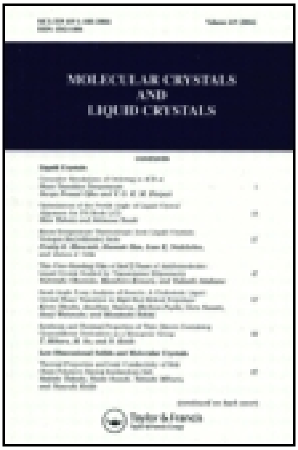

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Mesomorphic Properties of Some New Flurinated Liquid Crystals: the 4-n-Alkoxyperfluorobenzoate Series and Trifluoromethylbiphenyl Dervatives

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Mesomorphic Properties of Some New Fluorinated Liquid Crystals: the 4-*n*-Alkoxyperfluorobenzoate Series and Trifluoromethylbiphenyl Derivatives†

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(*Received July 19, 1984*)

We describe here the synthesis, the mesomorphic and the dielectric properties of two families of fluorinated compounds: the 4-alkoxyperfluorobenzoic acid 4'hydroxy-4-cyanobiphenyl esters and the 4-trifluoromethyl-4'-substituted biphenyl derivatives.

Some compounds exhibit only a wide temperature nematic range, while others have a wide temperature smectic A range with or without a nematic mesophase. These compounds are possible additives to mixtures of interest for displays.

INTRODUCTION

Until now, very few liquid crystal materials with perfluorinated aromatic ring structures have been studied. These compounds are mainly Schiff's bases,[1,2] biphenylene diamines,[3] terephtalates with 1, 2, or 3

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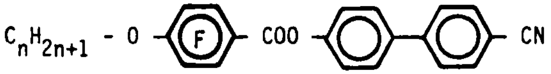
† Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

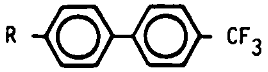
perfluorinated 1,4-phenylene groups[4] and perfluorinated hydroquinone bisbenzoates.[5]

A similar situation exists for liquid crystal materials having a trifluoromethyl group in their molecules.[6,7] In order to gain a better knowledge of fluorinated compounds and to compare them with the previously prepared non-fluorinated homologues, we have synthesized and studied two new families of compounds, with the following general formulae:



(I)

4-alkoxyperfluorobenzoic acid 4′-hydroxy-4-trifluoromethylbiphenyl esters with 2 ⩽ *n* ⩽ 12 and

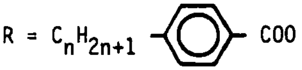


4-substituted 4′-trifluoromethylbiphenyls where:

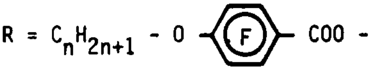
$R = C_7H_{15} - O -$ (II)

$R = C_9H_{19} - COO -$ (III)

(IV)



(V) with n = 5,8



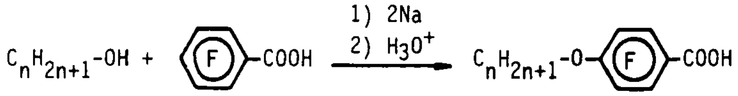
(VI)

with *n* = 5 and 7 ⩽ *n* ⩽ 12.

