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Highly fluorinated thermotropic liquid crystals: an update

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Abstract

Fluorine is used in liquid crystal materials in order to give them particular properties as compared to their hydrocarbon homologues. This leads to use of the new compounds as materials mainly in display devices such as Twisted Nematic Liquid Crystals Display (TNLCD) or for the development of Surface Stabilized Ferroelectric smectic C* display (SSFLCDs). In this paper, we describe recent studies and research effort concerning the liquid crystalline behavior of compounds incorporating a highly fluorinated part with more than one fluoromethylene units. We examine some of their mesophase properties and the impact of molecular shape on the resulting liquid crystal behavior. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Liquid crystal materials; Perfluorinated; Smectic; Ferroelectric

1. Introduction

The use of organofluorine compounds has generated much research effort. The replacement of one or several hydrogen atoms by fluorine confers to the resulting material unusual and peculiar properties which allow their use as good precursors with many applications: surface coating, fire retardants, biomedicine and much research has contributed to increase the knowledge of these compounds within the field of Molecular Organized Systems (MOS). From these, research has been carried out on mono or polyfluorinated compounds having liquid crystal (LC) character. The impact of fluorine in this field has been, up to now, little studied. This correlates with the relative difficulty to have the raw fluorinated materials available commercially. Despite this, intensive research has been carried out within this field over the last five years. Their use is not limited to laboratory research but assumes a particular interest since the discovery of ferroelectricity in liquid crystals.

We will describe, first, the terminology inherent to the liquid crystal field, then we will present the fluorine hypothesis, and in final step the description of the overall highly fluorinated or polyfluorinated structures with one or more number of fluoromethylene units against their impact on academic research or as potential materials within the ferroelectric liquid crystal field.

This present review, covering the literature from the end of 1995, concentrates on calamitic (rod-shaped) thermotropics (liquid crystals which change with heat) as compared to discotic [1], on low molecular weight compounds (polymers [2,3] or copolymers [4] will not be discussed) and will emphasize developments which have occurred since the beginning of 1992. For completeness, selected references are included to the earlier literature.

2. Thermotropic liquid crystals: definition

The term liquid crystal is used to describe a state which occupies an intermediate position between true solids (crystals) and true liquids (isotropic). This thermodynamic phase appears as a definite region on the phase diagram but is not however thought of as a fourth state, rather as a transition between the two states solid and liquid. It is a state in which the molecular order exhibits a size range similar to that of a crystal with the viscosity varying from that of oil to water. The terms mesophase and mesomorphous state can also be used to define this state. A mesogen is the molecule or a part of it, which gives rise to a mesophase. To completely

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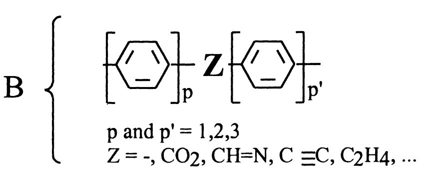
describe the liquid crystalline state, an optical investigation of morphology and typical structural characteristics using a polarizing microscope is required [5,6]. Mixing with a known mesophase will often confirm the assignment, since two identical mesophases are normally miscible. Further confirmation and assignment require differential scanning calorimetry (DSC) and low angle X-ray scattering in the mesophase. The basic structural information available on liquid crystals is that of texture, this is the analogue of morphology in the solid state. The term texture can be described as the total of topological elements sufficiently large to be seen by a polarizing microscope. All textures depend on short range molecular order, which is in itself dependent on the molecular structure. The two groups of liquid crystals, thermotropic and lyotropic, can be distinguished by their method of formation. Lyotropic liquid crystals are formed by the dissolution of solid crystals in certain solvents to form a concentrated solution. The stability of these last mentioned depends on both their concentration and the temperature. Lyotropic liquid crystals so formed will form a isotropic liquid on sufficient dilution. These compounds are of great scientific and biological interest, and mesophases are found in a large number of biological materials [7,8]. It is worth noting that the introduction of a perfluorinated tail leads to a particular MOS as compared to their hydrocarbon homologues [9–11]. Thermotropic liquid crystals, which we are going to discuss, appear as a function of the temperature. They are formed either by cooling isotropic liquids below the point of clarification (clearing point) or by heating solid crystals above the melting point. These thermotropic liquid crystals can be classified into two types, those which can be reached by both heating and cooling, i.e., those for which the formation is reversible, are called enantiotropic. In those for which the process is irreversible: the liquid crystal phase can only be reached from one direction in the thermal cycle, they are called monotropic. In a thermotropic mesophase, varying degrees of positional order are lost, giving fluidity, while orientational (supramolecular) order is retained, giving the anisotropy. A consequence of this anisotropy is that mesophases can have two (or even three) different refractive indices, magnetic susceptibilities and electric permittivities. As a result, some thermotropic molecules can be oriented by applied electric or magnetic fields. This is the basis of their considerable applications. Thermotropics can be further subdivided into calamitic (rodlike) and discotic (disklike). We will pay attention to the first which are classified as nematics (N) and smectics (S). In the least ordered phase, the nematic, the rodlike molecules line up approximately parallel to each other, along a direction defined by the director, *n*. The transition from the crystalline state (Cr) to the nematic phase (Cr → N) is often associated with an enthalpy change about ten times greater than the nematic to isotropic (I) transition (N → I). The introduction of a chiral center into a nematic molecule can give rise to cholesteric behavior, where the director is now helical. Smectic liquid crystals form a variety of layered phases, which offer additional order over that found for nematics, so-called S_A, S_B, S_C...[12].

Normally, the chemical structure of organic compounds possessing calamitic liquid crystal characteristics can be denoted by

$$A-B-C,$$

where A and C are terminal groups (including, if necessary, a chiral center or frequently a polar function) and B represents the rigid core, often made up of aromatic rings connected by linking group Z (i.e., CO_2, CH=N, C_2H_4,...) as described below.



