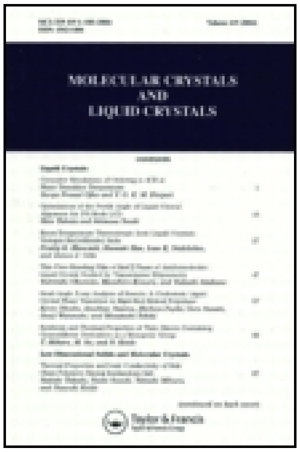

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Comparison of the Mesomorphic Properties Between Substituted Schiff's Bases Incorporating a Linear Hydrocarbon or Fluorinated Tail

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Comparison of the Mesomorphic Properties Between Substituted Schiff's Bases Incorporating a Linear Hydrocarbon or Fluorinated Tail

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We have developed new compounds within the perfluorinated series incorporating a Schiff's base as the connector between the aliphatic chain and the 4-biphenyl used as mesogen group. All members of the series are thermally stable and exhibit enantiotropic smectic behavior. A smectic polymorphism is observed only with F-butyl and F-hexyl tails. They show an oscillation in the smectic-isotropic transition temperature. The influence of the fluorinated chain and the shape of the connector on the stability or the reversibility of mesophases has been investigated by comparison with their hydrocarbon analogues and with a compound obtained by condensation of 2-(F-alkyl)ethylamine with 4-acetylbiphenyl. The fluorinated moiety strongly promotes enhanced smectic phases and the presence of a methyl group on the connector strongly decreases the stability of the mesophase. Exceptionally, it would seem that the fluorinated chain generates a liquid crystal behavior which can not be observed with the hydrocarbon homologous structures. The physical properties of these novel fluorinated materials are reported and the effect of fluorination on these properties is discussed. All these points are commented on and illustrated by the study realized from the differential thermal analysis and the light microscopy.

Keywords: Schiff's bases; 2-(F-alkyl) ethyl tail; smectic phase; thermal analysis

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1. INTRODUCTION

Several types of liquid crystals are currently employed for commercial liquid crystal displays. The particular mesomorphic structure that occurs not only depends on linear molecular shape but is intimately connected with the strength and position of polar groups within the molecule, the molecule's overall polarisability and the presence of chiral centers [1]. Molecular interactions that lead to attraction are dipole–dipole interactions, dispersion forces and hydrogen bondings. So, the presence of enough different elements can induce a microphasic separation, as in the case of semifluorinated alkanes which exhibit a thermotropic liquid crystal behaviour [2]. In order to obtain effective dipole–dipole interactions for liquid crystallinity, the molecule must contain polar groups and polarisable groups. In this case, electronic distortion is favored with the presence of cyclic groups and conjugated double or triple bonds. In this specified structure, there are three basic moieties: core units, a linking or bridging group and terminal groups. In our work, we are interested in the synthesis and the study of a series of compounds incorporating these structural elements necessary for a thermotropic mesomorphism. We have studied a series of compounds containing an aliphatic chain, a connector and a mesogen group. This connector is an imine function. In the past [3], it has been seen that the Schiff's base materials, being useful in liquid crystal devices, possess a sufficiently wide nematic range, low operating voltages and easy aligment characteristics. However, their sensitivity to moisture limits their use [4]. Nevertheless, they are useful materials for physico-chemical investigations [5, 6]. In our study, we have selected the Schiff's base as a connector between the aliphatic chain and the mesogen moiety represented by the 4-biphenyl in comparison with its location within MBBA. The aim of this work is to report on the unusual behavior observed between two homologous series, whose the nature of the alkylated chain is only different: hydrocarbon or perfluoroalkylated. In all cases, the studied tails are linear because Misaki *et al.* have remarked that this shape generates, when it can be observed, a wider smectogen range than the branched tails [7].

2. EXPERIMENTAL

Measurements

The liquid crystalline textures were observed with an Olympus BH-2 polarizing microscope equipped with a set of cross-polarizers and a Mettler model

FB-52 hot stage apparatus. The temperature of phase transition (melting, clearing temperatures and smectic transitions) was determined with a Perkin Elmer DSC 7 equipped with a Thermal Analysis Controller calibrated with pure indium as standard and also by a polarizing microscope described above. The heating and cooling curves were collected at rates of 10°C/min, in a nitrogen atmosphere. IR spectra were recorded with a Perkin Elmer FT-IR spectrometer Paragon 1000 at room temperature. ^{1}H-NMR (chemical shifts measured in deuterated solvents are given in ppm from TMS) and ^{19}F-NMR spectra ($CFCl_3$ as internal reference) were recorded with a Bruker AC 200 MHz spectrometer, using $CDCl_3$ 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 an Aldrich Kugelrohr with an Alcatel pump 2004 A.