RESULTS

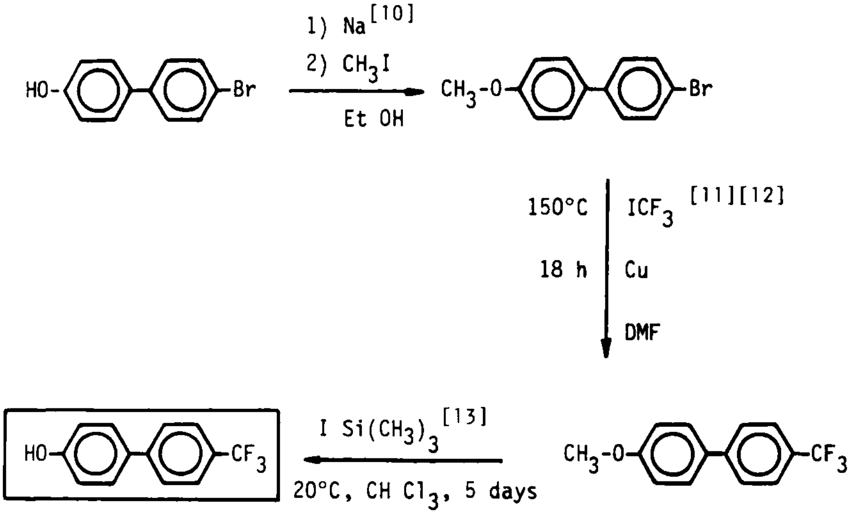
1. Synthesis

1-1. 4-alkoxyperflurobenzoic acids (VII). The 4-alkoxyperfluorobenzoic acids used here, were first prepared according to a method derived from ref. 8.



1-2. Trans-4-nonylcyclohexane-1-carboxylic acid. This acid was obtained by the method of Van Bekkum *et al.*[9]

1-3. 4-hydroxy-4'-trifluoromethylbiphenyl. The 4-hydroxy-4'-trifluoromethylbiphenyl was prepared according to the following reaction scheme:



1-4. Acid chlorides. Non-commercially available acid chlorides were obtained by heating the corresponding acids with SO Cl_2 under reflux for 3 hours.

1-5. Esters. The esters were prepared by interacting equimolar amounts of the relevant acid chlorides and phenols in pyridine for 48 hours at room temperature.

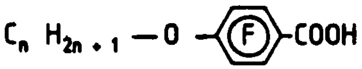
Purification of the esters was achieved by using chromatography on a column of silica gel; this was then eluted with toluene. The esters were crystallised from either hexane or methanol, until their transition temperatures remained constant.

2. Mesomorphic properties of the new compounds

The temperatures and enthalpies of transition were determined by means of differential scanning calorimetry. Textures of mesophases were observed through a polarizing microscope equipped with a programmable heating and cooling stage. The structures of the smectic phases were identified by isomorphism with a known reference compound (contact method);[14] this procedure applied to the compounds (I), (II), (III), (IV), (V). For the esters (VI), X-ray investigations were necessary to identify their mesophase as a smectic A, because glass slides and rubbed glass slides induced a spontaneous homotropic alignment, which made microscopic observations very

TABLE I

Mesomorphic properties of 4-alkoxyperfluorobenzoic acids

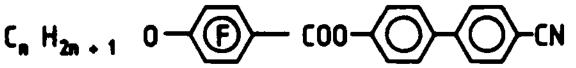


n	C_2	C_1	N	L
1(8)		● 122		●
2		● 114.5		●
3		● 84		●
4		● 87	(●57)	●
5	● 44	● 51	(●48)	●
6		● 53.5	(●52.5)	●
7		● 60		●
8		● 67		●
9		● 60		●
10	● 52	● 61		●
11	● 45	● 60.5		●
12		● 62		●

In this Table, and in the following Tables, the temperatures (°C) and molar enthalpy changes (material in smaller type—kcal/mole) correspond to the transitions between the phases indicated by full stops. Data in parenthesis correspond to monotropic transitions.

TABLE II

Mesomorphic properties of the compounds (I)

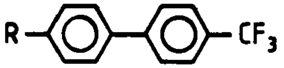


(I)

n	C	S_A	N	L
2	● 131		● 223	●
3	● 98		● 212.5	●
4	● 74		● 207	●
5	● 68		● 193.5	●
6	● 75	(●35)	● 187	●
7	● 68.5		● 176.5	●
8	● 66 9.1	● 120.5	● 172	●
9	● 58 8.5	● 139.5	● 160.5	●
10	● 72 11.3	● 150	● 161.5	●
11	● 62.5 10.9	● 153.5	● 157	●
12	● 63.5 12.1	● 155	● 156.5	●