The resulting rodlike polarizable core, together with the flexible end chains, increases molecular anisotropy and facilitates liquid crystal formation.

The mesomorphic structure depends on many factors: mainly the linear molecular shape but also on the position and strength of the polar groups and the presence or absence of a chiral center within the molecule as well as on the molecular interactions of the molecule, e.g., dipole–dipole interactions and hydrogen bonding. The compounds considered in this review allow further investigations of these factors.

3. The fluorine hypothesis

3.1. Why introduce fluorine?

The introduction and the choice of the fluorine atom position within liquid crystal systems allow formation of materials which present a considerable technological interest [13] for display [14] or non-display [15] applications: the nematics and smectics.

The involvement in the nematogenic devices is generally obtained from the introduction of fluorine on to the rigid core [16] so-called fluoro-substituents. In fact, the properties required are those for materials used in the electronic industry: optical and chemical stability, wide mesomorphic temperature range, low melting point, low viscosity and low conductivity. Much attention is paid in the nematogen design based on fluorinated systems because they have low conductivities and viscosities. Furthermore, the controlled choice of the position of fluoro-substituents allows tailoring of appropriate dielectric anisotropies for commercial applications [14].

On the other hand, the ferroelectric smectogens can also be obtained with fluoro-substituents or by the introduction of a highly fluorinated part. The development of ferroelectric liquid crystal materials requires [17] low viscosities, wide mesophases and low melting points. Fluorine substituents are of major interest for these requirements.

The use of fluorine within liquid crystal materials can prove useful as short term prospects as interesting alternatives to avoid defaults or instabilities asserted in hydrocarbon series. In fact one of the most important points for potential use as liquid crystal materials is, the wide temperature range of mesomorphism, with enantiotropy and reproductibility during the phase transition phenomena, but also chemical stability. The perfluorinated species are chemically stable and can, in suitable cases, dope the stability of the resulting mesomorphic phases.

3.2. *Where to introduce fluorine atoms?*

From the description of classical rodlike liquid crystals (see Section 2), the introduction of fluorine atoms can be effective on each molecular groupings as described in Fig. 1 specifically, they can be introduced

i. on the main aliphatic core (see part 4),
ii. on the rigid core,
    - between the rings [18],
    - on the aromatic rings [19–26],
iii. in the chiral center [27,28],
iv. near the chiral center or as a polar head group [29].

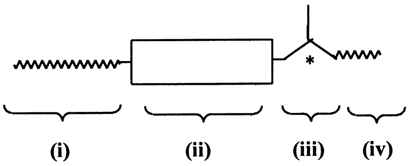


Fig. 1. Different features of rodlike liquid crystals.

Furthermore, fluorine atoms can be introduced, in several parts at the same time : e.g. (ii) + (iii) [30,31]. Examples of molecules (compounds **1–6**) to illustrate these points are given in Fig. 2.

The introduction of a fluorine atom instead of hydrogen in the so-called fluoro-substituent has been described in several papers, and a recent review describes their effect on the liquid crystal behavior [41]. Little attention has been paid on the influence of fluorine in (i) or (iv) moiety [42]. The aim of the present paper is to focus our attention on highly fluorinated liquid crystals which include a tail such as –$(CF_2)_m$ with "*m*" more than one.

4. Within highly fluorinated series

In all cases, the studied tails are linear because, as Misaki et al. have noted, this design generates, when it can be observed, a wider smectogen range than the branched tails [43].

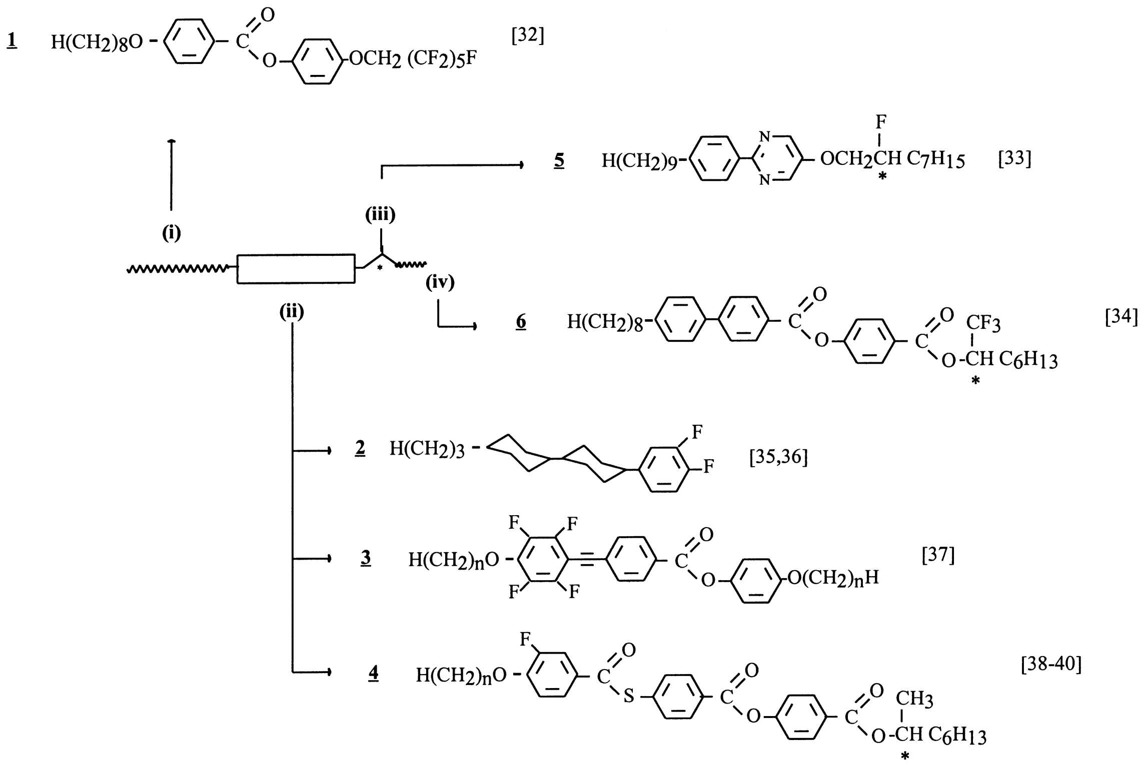


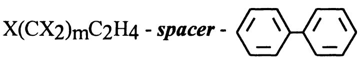
Fig. 2. Example of molecules versus position of fluorine atom in the molecular shape. [32–40]