Synthesis

4-biphenylcarboxaldehyde, 4-acetylbiphenyl and hydrocarbon amines were purchased from Aldrich and were used without further purification. The 2-(F-alkyl)ethylamines [8] (3a–3d) have been prepared from 2-(F-alkyl) ethyliodides via the corresponding azides [9] (2a–2d). The compounds 4a–4d, 5a–5d et 6a have been synthesized by reaction of 4-biphenylcarboxaldehyde or of 4-acetylbiphenyl on a hydrocarbon or fluorocarbonated amine according to the standard procedures and illustrated by Figure 1. The reaction mixture in a solvent as methanol or chloroform was stirred at

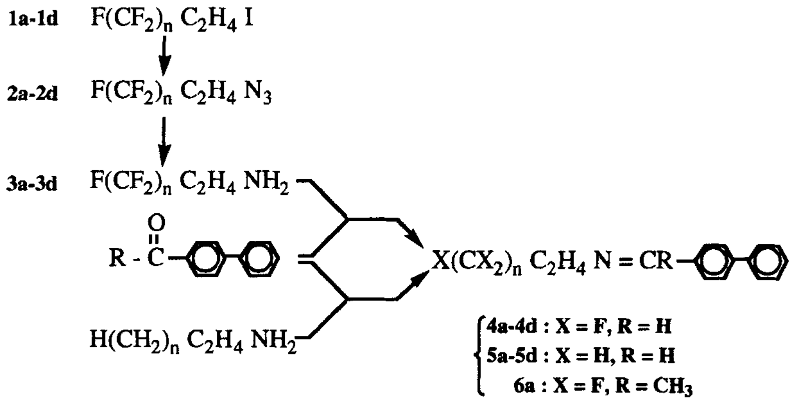

FIGURE 1 Procedure for the synthesis of compounds 4a–4d, 5a–5d and 6a.

room temperature until the disappearance in gas phase chromatography of starting products derivated from 4-biphenyl (4–12 hours). Then, the solution was concentrated under reduced pressure and the product was collected as a solid precipitate. Two or three recrystallizations from absolute methanol (4b–c, 5a–d, 6a), diethyl ether (4d) or purification by distillation (4a) afforded the pure product (yield 82–92%).

^{1}H NMR ($CDCl_3$/TMS), δ(ppm), J(Hz); 4a–4d: 2.5 (Tt, 2H, $C\underline{H}_2-R_F$, $^3J_{H-F}=18.8$, $^3J_{H-H}=7.6$), 3.9 (*t*, 2H, $C\underline{H}_2-N=$, $^3J_{H-H}=7.6$), 7.2–7.8 (*m*, $9H_{arom.}$), 8.4 (*s*, 1H, $C\underline{H}=N$); 5a–5d: 0.9 (*m*, 3H, $C\underline{H}_3$), 1.3 (*m*, $2(n-3)$H, $(C\underline{H}_2)_{n-3}$), 2.55 (*m*, 2H, $C\underline{H}_2-CH_2-N$), 3.6 (*t*, 2H, $C\underline{H}_2-N=$, $^3J_{H-H}=6.9$), $7.2-7.8$(*m*, $9H_{arom.}$), 8.3 (*s*, 1H, $C\underline{H}=N$); 6a: 2.3 (*s*, 3H, $C(C\underline{H}_3)=N$), 2.6 (Tt, 2H, $C\underline{H}_2-R_F$, $^3J_{H-F}=18.9$, $^3J_{H-H}=7.8$), 3.8(*t*, 2H, $C\underline{H}_2-N=$, $^3J_{H-H}=7.8$), $7.2-7.8$ (*m*, $9H_{arom.}$);

^{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: -81.3 (CF_3), -114.5 ($CF_{2\alpha}$), -122.4 ($CF_{2\beta}$), $-$ 123.3 to -124.0 $(CF_2)_2$, -126.5 ($CF_{2\omega}$); 4c: -81.3 (CF_3), -114.3 ($CF_{2\alpha}$), -122.5 (3*CF_2), -123.3 to -124.3 (2*CF_2), -126.6 ($CF_{2\omega}$); 4d: -81.3 (CF_3), -114.1 ($CF_{2\alpha}$), -122.3 (5*CF_2), -123.3 to -124.3 (2* CF_2), -126.6 ($CF_{2\omega}$);

IR (KBr film): 1660, 1640, 1100–1220;

MS (70 eV), m/z (%) examplified for 4b: 527 (100%), 208 (9.7), 194(11.2), 180 (13.1), 169 (2.1), 119 (3.0), 69 (12.0).