TABLE III

Mesomorphic properties of 4-substituted-4′-trifluoromethyl-biphenyls



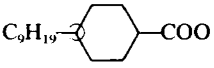
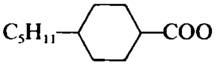
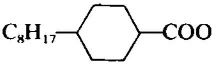
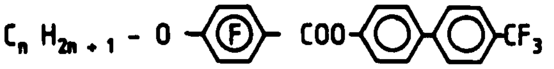
R	C	S_E	S_B	S_A	L
C_7H_{15}—O—	● 69 4.9		● 114,5 3,8		●
C_9H_{19}—COO—	● 63,3 2,9	● 74 0,2	● 108.3 2.8		●
	● 113.2 4.7		● 141 0.7	● 170.5 1.2	●
	● 144.2 5.8		(● 137) 0.6	● 201.7 3.8	●
	● 112 3.9		● 149 0.8	● 195 2.1	●

TABLE IV

Mesomorphic properties of the compounds (VI)


(VI)

n	C	S_A	L
5[a]	● 78.5	● 140.5	●
	3.4	1.1	
7	● 72	● 148	●
	4.0	1.15	
8[b]	● 71	● 147.5	●
	4.0	1.4	
9	● 74.5	● 146.5	●
	4.9	1.25	
10	● 76	● 146	●
	5.5	1.4	
11	● 78	● 143.5	●
	6.0	1.35	
12	● 80	● 141	●
	6.5	1.4	

[a] thickness of the smectic A layer: $d = 24,91$ Å

[b] thickness of the smectic A layer: $d = 28,64$ Å

difficult. Moreover, we noticed that the mesophase of the esters (VI) seemed less viscous than a normal smectic A.

Results are given in Tables (I), (II), (III) and (IV).

3. Dielectric properties

Permittivity measurements were made using a parallel-plate cell. For the different mesophases, measurement was achieved in two main directions: the measurement electric field was either parallel ($\epsilon^*_\parallel$) or perpendicular ($\epsilon^*_\perp$) to the optic axis of the sample. In this paper, the experimental results are presented in the following forms:

- quasi-static: $\epsilon'_i(T)$; the dielectric constants are given at a fixed frequency as a function of temperature.
- dynamic: $\epsilon^*_i(f, T)$ ($\epsilon^* = \epsilon' - j\epsilon''$); the complex permittivities were obtained at a fixed temperature using Hewlett-Packard impedance-analyzers driven by a H.P. table computer.[15] The frequency range investigated was 1 Hz-1 GHz.

As an example, in Figures 1 and 2 are shown the results obtained in the case of the ester (I) with $n = 8$.

