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Rod-like mesogens with antipathetic fluorocarbon and hydrocarbon tails

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A perfluorinated (or semi-perfluorinated) chain is affixed to various classical mesogenic moieties in lieu of the usual hydrocarbon tail. The consequences of this modification on the mesogenic behaviour are discussed by comparison with the perhydrogenated homologues. Smectic A phases are highly favoured. Their layer spacings show a trend to bilayer stacking in many cases likely to result from microsegregation among incompatible portions of the molecules.

1. Introduction

A conventional model for a mesogen is a long rod-like object sometimes detailed as formed by a rigid core with two flexible, more or less symmetric hydrocarbon tails. However numerous deviations from this simplistic model have been found in the course of the study of correlation between molecular structure and mesomorphic properties [1]. It was initially demonstrated that a simple change in the length of the aliphatic tails in classic liquid crystals can strongly influence the polymorphism [2]. Also, in recent years more sophisticated molecules in which the number, location and length of the aliphatic parts are varied on both sides of a rod-like core have been prepared. The relationships resulting from the variable ratio flexible aliphatic moiety versus rigid aromatic moiety and mesomorphism are complex and here three molecular parameters influence the structure of the mesophases in these so-called polycatenar liquid crystals [3]. Introducing disymmetry in the molecule also significantly influences the liquid-crystalline behaviour. This has been especially demonstrated by the study of polar mesogens in which the replacement of one tail by a cyano or a nitro group adds an up and down property to the molecule and leads to smectic phases with bimolecular character [4]. Notably this effect is preserved if the strong polar group is connected to the core by a medium length aliphatic segment; such molecules appear to be close to amphiphilic systems [5]. It has also been proposed that some smectic structures for side chain polymers result from the disymmetry structurally carried by the mesogenic group which is attached to the backbone on one side while the other is free [6]. The prominent role of two molecular characteristics upon the liquid-crystalline behaviour, namely the overall flexibility and the compatibility of both ends of the molecule are thus stressed by these preliminary comments.

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As shown above, these parameters have been analysed either by changing the length of the tails and/or replacing one of them by a more or less polar head. But so far no systematic study has been performed changing the nature of the flexible parts. The reason for this is that very few chemical modifications are feasible. In this framework no other tetravalent element can be substituted for the carbon atoms. For example hydrogens in R–SiH$_2$–R' are reactive and the hindrance of the methyl groups in R–Si(CH$_3$)$_2$–R' readily suppresses the mesomorphism.

The next tetra-functionalized atom is tin which is too large in its own right and the hydrogen atoms are also reactive. Thus one is compelled to keep the carbon chain and only the persubstitution of halogens for the hydrogens appears possible. In fact chlorine, iodine and bromine are ruled out owing to their steric hindrance and general lack of availability of these perhalogenated alkanes; only perfluorocarbon chains can be used instead of hydrocarbon ones [7–9].

The purpose of this paper is to present the first observations which can be deduced regarding the liquid-crystalline properties resulting from systematic substitution of one such chain on some classical rod-like cores. At this point it is also worth recalling two important characteristics of a perfluorinated chain:

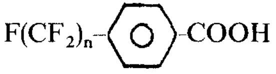
(i) The larger fluorine atoms favour an all *trans* conformation (see table 1) [10]. The actual configuration of the chain is helicoidal [11]. As a consequence of this higher order, it is much stiffer than the hydrocarbon homologue;

(ii) Fluorocarbons are known to be highly incompatible with both saturated and aromatic hydrocarbons [12].

So using perfluorinated and semiperfluorinated chains as tails for mesogenic compound should allow us to study the consequences of a step by step variation of both the flexibility and the disymmetrization of the molecule.