3. RESULTS AND DISCUSSIONS

Figure 2 illustrates the curves obtained from differential thermal analysis. All data obtained from heating, cooling curves and concerning the temperature range of the mesophase are collected in Table I. The lengthening of the hydrocarbon chain results in an increase in melting point. When the two series, which differ only by the nature of the aliphatic chain, fluorinated (4a–4d) or hydrocarbon (5a–5d), are compared, we observe an unusual behavior. The monocatenar structures, within the hydrocarbon series, do not have a liquid crystal behaviour which can be observed. Nevertheless, it is worth noting that this result in not surprising when compared with many works published concerning 4-biphenyl. The variation of the nature of the connector of type ether [10], ester [11], thioether [12], ketone [13] and others [14], does not show, according to their authors, thermotropic mesomorphism. The same behavior has been seen when the hydrocarbon aliphatic chain is directly connected to 4-biphenyl [15]. Conversely, in our

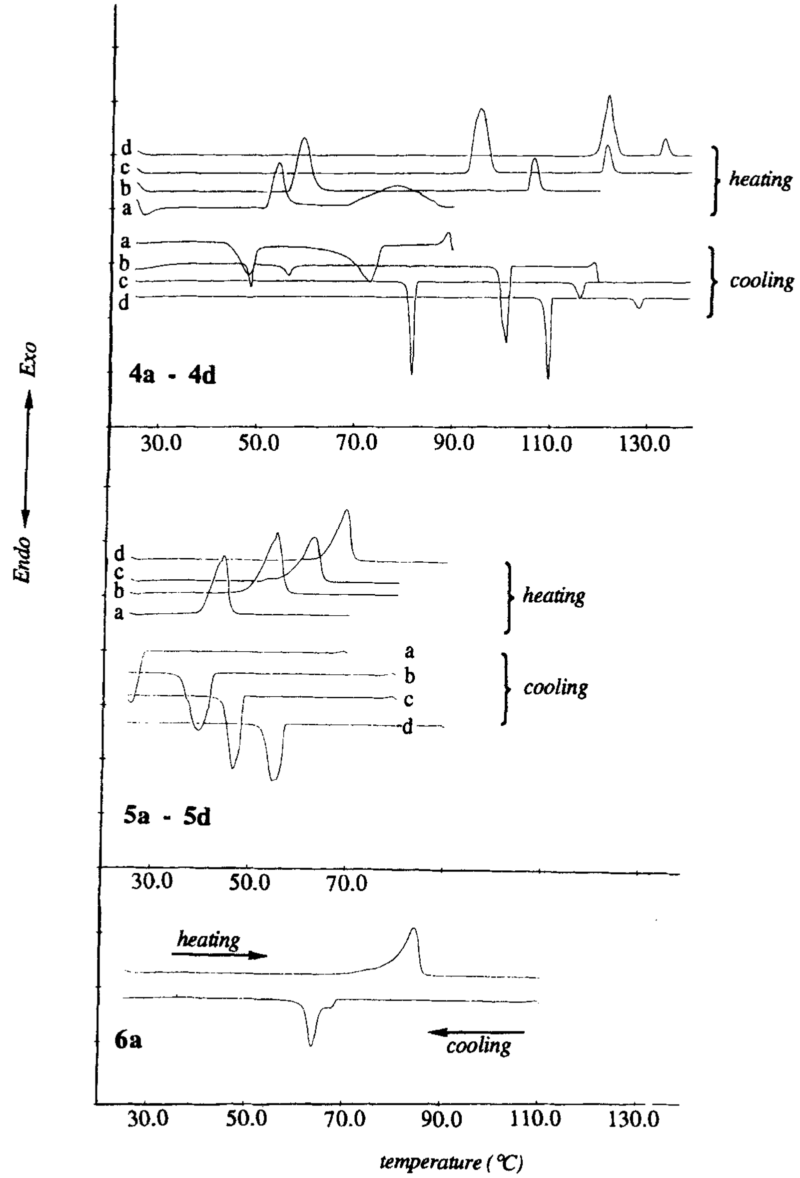

FIGURE 2 DSC curves for compounds 4a–4d, 5a–5d and 6a.

work, the presence of a fluorinated tail with the same length as their hydrocarbon analogues generates a liquid crystal behavior. This unusual result is remarkable. In the past, many studies have been undertaken in order to increase understanding concerning the influence of the replacement

TABLE I Phase transition temperatures and yields obtained from series 4, 5, and 6