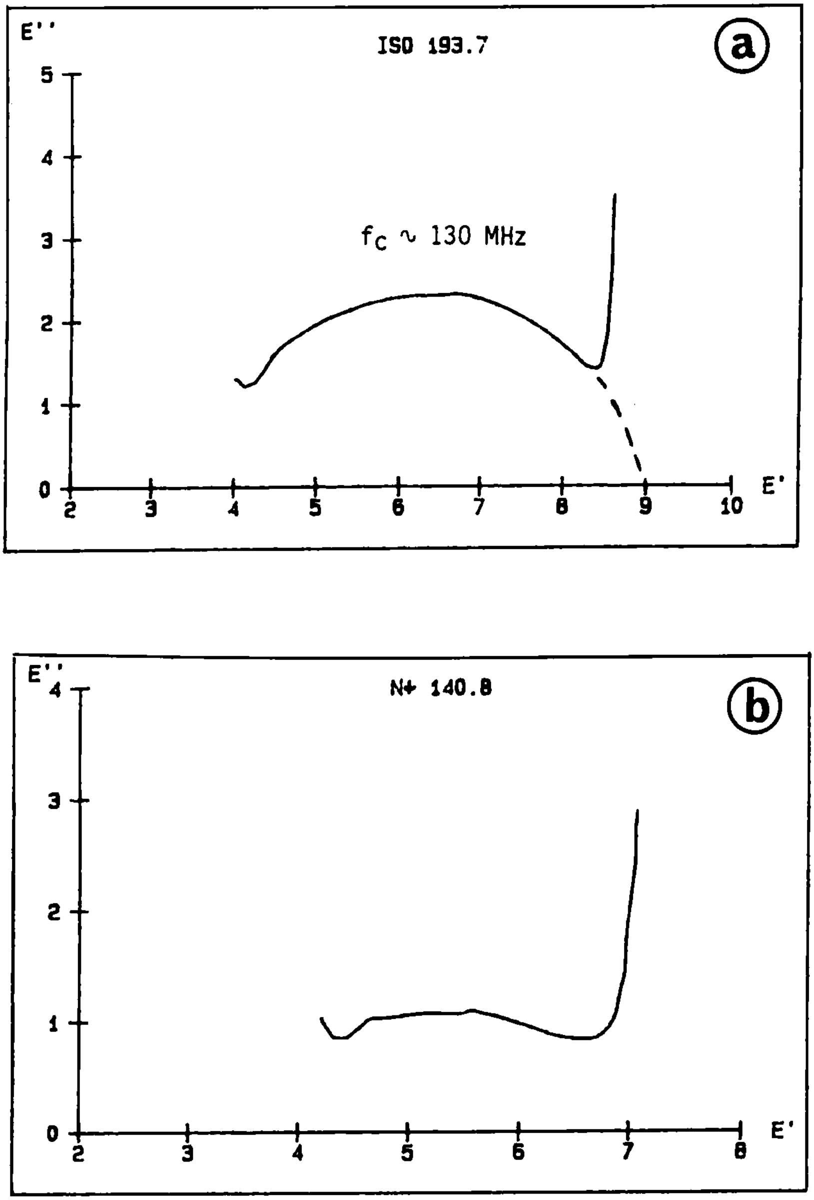
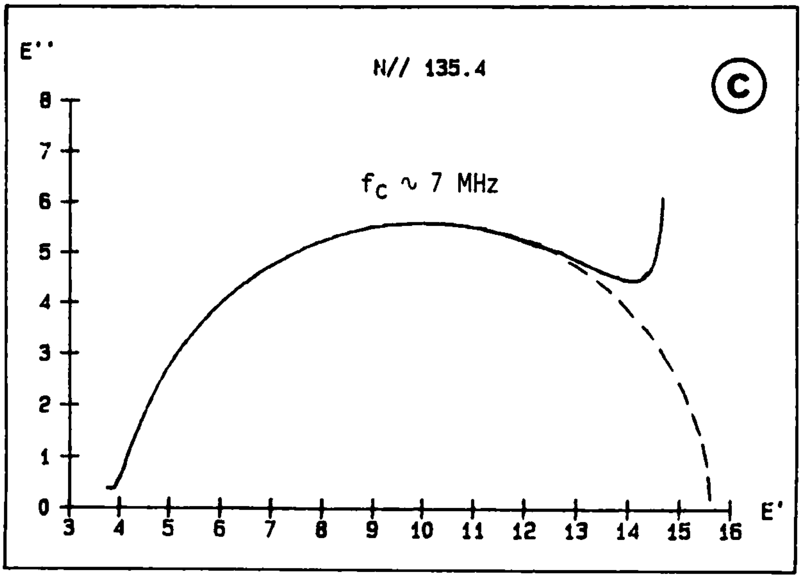


FIGURE 1 a: Cole-Cole diagram obtained for ester (I) with $n = 8$ in the isotropic phase ($T = 193,7$°C). b: Cole-Cole diagram obtained for ester (I) with $n = 8$ in the nematic mesophase ($T = 140,8$°C), when the electric field **E** is perpendicular to the director **n**. c: Cole-Cole diagram obtained for ester (I) with $n = 8$ in the smectic A mesophase ($T = 135,4$°C) when **E** is parallel to **n**.