2. Materials

The essential intermediates used to synthesize the materials for this study are the following perfluoroalkyl and semi-perfluoroalkyloxy benzoic acids



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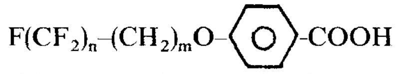


The former were prepared by a coupling reaction between 4-iodobenzoic acid and perfluoroalkyl iodide with an excess of copper in DMSO [13]

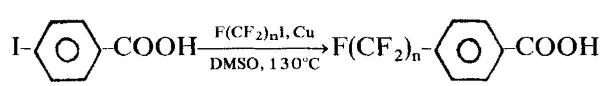
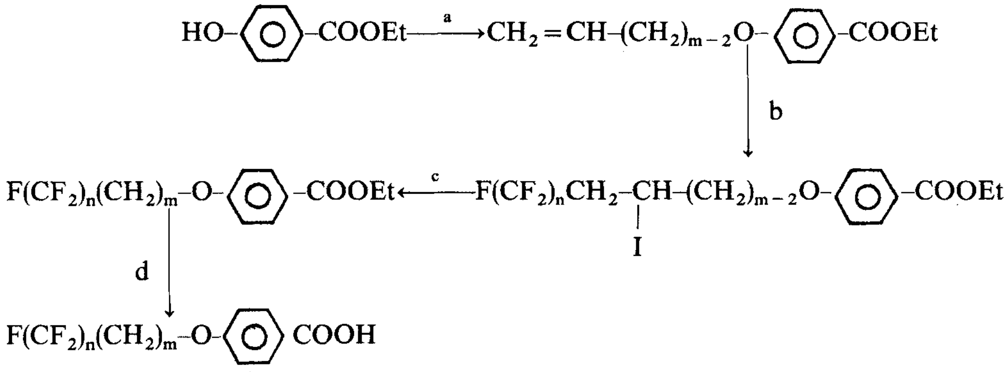


Table 1. *Trans* configuration energy (kJ mol^{-1}) of butane and decafluorobutane and their contribution ratio of *trans* and *gauche*.

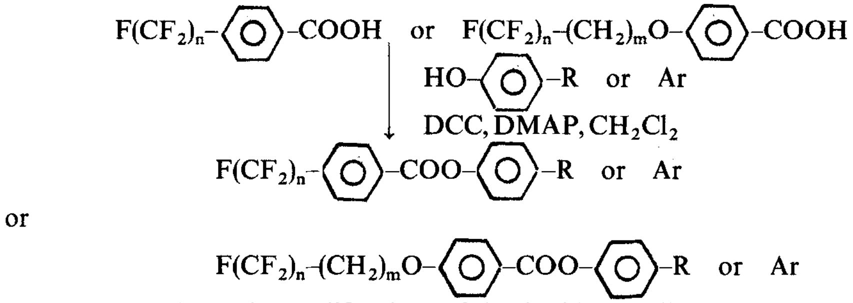
	Energy *Trans*→*Gauche*/kJ mol^{-1}	Ratio *Trans*/*Gauche*
C_4H_{10}	3·4	69/31
C_4F_{10}	9·1	95/05

The latter were prepared following the scheme [14, 15]



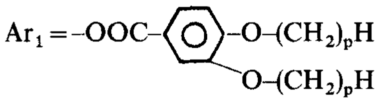
(*a*) $CH_2=CH-(CH_2)_{m-2}-Br$, KOH, EtOH
(*b*) $F(CF_2)_nI$, AIBN, Δ
(*c*) Zn, HCl(g), EtOH
(*d*) KOH, EtOH, H_3O^+

These acids can then be connected via classical methods to a variety of substituted phenols

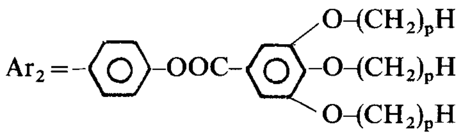


In order to evaluate the modifications of the liquid-crystalline properties induced by the fluorine chain the following substituents have been selected

$R = -O-(CH_2)_pH, -CN, -NO_2$ classic rod-like



forked rod-like



polycatenar rod-like

The synthesis of these benzoic acids and all the series will be published elsewhere.

3. Results and discussion

The phase behaviour of the various mesogens containing fluorine are given in table 2. Table 3 provides the same information for hydrocarbon homologues or for compounds differing only slightly by the length of the aliphatic parts since data on strictly similar ones are not available from the literature [16].