Cpd N	*n value*	*Yield(%)*	*transition temperatures (°C)* *heating*	*cooling*
4a	4	66†	K 52 S1 76 I	I 72 S1 50 S2 25* K
4b	4	73†	K 57 S1 105 I	I 101 S1 57 S2 (49 S3)‡ 52 K
4c	8	70†	K 93 S1 120 I	I 117 S1 83 K
4d	10	54†	K 119 S1 132 I	I 129 S1 110 K
5a	6	82	K 45 I	I 28 K
5b	8	85	K 55 I	I 39 K
5c	10	87	K 62 I	I 47 K
5d	12	84	K 70 I	I 56 K
6a	6	72†	K 81 I	I (75 S1)‡ K

(†)Yield from 2-(F-alkyl)ethyl iodides (three steps).
(‡) Monotropic transition.
*Not observed by DSC.

of hydrogen atoms by fluorine atoms on an aliphatic chain. All the results obtained from compounds containing perfluoroalkyl chains, concerning the thermotropic mesomorphism, are different to those achieved from structures having one or two fluorine atoms or a trifluoromethyl group. These last structures show interesting characteristics for display devices. It has been seen that increasing the number of fluorine atoms could produce a favorable effect on the physico-chemical properties notably the viscosity or the dielectric characteristics [16]. It is worth noting that in the most studied cases, within the perfluorinated series, it appears that the introduction of fluorine atoms induces the suppression of the nematic or cholesteric phase [17], when it exists, and the increase in thermal stability of mesophases and the temperature range of smectic phase [18]. Nevertheless, it appears, according to Fialkov *et al.* that the total substitution of hydrogen atoms by fluorine atoms on the tail of the derivatives of 4-benzoic acid leads to the total suppression of the liquid crystal behavior observed with their hydrocarbon analogues [19]. So, it seems that this unusual mesomorphism shown by the structures 4a–4d is directly connected to the presence of a perfluorinated chain which is chemically and thermally more stable, but also to an ethylenic spacer. It appears that the presence of a methylene group is necessary to intensify the thermotropic mesomorphism which is absent when the fluorinated chain is directly connected to the mesogen unit. For example, when the perfluorinated chain is directly linked to 4-biphenyl, any mesomorphic property has been observed by their authors [20] and has been explained in function of the methylene group number as spacer between the fluorinated tail and the rigid core [21]. So, the introduction of the perfluorinated chain, notably partially fluorinated, can be considered as an interesting alternative for the obtaining of smectic phases: Janulis *et al.* have shown the influence of a such spacer on the nature of the mesomorphic phase notably for the obtention of smectic C behavior [22].

The phase diagrams obtained on heating and cooling for the F-alkylated series (4a–4d) are illustrated by Figrue 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 units in the fluorinated tail. An oscillation is observed for the smectic isotropic transition. 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 increases ($n > 4$). The structures incorporating F-butyl and F-hexyl are polymorphic liquid crystals, which have two or three smectic mesophases, respectively, between the crystal and the isotropic liquid phases, in comparison with the compounds containing a perfluoroctyl or perfluorodecyl chain which present a monomorphic smectic mesomorphism. By optical microscopic observation, the mesophases of all members of this series 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 characteristic textures of observed phases are illustrated in Figure 4.

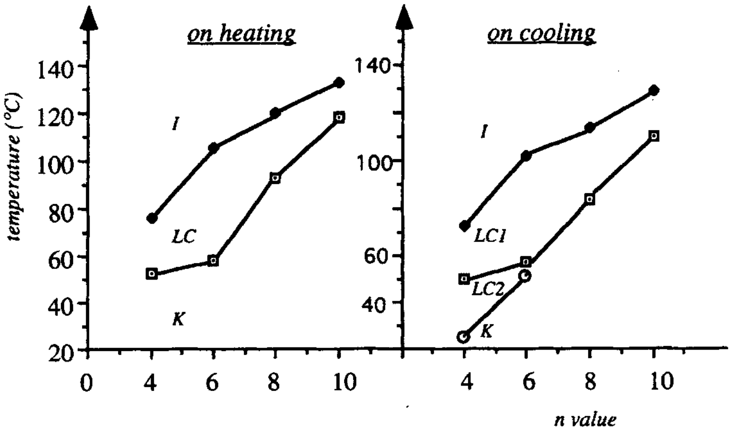

FIGURE 3 Phase diagrams for compounds 4a–4d.