4.1. Academic studies

4.1.1. Polycyclic

The simplest polycyclic core referred to in Section 2 is when Z does not exist and is found in biphenyl derivatives which have commercial application for the preparation of room temperature nematic liquid crystals [44,45]. For the 4-biphenyl derivatives mainly two facts were studied: the impact of the perfluorinated tail and the influence of the spacer.

1. Influence of the introduction of a perfluorinated tail as compared with their hydrocarbon homologues. When two series, which differ only in the nature of the aliphatic chain, hydrocarbon (**7**,**8**) or fluorinated (**9**,**10**) are compared [46–48], we observe an unusual behavior. The hydrocarbon series do not have an observable liquid crystal character as compared to the fluorinated compounds. Nevertheless, it is worth noting that this result is not surprising when we examine the literature on 4-biphenyl derivatives. Variation of the connectors of type ether, ester, thioether, ketone [49,50], within the hydrocarbon series does not show, according to those authors, thermotropic mesomorphism. The same behavior has been seen when the hydrocarbon aliphatic moiety is directly connected to the 4-biphenyl unit. Conversely, the presence of a fluorinated tail with the same length as their hydrocarbon analogues generates liquid crystalline behavior. In the past, many studies [51–59] have been undertaken in order to increase understanding of the influence of the replacement of hydrogen atoms by fluorine atoms on an aliphatic chain on thermotropic mesomorphism. All the results obtained from the compounds containing perfluoroalkyl chains are different from those for structures having only one, two or three fluorine atoms. It has been seen that increasing the number of fluorine atoms produces a favorable effect on the physico-chemical properties, particularly viscosity or the dielectric constant [60]. It is worth noting that in the most studied cases, within the perfluorinated series, it appears that the introduction of fluorine atoms induces suppression of the nematic or cholesteric phase [61], when it exists, and increases the thermal stability of the mesophases and the temperature range of the smectic phase [62]. Nevertheless, it appears, according to Fialkov et al. that the total substitution of hydrogen atoms by fluorine atoms on the tail of derivatives of 4-benzoic acid leads to the total suppression of the liquid crystalline behavior observed with their hydrocarbon analogues [63]. So, it seems that the unusual mesomorphism shown by the structures **9** and **10**, is directly connected not only to the presence of a perfluorinated tail which is chemically and thermally stable, but also to the 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 group, no mesomorphic property has been observed [64] and this property has been explained as a function of the number of methylene groups as spacer between the fluorinated tail and the rigid core [65]. So, the introduction of the perfluorinated chain, particularly partially fluorinated, can be considered as an interesting alternative for obtaining smectic phases. Janulis et al. have shown the influence of such a spacer on the nature of the mesomorphic phase notably for obtaining a smectic C phase [32].

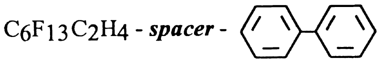


spacer = -N=CH-; -SC(O)-

7,8 X = H; m=4,6,8; Cr ⟷ I

9,10 X = F; m=4,6,8; Cr ⟷ LC ⟷ I

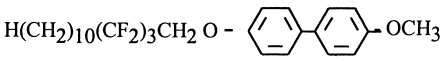
2. Intrinsic impact of the spacer bonding the semifluorinated tail to the 4-biphenyl moiety. Evaluation of the mesomorphic behavior of 4-biphenyl derivatives, incorporating different spacers bonding the mesogenic core to the fluorinated tail, shows some interesting properties and highlights some peculiar properties for the overall structures. Some spacers like amide **11**, **12** or thioether types **16** as well as hemithioacetal derivatives **15** give total suppression of smectic character. Others like the ester spacers of type –OC(O)– **14** lead to a very short range smectic behavior or for the esters with a C(O)O spacer **13**, ether **17**, imine **9b** or thioester **10b** compounds to a broad range enantiotropic S_A behavior, and in one case (**17**) with an additional smectic E phase. The data collected from the synthesized biphenyl derivatives leads first to confirm about the enhancement of the smectic properties because of the perfluorinated tail, but also shows the impact of the spacer on those properties which can increase the smectogenic potential of the fluorinated tail. It is clear from the above results [66–68] 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 behavior.



	spacer	transition temperatures on heating
9b	-N=CH-	Cr 57 S_A 105 I
11	-NHC(O)-	Cr 175 I
12	$-N(CH_3)C(O)-$	Cr 87 S_A 90 I
13	-C(O)O-	Cr 80.5 S_A 113.2 I
14	-OC(O)-	Cr 70.5 S_A 72 I
10b	-SC(O)-	Cr 51.6 S_A 152 I
15	$-SCH_2O-$	Cr 71.6 I
16	$-SCH_2-$	Cr 59.7 I
17	-O-	Cr 81.4 E 96.1 S_A 105.5 I

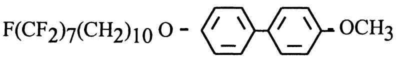
The study of polyphilic compounds **18–20** leads to understanding of the segregation of these chemical fragments onto the molecular design [69,70]. The molecule with a central hydrocarbon moiety **19** exhibits only an S_A phase with interdigitation of the aliphatic and aromatic parts and can be considered as a biblock compound: perfluorinated and hydrocarbon (both aliphatic and aromatic), as compared to the structures **18** and **20**, where the position and the nature of the perfluorinated tail lead to well segregated arrangements. From the polyphilic concept, some other compounds have been synthesized from 4,4′-cyanobiphenyl derivatives and incorporating a carboxylic acid function at the omega position in order to induce a multi-block arrangement from hydrogen bonds [71].