The comparison of the two tables is striking. All but one of the perfluorinated compounds show a smectic A mesophase while all but one corresponding hydrogenated compounds are nematic. The liquid-crystalline behaviour of these fluorinated materials is also characterized by high clearing temperatures some 80–100°C higher than for the corresponding hydrocarbon mesogens. We compared these temperatures for two series of cyano compounds (see tables 2 and 3) in the figure. In the case of a hydrocarbon chain, the evolution of the stability of the mesophase as a function of the number n of methylene units show the classic pattern: a gradual increase which eventually levels off for longer chains. In contrast, the temperatures of transition of the perfluorinated compounds increase strongly and regularly up to $n=10$ and do not

Table 2. Phase behaviour of perfluorinated and semi-perfluorinated compounds.

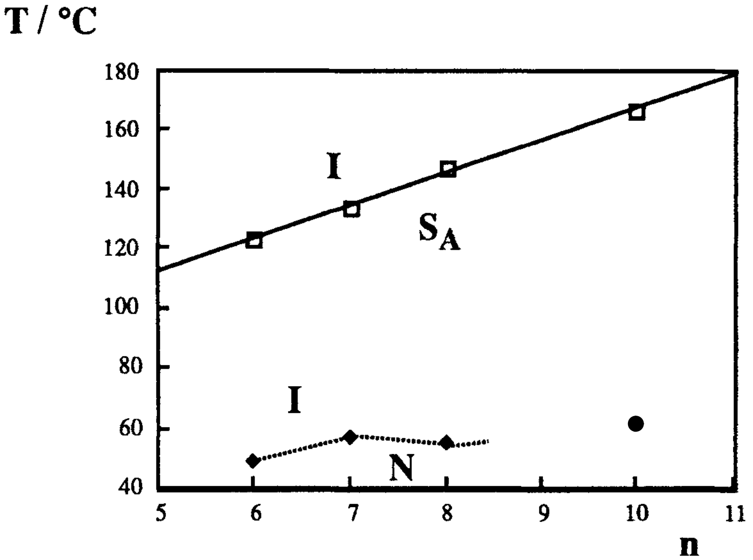
n	m	R or Ar	p	Transition temperatures/°C							Index
8	—	OCH_3	—	C			126	S_A	133	I	**1f**
7	—	OC_6H_{13}	—	C			108	S_A	117	I	**2f**
10	—	OC_6H_{13}	—	C			134	S_A	143	I	**3f**
6	—	CN	—	C			101	S_A	123	I	**4f**
7	—	CN	—	C			108	S_A	134	I	**5f**
8	—	CN	—	C			119	S_A	147	I	**6f**
10	—	CN	—	C	141	[S_C	138]	S_A	167	I	**7f**
6	—	NO_2	—	C			82	S_A	98	I	**8f**
7	—	NO_2	—	C			98	S_A	118	I	**9f**
8	—	Ar_1	10	C	105	$S_{\tilde{C}}$	109	S_A	122	I	**14f**
10	—	NO_2	—	C	107	[S_B	91]	S_A	155	I	**11f**
12	—	NO_2	—	C	118	S_B	135	S_A	168	I	**12f**
6	—	Ar_1	10	C	97	[$S_{\tilde{C}}$	87]	S_A	105	I	**13f**
8	—	Ar_1	10	C	105	$S_{\tilde{C}}$	109	S_A	122	I	**14f**
6	4	Ar_1	10	C			88	$S_{\tilde{C}}$	105	I	**15f**
6	4	Ar_1	12	C			108	$S_{\tilde{C}}$	129	I	**16f**
8	—	Ar_2	12	C			71	Cub.	108	I	**17f**

C, crystal; S_A, smectic A; S_C, smectic C; S_B, smectic B; $S_{\tilde{C}}$, modulated ribbon phase; Cub., cubic; I, isotropic liquid. [ ] indicates monotropic transition and metastable phase.