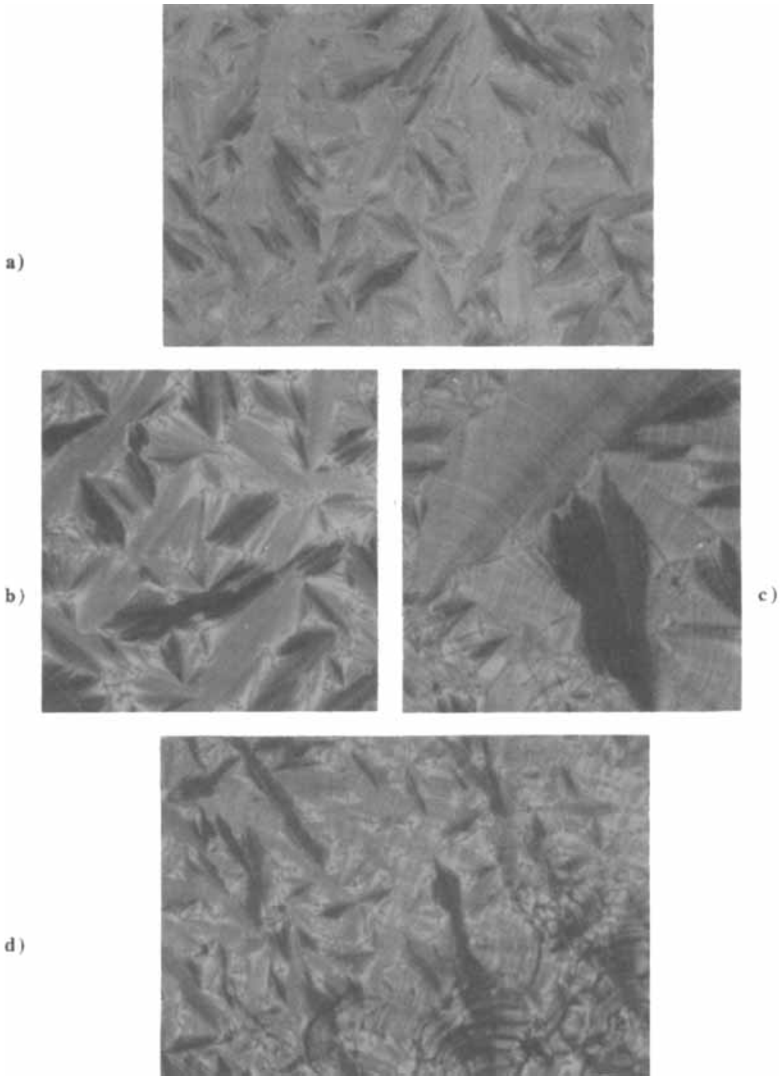

FIGURE 4 Optical polarizing micrograph displayed by the fluorinated series (4a–4d) on cooling from the isotropic melt; a) $n = 10$, $T = 112°C$(S1); b) $n = 8$, $T = 80°C$ (S1); c) $n = 6$, $T = 49°C$ (S2); d) $n = 6$, $T = 28°C$ (transition S2 to K). Note the stripe pattern in c) and d). (See Color Plate II).

Furthermore, we are interested in the nature of the connector. The introduction of a methyl group on the imine function suppress the mesomorphic structure observed for the compound 4b, leading to a monotropic behavior in which the appearance of mesophase is related of the scanning rate on cooling from the isotropic state. This behavior is shown clearly by the recording of DSC spectra represented by Figure 2. It would seem that, for these structures, the shape of the connector has a great influence on the stability of the mesophase. At the present time, these results allow us, within our laboratory with a systematic approach, to study the influence of the nature of the chemical function, linking the perfluoroalkylethyl moiety to the rigid core, on the thermotropic mesomorphism.

4. CONCLUSION

The synthesis of a series of partially fluorinated liquid crystals has been reported. Some examples have shown, in the past, that the introduction of perfluorinated chain could lead to the suppression of the liquid crystal character. We report, for the first time, in this work, on the great effect of the introduction of 2-(F-alkyl)ethyl chains connected to 4-biphenyl through a Schiff's base. Even though their hydrocarbon analogues are not mesomorphic, the overall compounds of the F-alkylated series have a smectogenic enantiotropy within a wide temperature range. Smectic enhancement through incorporation of fluorine into the tails of a liquid crystalline system appears to be quite general in this series of compounds. The decrease in number of fluoromethylene groups leads to a thermotropic polymorphism notably remarkable for F-butyl or F-hexyl. However, the introduction of the methyl group, branching the spacer, strongly reduces the stability of the mesophase and leads to a monotropic behavior. The chemical and thermal stability of fluoroalkyl groups and their mesophase, respectively, allow us to consider them as new liquid crystal materials and to increase the value of the 2-(F-alkyl)ethyl moieties as noteworthy precursors in this field.

Acknowledgments

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