18



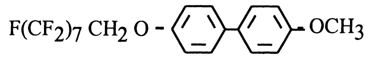
Cr 60.0 S_E 87.5 I

19



Cr 123 S_A 145 I

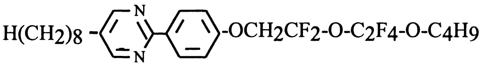
20



Cr 72 S_E 138 S_A 168 I

In a more recent study, some other compounds derived from phenylpyrimidine with one alkyl and one polyfluoroalkyl end group such as **21** synthesized at 3 M Corporation [72] allow some interesting studies on the critical heat capacity at the S_A–S_C transition [73].

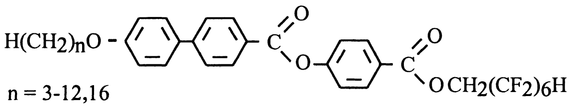
21



$S_C \longleftrightarrow S_A \longleftrightarrow I$

For compounds **22**, lengthening of the hydrocarbon tail leads to decrease in the span of the mesophase (88.1°C for $n = 3$ to 46.7°C for $n = 16$). In this series, the mesogens with a short terminal hydrocarbon chain, $n = 3$, 4 possess a wide monophasic mesomorphic range of type A. Lengthening of the hydrocarbon tail and more particularly when "n" is up to 5 leads to the appearance of a broad enantiotropic S_C phase to the detriment of the S_A phase. For the last member of the series $n = 16$, only a S_A phase appears [74].

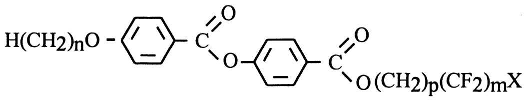
22



n = 3-12,16

For the compounds **23** derived from phenylbenzoate, the introduction of fluorine leads to emphasis of the S_C phase. When the fluorine is introduced in the terminal position, an enantiotropic S_C phase appears for all members of the series. Increase of the perfluorinated tail leads to suppression of the S_A phase, and as a consequence direct transition from S_C to I occurs [75].

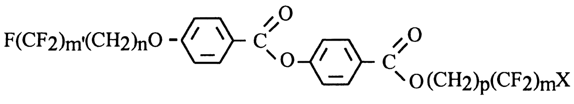
23



p/m/X=1/3/F, 1/4/H, 2/6/F; n=6-14

For compounds **24** when n is even, both S_A and S_C mesophases exist, whereas when n is odd, there is only the S_C mesophase. The exclusive presence of smectic A and C phases is stabilized by the perfluorinated moiety and the dibenzoate core. Increase of fluoromethylene units leads to an increase in the clearing temperature [76].

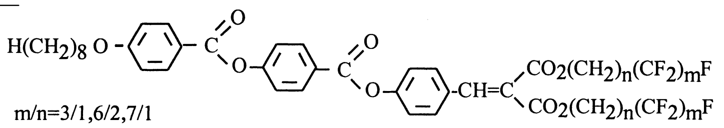
24



p/m/X=1/3/F, 1/4/H, 2/6/F; n=4-6; m'=4,6

Another molecular shape that has been studied is highly fluorinated swallow-tailed compounds **25** and **26**. Only the substance with one methylene unit ($n = 1$) between the carboxylic groups in the swallow-tail (**25a**), has a short nematic phase above the smectic phase. There is an increase of the clearing points and a stabilization of the smectic phases compared to the non-fluorinated swallow-tailed compounds. The mixture of **25** and **26** leads to design dimer pairs with dipoles in one direction. However, the observations do not indicate ferroelectricity [77–79].

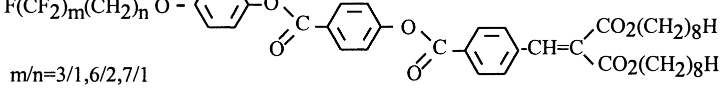
25



m/n=3/1,6/2,7/1

25a m/n=7/1 : Cr 119 S_C 137.8 S_A 143 N 147.2 I

26



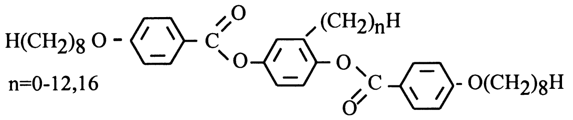
m/n=3/1,6/2,7/1

26a m/n=7/1 : Cr 59 (S_X 56.1) S_C 68.3 S_A 154.8 I

To obtain a nematic phase, a side-chain is often added to a calamitic structure, within a hydrocarbon series (**27**). In the case of fluorinated series, compounds **28** and **29**, the introduction of a side-chain (methyl or *n*-alkanoylmethylene) has no effect on the nucleation of the nematic phase. It seems that microsegregation between the fluorinated part and hydrocarbon moiety in the main axis governs the order of the layer. However, the presence of a lateral substituent allows a decrease of the S_C–S_A transition and stabilizes, at the same time, the S_A mesophase [80]. This is in contrast with the fact that the side-chains disrupt smectic layering and stick out again the high potentiality smectogenic to the *F*-alkyl chain which can occur to the detriment of the other phase.

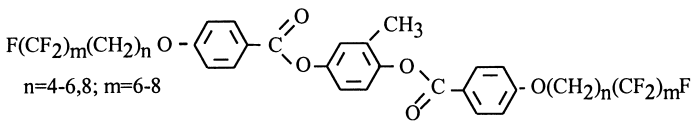
In the side-chain substituted mesogens (**30**–**33**) with an *F*-alkylalkoxy chain in the terminal position leads to an increase of the clearing points and a stabilization of the smectic phase as compared to the hydrocarbon homologues [81]. The position of the *F*-alkyl tail **30** or **31** of the molecule has only a small effect on the height of the transition temperature and none on polymorphism in these series. As Janulis et al. have observed, the introduction of a fluorinated tail instead of an hydrocarbon chain stabilizes the smectic phase to the detriment of the nematic phase. In fact, exchange of the perfluorinated tail by an octyloxy group in compound **32** yields the appearance of a nematic phase.

