-7.78 (m, 8H arom); ^{19}F NMR

($CDCl_3/CFCl_3$), δ(ppm); **4a**: -81.6 ($C\underline{F}_3$), -114.8 ($C\underline{F}_2\alpha$), -124.9 ($C\underline{F}_2\beta$), -126.6 ($C\underline{F}_2\omega$); **4b, 5b, 6b, 7b**: -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($C\underline{F}_2\omega$); **4c** : -81.3 ($C\underline{F}_3$), -114.3 ($C\underline{F}_2\alpha$), -122.5 (3 $C\underline{F}_2$), -123.3 to -124.3 (2 $C\underline{F}_2$), -126.6($C\underline{F}_2\omega$).

MS (70 eV), m/z (%): examplified for **6b**: 569 (2.9), 375 (2.5), 222 (<1), 195 (100), 179 (1.3), 170 (6.2), 131 (<1), 119 (<1), 69 (2.7).

RESULTS AND DISCUSSION

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. Transition temperatures (°C) are reported in table 1.

TABLE 1 Yields and transition temperatures for compounds 4-7.

Cpd N°	R_F / Z	Yield (%) •	transition temperatures (°C) ‡						
			C		S_E		S_A		I
4_a	C_4F_9/H	60.5	•	64.2			•	79.4	•
4_b	C_6F_{13}/H	58.8	•	80.5			•	113.2	•
4_c	C_8F_{17}/H	59.4	•	95.5			•	127.6	•
5_b	C_6F_{13}/OCH_3	52.0	•	85	•	112	•	148	•
6_b	C_6F_{13}/CN	56.3	•	92			•	161	•
7_b	C_6F_{13}/Br	48.3	•	149			•	153	•

(*) Yield from 2-F-alkylethyl iodides
(‡) From DSC spectra.

By optical microscopic observation, the mesophase of all members of these compounds 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 the smectic A and smectic E type. According to the DSC spectra, the liquid crystal phase is observed from heating and cooling which characterize an enantiotropic character.

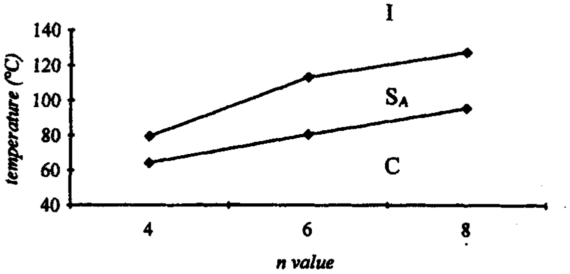


FIGURE 2 Phase diagram of compounds 4a-c on heating.

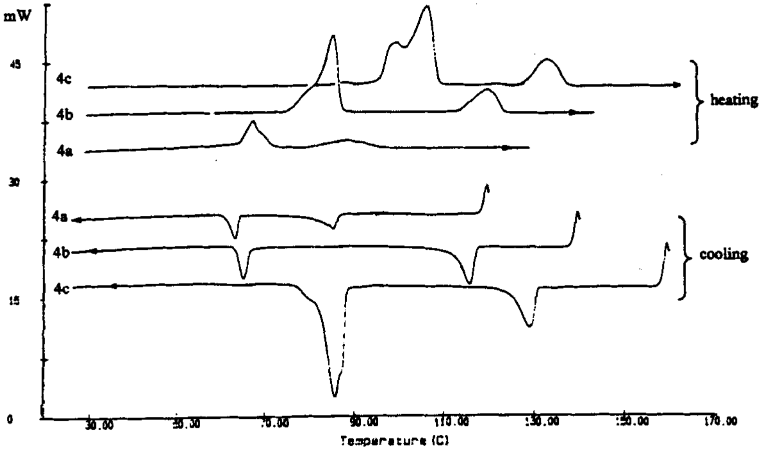


FIGURE 3 DSC curve for compounds 4a-c (heating and cooling rate : 10°C min^{-1}).

The phase diagram obtained on heating and plotted against the carbon number n of the terminal perfluoroalkylated moieties for the 4-biphenyl series (4a-c) is illustrated by figure 2. The curves obtained from differential thermal analysis is shown in figure 3. No significant change occurs in the transition temperatures after prolonged heating above the isotropic transition. These diagrams show the behavior of the transition temperatures as a function of the number, n, of fluoromethylene unit in the fluorinated tail. It is worth noting that the decrease in fluorinated tail length leads to a simultaneous reduction of the melting and clearing temperatures. However, the vertical spacing of these points, which represents the temperature span of the mesophase, becomes narrow as n decreases.

The comparison with the behavior of the compound 4b (Z = H, R_F = F-hexyle) allows us to emphasize the impact of the introduction in 4' position of different moiety instead of hydrogen (Figure 4).

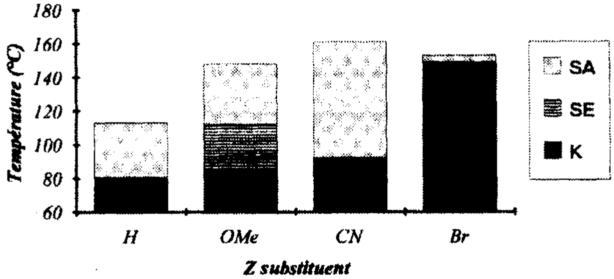


FIGURE 4 Comparison of the span of the mesophase against Z substituent

In fact, when *Z = OMe et Z = CN* : we can observe an increase of the smectic phase. Furthermore in the case of the compound 5b the methoxy group lead to an enantiotropic dimorphism. For CN substituent, the observation carried out from light microscopy and from the DSC studies, show a smectogen liquid crystalline behavior over a wide temperature range; On the other hand, when Z = Br, the span of the mesomorphic state become narrow : the liquid crystal character appear only over few degree celsius.

CONCLUSION

In a previous work[4, 15], we have seen that the nature of the connector (bonding the aliphatic tail to the rigid core) can govern the liquid crystal behavior within the fluorinated series. In this work, it is worth noting that the nature of the 4' substituent can affect the evolution of the mesomorphic behavior : the mono or dimorphism but also the span of the mesophase. This fact have to be put in correlation with the molecular architecture.

Acknowledgments

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