Table 3. Phase behaviour of perhydrogenated compounds.

n	m	R or Ar	p	Transition temperatures/°C							Index
—	9	ORH	1	C			53	[N	46]	I	**1h**
—	6	ORH	6	C			46·3	N	53	I	**2h**
—	10	ORH	—	C	47·1	[S_A	44·1]	N	59	I	**3h**
—	6	CN	—	C			44	N	48·6	I	**4h**
—	7	CN	—	C			44	N	56·5	I	**5h**
—	8	CN	—	C			46	N	55	I	**6h**
—	10	CN	—	C			59	N	61	I	**7h**
—	5	NO_2	—	C			48·5	[N	25·5]	I	**8h**
—	8	NO_2	—	C	50	[S_A	24	N	35]	I	**9h**
—	6-O	Ar_1	6	C			112	N	117	I	**10h**
—	CN	Ar_2	12	C					108	I	**11h**
—	12-O	Ar_2	12	C			73·4	[Cub.	60]	I	**12h**

K, crystal; N, nematic; S_A, smectic A; I, isotropic liquid; Cub., cubic. [ ] indicates monotropic transition and metastable phase.



Clearing temperatures for perfluorinated tail mesogens (**4f–7f**, S_A–I) versus analogous hydrocarbon tail mesogens (**4h–7h**, N–I).

show any sign of decreasing. It is thus clear that the lamellar structure is highly stabilized at the expense of the nematic phase by the introduction of one perfluorinated chain.

This absence of the nematic phase is surprising since stiffness is a property which is favourable to this state. Now we have to take into account in the discussion the other specific feature of these molecules which contain incompatible (antipathetic) parts. In fact a lamellar structure can be expected as a result of microphase separation among highly incompatible parts (perfluoro chains against hydrocarbon chains and/or aromatic cores). In this regard it must be noted that a previous thermodynamical and structural study of semi-fluorinated *n*-alkanes has identified several crystalline phases in these compounds depending on the respective length of each moiety; different models of antiparallel or parallel packing of the molecules have been proposed to explain the differences in the X-ray patterns [15 (*a*), 17]. The structural analysis of the smectic A phases in this work is thus of great interest since such behaviour is usually revealed through anomalies of periodicities in the stacking of lamellae (i.e. partial bilayer structures incommensurate with the molecular length or bilayer structures [4]). The results of a preliminary study of some compounds are reported in table 4. Two of them are particularly remarkable:

(i) True thermotropic bilayer structures are observed with short aromatic cores (see **6f** and **12f** in table 4);

(ii) A partial bilayer structure is observed for the first time in a pure non-polar low molar mass mesogen (see **14f** in table 4).

The qualitative comparison of the bimolecular properties of the smectic layers in fluorinated and non-fluorinated compounds are summarized in table 5. Generally speaking the trend towards bimolecular organization is stronger in fluorinated systems. However it is puzzling to note that the smectic A phase of compound **2f** is not

Table 4. Characteristics of the smectic A phase for some perfluorinated compounds of table 2.

Compound	Layer spacing	Molecular length	Ratio *d*/*l*	Smectic type
2f	30·4	29·8	1·02	Monomolecular S_{A1}
6f	41·5	24·8	1·67	Bimolecular
12f	49·8	29·4	1·69	S_{A2}
13f	59	42	1·40	Partial bimolecular S_{Ad}

Table 5. Comparison of the bimolecular properties of the smectic layers in fluorinated and hydrogenated compounds.

	Bimolecular organization in the smectic A state	
Molecular parameters	Fluorinated	Non-fluorinated
Non-polar, non-forked, short core	No	No
Non-polar, forked, long core	Yes	No
Polar, non-forked, short core	Yes	Yes

Table 6. Comparison of density (*d*) and molecular parameters (*v*: volume, *l*: length in all *trans* conformation, *s*: area of the cross-section) between a hydrocarbon and a fluorocarbon.