27



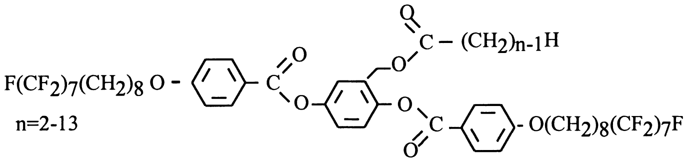
$Cr \leftrightarrow N \leftrightarrow I$

28



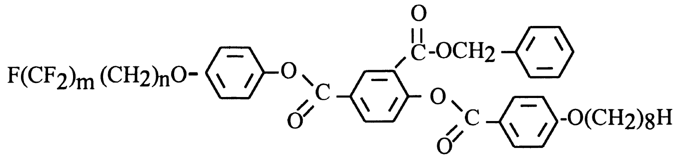
$Cr \leftrightarrow S_C \leftrightarrow S_A \leftrightarrow I$

29



$Cr \leftrightarrow S_C \leftrightarrow S_A \leftrightarrow I$

30



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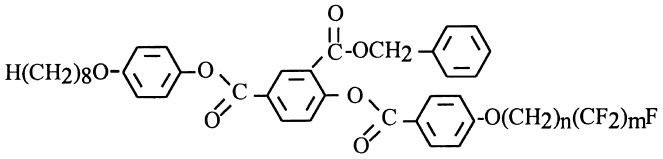

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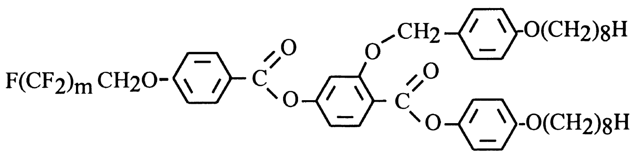

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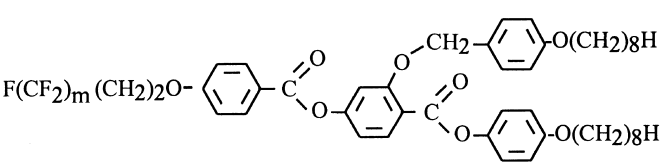
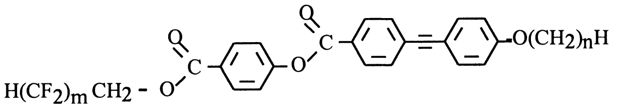


m=3,6-9,11; n=1,2

Other work has led to synthesize twin molecules which consist of symmetric bimesogenic parts bonded by a spacer. These compounds **35–37** have not exhibited liquid crystalline properties, but have been used in mixtures to lead to binary systems with particular LC behavior [82]. No liquid crystal behavior has been detected for compounds including a CF_2 unit as a spacer in the twin shape as compared to a homologous hydrocarbon spacer (**34**). The introduction of a highly fluorinated tail at the end position shows that **34** strongly changes the thermotropic behavior with the appearance of a LC phase but also a dramatic increase of the melting point (to 350°C) which prevents further investigations. These results are not due to the molecular shape (twin) but rather to the relative rigidity of the twin center. In fact, other work which has been carried out on twin molecules containing organosiloxane units with a bimesogenic part including a chiral center, leads to high spontaneous polarization (200–450 nC cm^{-2}) and high tilt angle (about 38°) over a 100°C wide temperature range and exhibits an antiferroelectric phase [83].

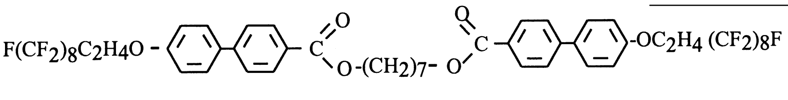
38



m=2,4,6; n=4-10,12

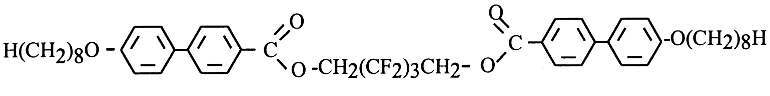
38a m/n=2/6 : Cr 122.8 S_C 150.1 S_A 208.3 I
38b m/n=4/6 : Cr 105.0 S_C 169.1 S_A 210.2 I
38c m/n=6/6 : Cr 112.8 S_C 181.1 S_A 219.1 I

34



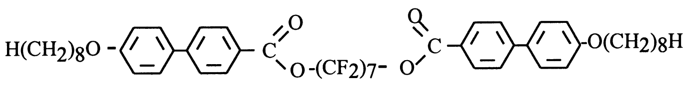
Cr 369 N > 400 I (decomp.)

35



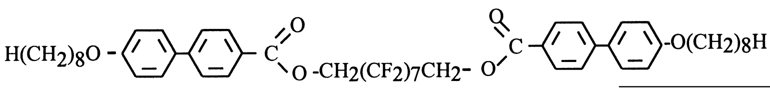
Cr 115 I

36



Cr 143 I

37

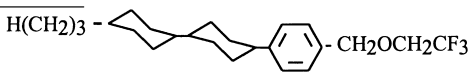


Cr 157 I

The synthesis of some toluene derivatives **38** incorporating a partially fluorinated tail with hydrogen at the omega position [84] shows that most of them exhibit an enantiotropic thermotropic liquid crystalline behavior with S_A–S_C phase transition over a wide temperature range except for compounds with low values of "*m*" and "*n*" which exhibit an S_A–N phase sequence instead of S_C–S_A transition. The increase of "*m*" part at a threshold value of four leads to the appearance of an S_B phase with the lengthening of hydrocarbon tail. It seems that the increase of the number of the difluoromethylene units stabilizes the smectogenic character but it is worth noting that at the same time an increase recorded for the temperature range of the S_C phase.

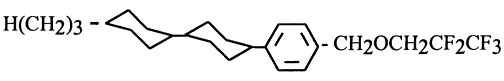
The liquid crystal benzyl fluoroalkylethers incorporating cyclohexyl units **39–42** exhibit S_B phases. The span of the mesophase is higher without the chiral center exhibiting enantiotropic behavior over 100°C for compounds **39–41**, as compared to **42** which leads to a monotropic state. The removal of one cyclohexyl ring leads to suppression of the liquid crystal character. It is worth noting that these materials exhibit low refractive anisotropy and can be used as additives for lowering the refractive anisotropy in ZLI 1132 as a nematic solvent but with a slight increase of viscosity in a 15 wt% mixture [85].

39



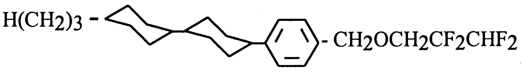
Cr 32.1 S_B 167.4 I

40



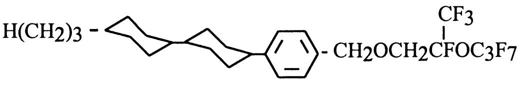
Cr 36.5 S_B 160.6 I

41



Cr 34.0 S_B 148.7 I

42

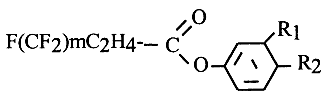


Cr 146.4 (S_B 144.5) I

4.1.2. Monocyclic

Work previously described and carried out by different groups on liquid crystals with polyfluoroalkyl or polyfluoroalkoxy chains showed enhancement of the smectic mesophase and the mesophase thermal stability. This can be correlated with the behavior of hydrocarbon homologues behavior. As a consequence, molecules with polyfluoroalkyl terminal chains became an important topic in the study of new liquid crystal materials. In recent years, it can be observed that the introduction of a fluorinated tail could decrease, for the first time, the number of aromatic rings required for mesogenicity, and lead to monophenyl derivatives exhibiting unexpected LC properties. This is remarkable because such behavior would not be expected within the hydrocarbon series without hydrogen bonds. This shows the fundamental interest of a fluorinated tail for easy access to raw precursors apparently less expensive than biphenyl derivatives.

47



$F(CF_2)_mC_2H_4-C(=O)O-C_6H_3(R_1)(R_2)$

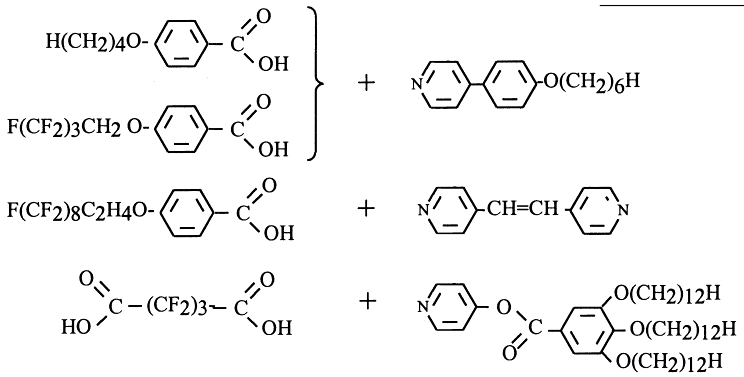
n=6,8,10 R_1=H,NO_2,CN,CH_3,F,Br; R_2=OCH_3,F,CN,CF_3, H,C_4H_9,$OC_{10}H_{21}$,OC_6H_{13}

47a n=10; R_1=NO_2; R_2=H : Cr 62 S 92 I

47b n=10; R_1=CN; R_2=H : Cr 77 S 90 I

The development of liquid crystals having a single benzene ring as the mesogenic core is of importance and current interest. Single benzene ring compounds would be expected to have low molecular anisotropy and should not readily display liquid crystalline properties.

As introduction to this part, it is important to notice that a special study has been carried out on fluorinated alkyl chains and their effect on the stabilization of hydrogen bonded liquid crystals **43**–**46**. The presence of hydrogen bonds for the appearance of mesomorphic states has been described in the past [86–89]. The association of the *F*-alkyl moiety in such a concept led us to stabilize the smectic phase [90].



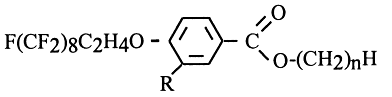
43 **44** **45** **46**

The results observed for some derivatives of 2-*n*-perfluoroalkylethyl-3 and/or 4-substituted benzoates **47** indicate the necessity to have a long perfluoroalkyl group, and a lateral substituent is indispensable and a dipole within the substituent desirable. The substituents at positions 3 or 4 can govern the existence of the mesophase. The presence of R_1 which can confer a bent structure on the molecule is indispensable, according to the authors, for a layered molecular arrangement [91].

Usually, a lateral substituent reduces the mesomorphic properties or reduces order in the molecular arrangement. In this cases the lateral substituent could induce spatial shape (bent) for nucleation of the enantiotropic mesophase **47a**–**47b**.

Another example is described with substitution at positions 2 and 4 (**48**). All the members of this series exhibit monotropic transitions. The smectic A-isotropic transition temperature and the latent heat decrease with the lengthening of the hydrocarbon tail with the total suppression of the mesomorphic character for an hexyl moiety [92].