	Octane	Perfluorooctane
$d/\mathrm{g\,cm^{-3}}$	0·7	1·73
$M/\mathrm{g\,mol^{-1}}$	114	438
$v/\text{Å}^3$	270	420
l/(all *trans*)Å	12·6	13·4
$s/\text{Å}^2$	21·4	31·3

Table 7. X-ray diffraction results of compound **16f**.

h, *k* reflections	Reticular spacing/Å	Intensity (arbitrary units)
10	270	1000
$\bar{1}1$	—	—
01	—	—
11	100	100
$\bar{1}2$ 02	61	10000
12	—	—
03	—	—
$\bar{1}4$	32	1000

bimolecular at all. Table 6 shows a comparison of density and molecular parameters for octane and perfluorooctane. Note that the density of the fluorocarbon tail is about two and a half times the density of the hydrocarbon tail and that the ratio of their cross-sections assuming the all *trans* conformation is about one and a half. Such differences in density and molecular area would be intolerable to adjacent layers and this certainly explains why the monolayer structure is the stable one although it implies mixing of the unlike chains (fluorocarbons and hydrocarbons usually become miscible above 100°C even though they undergo phase separation at low temperature). In the case of forked compounds (see compound **14f**) adding a second aliphatic chain is likely to balance the molecular areas on both sides of the molecules, allowing then for some segregation and partial bilayer character may show up. In a study of ferroelectric liquid crystals with semi-perfluorinated chains Janulis *et al.* [18] reported incidentally the observation of a partial bilayer smectic phase. In agreement with the subject of this discussion, this result could be explained by the increase in molecular area and stiffness of the chiral tail owing to its additional methyl group on the asymmetric carbon. Alternatively, the actual separation into bilayers can be achieved in fluorinated compounds with the total elimination of the hydrogenated chain and its replacement by a strong dipole which enhances the bimolecular organization.

Another confirmation of the importance of the disymmetry introduced by the perfluorinated chains has been found by the occurrence of a modulated ribbon $S_{\tilde{C}}$ phase [19] in the semi-perfluorinated compounds **15f** and **16f**. Previously this kind of phase was known in polar thermotropic systems and is an intermediate toward a bilayer lamellar phase [2]. It is likely from textural observations that the low temperature smectic phases in compounds **13f** and **14f** are of the same type.

From X-ray diffraction studies of compound **16f**, we deduce a short range liquid-like order. But the striking feature is that we can index five scattering vectors 10, 11, $\bar{1}2$, 02 and 14 (see table 7) at small angle (if we assume a two-dimensional oblique lattice $S_{\tilde{C}}$ phase suggested by textural observations). We remark that $\bar{1}2$ and 02 scattering vectors are nearly superimposed and for example 01, $\bar{1}1$ and 12 scattering vectors are not visible. From the values of the experimental scattering vectors we can deduce the lattice constants $a = 270$ Å, $c = 122$ Å and $\beta = 105$°C. This superlattice can be interpreted in terms of associated molecules and segregation between sublayers due to the three antipathetic parts (i.e. fluorinated chains, aromatic cores and hydrogenated chains).

4. Conclusion

We can summarize the previous discussion as follows.

(i) Rod-like mesogens with one perfluorinated (or semi-perfluorinated) chain are likely to form lamellar phases, mostly smectic A and no nematic phase.
(ii) In most cases the structures of these smectics show bilayer characteristics.

Thus the behaviour of these liquid crystals appears to be driven by the strong incompatibility between the perfluorinated and both the aromatic cores and hydrogenated chains, which tends to segregate the unlike parts in layers and sublayers. Similar properties are found in polar thermotropic mesogens and in amphiphilic lyotropic molecules to which the materials of the current study can be compared. If one adds that these antipathetic properties can be used in mixtures (a critical consolute point and a macroscopic phase separation have been observed for the first time in a smectic A solution [20] using the compound **2f**) one can conclude that this class of liquid crystals, little investigated so far, should provide a variety of new insights into the molecular interactions that stabilize mesophases. For instance, this remark could show some relevance in further studies of the cubic mesophase of polycatenar mesogens. Its stability is strikingly enhanced in compound **17f** (with a perfluorinated chain) compared to compounds **11h** (metastable cubic phase with a perhydrogenated chain) and **12h** (no cubic mesophase with a cyano polar end). Moreover, the presence of fluorinated parts could be very helpful in the analysis of the molecular packing in these superlattices through neutron scattering experiments.

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