48

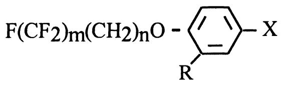


$F(CF_2)_8C_2H_4O-C_6H_3(R)-C(=O)O-(CH_2)_nH$

n=1-6; R=H,Br,NO_2

In contrast with **47** substitution (R) on the benzene ring for **49** is not necessary to achieve mesomorphism. The ability to form lamellar liquid crystals requires an hydrocarbon/perfluorinated segments (*m*/*n*) ratio less than unity when $n + m = 10$ and 12. Increasing the length $(m + n)$ of the semiperfluorinated part stabilizes the liquid crystalline phases. The wider mesomorphic range is about 12°C. For the other members which exhibit liquid crystal behavior, the mesophase appears enantiotropically over 1°C or 2°C. An unique compound which exhibits a mesophase width of 28°C with triphasic behavior is of benzoic derivatives [93]. In this case, it is not possible to consider that the wide range of the mesophase is due only to the fluorinated tail because hydrogen bonds occur, which is well known effect even for non-mesogenic precursors [86–88], and as a consequence, can mask the real fluorophobic effect. Another molecular shape has been also developed which leads to enantiotropic materials with a mesophase of over 30°C [94] based only on fluorophobic effects.

49



m=0,4,6,8
n=4,6,8,12
X=CN,NO$_2$,CO$_2$CH$_3$,OCH$_3$,CH$_2$OH,CO$_2$H,COCH$_3$
R=H,CH$_3$

The incompatibility of fluorocarbons with both saturated and aromatic hydrocarbons leads to microsegregation favorable for expressing LC behavior even in monocyclic derivatives which cannot be expected within the hydrocarbon series. However, it is important to recall that high incompatibility (oleophobic and fluorophobic effects) is enough to lead to microsegregation favorable to induction of LC phase. This fact arose, in the past and more recently, from a succession of blocks of fluoromethylene and methylene units, so-called di- [95] or tri-blocks, [96–98], and more recently functionalized di-blocks [99] such as bromo derivatives **50**.

50 $F(CF_2)_m$- $(CH_2)_n$ Br

m	n
8	2,4,6.10
10	10
12	10

As a conclusion of this part, the chemical and thermal stability of the fluoroalkyl groups and their ability to form mesophases with different spacers and molecular shapes give short term prospects for the synthesis of mesogenic chiral compounds in order to obtain new liquid crystalline materials for applications in display devices.

4.2. Application to ferroeletric liquid crystals (FLC)

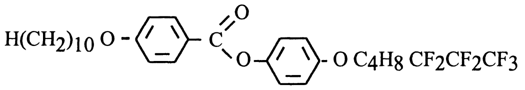
The discovery of ferroelectricity in a chiral smectic C (S_{C*}) phase by Meyer in 1975 and the proposal of electro-optical devices using ferroelectric liquid crystals by Clark and Lagerwall in 1980, have generated a great deal of interest in academic and industrial research laboratories. Subsequently, extensive studies have been made on ferroelectric liquid crystal materials and their application. In addition to high-speed electro-optic shutters, spatial light modulators working in real time, hardware for optical processing and applications requiring very high intrinsic speed in repetitive operation, ferroelectric liquid crystal technology offers the possibility to make large area, high resolution screens without the need for transistors or other active elements usually used in classical nematic liquid crystals. In principle, ferroelectric liquid crystals have the potential to do what no other liquid crystal technology could do, and are used as interesting alternatives for classical twisted nematic or super twisted nematic devices. To study the correlation between molecular structure and mesomorphic properties so as to prepare desirable materials, various molecular designs have been made, and a great number of ferroelectric liquid crystals have been synthesized. It was initially found that these materials require at least two aromatic rings in the core and two terminal chains at the end, one of which contains one chiral group. We will see, in this part, that ferroelectric properties can be obtained without a chiral center.

The previous studies highlighted the great smectogenic character of the perfluorinated tail. Association of *F*-alkylated moiety with a chiral unit via a mesogen connector appears to offer a further attractive alternative. To this aim, several series of compounds containing a semiperfluorinated tail, two or three aromatic rings and an aliphatic chiral tail at the other extremity, have been prepared. We will present work published in scientific journals but it is worth noting that due to their technological interest, many results are described through patents (for example see [100–102]).

4.2.1. With a chiral moiety

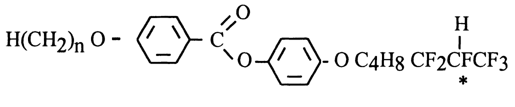
Compared to the compound **51** which exhibits a I–S_A–S_C–B–Cr phase sequence on cooling, the introduction of an asymmetric carbon in the perfluorinated chain causes the disappearance of the tilted smectic C phase (**52**,**53**). However, increase of the number of fluorine atoms on the other side contributes to the appearance of the smectic C phase, and probably stabilizes this phase with increase in the fluorine density in the molecule. The spontaneous polarization of these 4-2H-perfluoropropyl-1-butanol tail derivatives are also smaller (below 50 nC cm^{-1}) compared to 2-fluoro-octanol tail analogues [103].

51



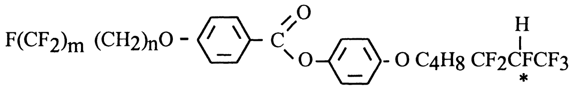
Cr (9.1 B 51.8 S_C) 66.4 S_A 104.5 I

52



n=10 : Cr 70.9 (B 46.6) S_A 80.6 I

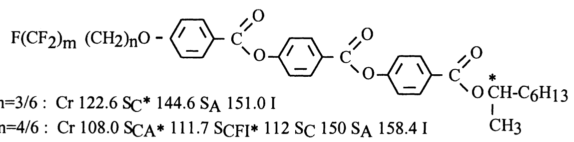
53



m/n=6/3 : Cr 80.0 (S_C or S_C* 78.0) S_A 115.1 I

It is worth noting that, within the same series, the length of the linear tail induces a modification of the phase sequence. This is the case, for example, for **54** [104]. These structures exhibit a ferroelectric S_{C*} phase and a paraelectric S_{A*} phase. In such structures, the phase sequence depends on the length of fluoromethylene and methylene sequences [105].

54



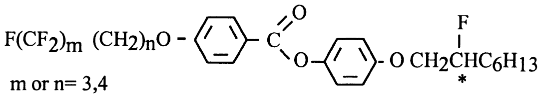
54a m/n=3/6 : Cr 122.6 S_C* 144.6 S_A 151.0 I

54b m/n=4/6 : Cr 108.0 S_{CA}* 111.7 S_{CFI}* 112 S_C 150 S_A 158.4 I

The helical pitch was found to be nearly temperature-independent. Compound **54b** shows a rather wide antiferroelectric phase as compared to compound **54a** which does not have this phase sequence. However, the tilt angle and spontaneous polarization are of the same order.

As compared to previous work [105], for compounds **55–57**, the orientation of the carbonyloxy group drastically influences the mesomorphic behavior. **56** exhibit an increase and a stabilization of the S_{C*} phase as compared to compounds **55** where stabilization of the smectic A occurs to the detriment of the S_{C*} phase which appears monotropic with a small spontaneous polarization (**55a**). The monocyclic derivatives (**57**), although showing no mesomorphic state, have been used as ferroelectric liquid crystal dopants with host liquid crystal mixtures of a series of phenylpyrimidines to lead to room temperature liquid crystal transitions with a S_{C*} phase [106,107].

55

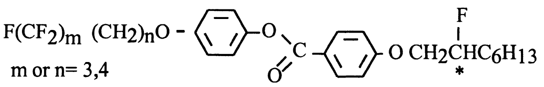


m or n= 3,4

55a m/n=4/3 : Cr (76.0 S_C*) 79.4 S_A 129.2 I

55b m/n=6/3 : Cr 83.7 S_C* 92.0 S_A 149.5 I

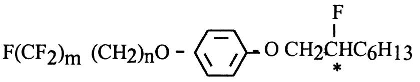
56



m or n= 3,4

56a m/n=4/3 : Cr 62.6 S_X 65.3 S_C* 103 S_A 119.6 I

57

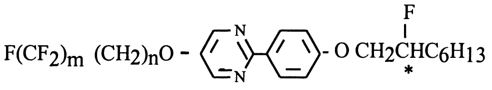


m or n= 3,4

The tilt angle increases with the lengthening of the fluorinated tail. However, even with structure **55** lengthening of the fluorinated tail contributes to stabilizing the S_{C*} phase which appears enantiotropic with six fluoromethylene units **55b** [106].

The series of compounds **58** which includes fluorine atoms both at the chiral center and at the terminal position is derived from phenylpyrimidine. The overall series exhibits an enantiotropic chiral smectic C phase. The increase of the fluorine density from the achiral part favors the chiral smectic C phase to the detriment of the smectic A phase but also shows a large spontaneous polarization in the pure state [108,109].

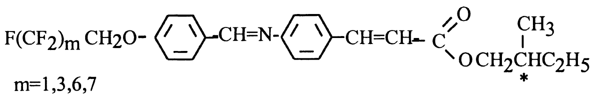
58



m = 2-4,6; n = 3-6,8,9

Work carried out from cinnamate derivatives incorporating a Schiff's base between the two aromatic rings (**59**) indicates that increasing the length of the fluorinated tail with one, three, six or seven di-fluoromethylene units enhances the stability of the smectic A phase to the detriment of the S_C phase. As compared to their hydrocarbon homologues, the introduction of fluorine atoms at the end of the linear tail stabilizes the mesophase at higher temperatures than for hydrocarbon homologues. When a smectic B phase appears in the hydrocarbon compounds, the formal substitution of hydrogen by fluorine leads to the replacement of the S_B phase by a S_C phase [110].

59

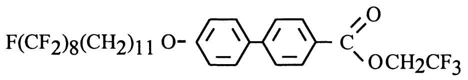


m=1,3,6,7

4.2.2. *Without a chiral center*

Achiral polyphilic molecules have been performed [111] including biaryl derivatives substituted either by two perfluorinated tails at the end position **61** [112,113] or by one perfluorinated tail and a trifluoromethyl group **60**, **62** [114]. These compounds exhibit unconventional ferroelectric liquid crystal properties. **61** is reported to have a smectic C phase with a temperature range of 19°C.

60



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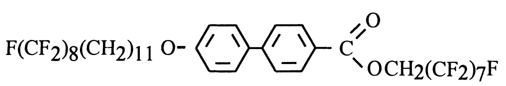

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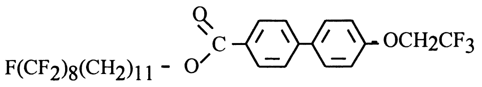

It is worth noting that the chiral center is not necessary for ferroelectric properties [115] because the molecular shape can also induce this character as for example for the case of banana-shaped molecules [116,117].

5. Conclusion

The results obtained from DSC, polarized optical microscopy, dielectric measurements, and tilt angles show, that in most cases, the association within the same molecule of a chiral center, a perfluorinated tail and a mesogenic core is an important topic for obtaining ferroelectric thermotropic liquid crystals.

The fluorine hypothesis has now been improved and leads to new developments within the liquid crystal field [118–123]. It is important to emphasize that, at the present time, only some intrinsic fluorine properties are understood in particular its strong electronegativity which allows it to be a good substituent on the mesogenic core, its strong incompatibility which allows it to induce, under special conditions, a microphasic separation in a favorable manner for the nucleation of liquid crystal properties. Furthermore, it is possible to foresee ferroelectric properties with or without a chiral center, either as polyblocks or as banana-shaped liquid crystals with or without Shiff's bases, which lead to a significant decrease in the cost of the resulting liquid crystal devices. These properties also allow for the first time, monocyclic liquid crystals without hydrogen bonding. Moreover, the organofluorinated moieties have surfactant properties which have been less described within the liquid crystal development [124] but are well known. Their particular surfactant properties occur at lower concentrations as compared to hydrocarbon compounds. For these reasons fluorinated compounds find use as autolubrication or coating materials. These surface energy properties in association with liquid crystal effect which require the formation of surface stabilized and stickiness control and adsorption will prove effective for short term prospects.

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