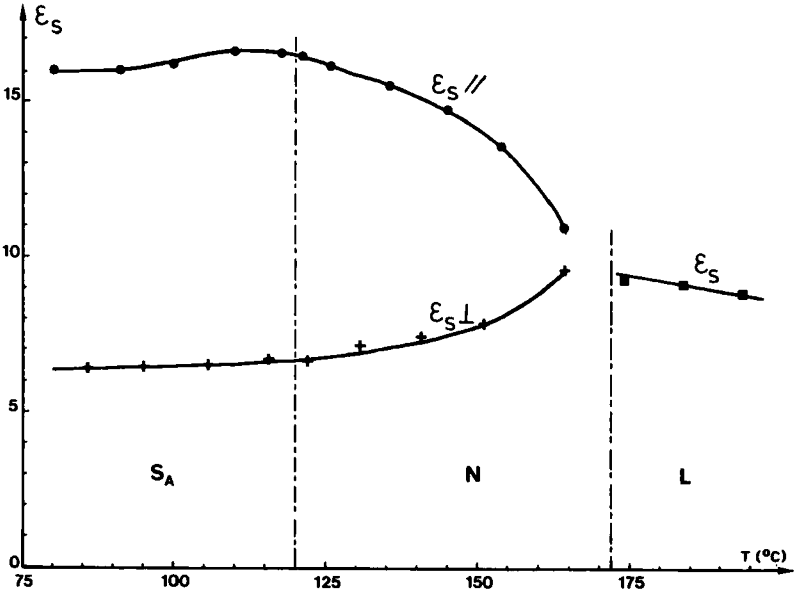


FIGURE 2 Quasi-static permittivity for ester (I) with $n = 8$.

DISCUSSION

1. Mesomorphic properties

1-1. 4 alkoxyperfluorobenzoic acids. Most of the 4 alkoxyperfluorbenzoic acids are not mesogenic, except for the compounds with $n = 4$, 5 and 6, which exhibit monotropic nematic mesophase. This result is quite surprising, when compared with the mesomorphic properties of the 4-alkoxybenzoic acids[16] (Table V). A comparison of the data in Tables (I) and (V) shows that complete substitution of the 1,4-phenylene ring by fluorine decreases the melting point of the acids and modifies molecular interactions in such a way that mesomorphic properties are diminished.

1-2. 4-alkoxyperfluorobenzoic acid 4'-hydroxy-4-cyanobiphenyl esters. Esters (I) with a short alkoxy chain ($n \leqslant 5$) are nematic over a wide temperature range. When the length of the alkoxy chain increases, a smectic A mesophase appears (monotropic when $n = 6$, eniantiotropic when $n \geqslant 8$). The decrease in the clearing temperature as n increases is regular. Odd-even effects are *not* observed. When $n \geqslant 8$, the nematic range becomes smaller, while the smectic A range becomes larger (Figure 3). The largest nematic temperature range is obtained when $n = 4$ ($\Delta T_N = 133°C$) and the widest smectic A temperature range is found when $n = 9$ ($\Delta T_{S_A} = 81{,}5°C$). Such a wide S_A temperature range is not commonly observed.

The behaviour of the compounds (I) is quite different from that of the non-fluorinated ester analogues (Table VI):

- the melting points are lowered (from 20,5°C when $n = 7$, to 46°C when $n = 4$)
- the mesomorphic thermal stability decreases
- the re-entrant nematic phenomenon does not exist.

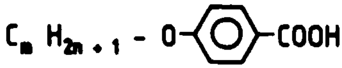
1-3. 4-substituted-4'-trifluoromethylbiphenyls (II), (III), (IV) and (V). These compounds exhibit only one or two smectic mesophases. Very often, the smectic mesophase is an ordered one. The corresponding cyano-compounds (Table VII) have

- lower melting points;
- higher clearing points and wider mesomorphic range for esters (VII-3) and (VII-4), but lower clearing points and narrower mesomorphic ranges for compounds VII-1 and VII-2;
- less ordered mesophases.

1-4. 4-alkoxyperfluorobenzoic acid 4'-hydroxy-4-trifluoromethylbiphenyl esters. All these compounds have only a smectic A

TABLE V

Mesomorphic properties of 4-alkoxybenzoic acids



n	C_2	C_1	S_C	N	L
3(12)	● 121	● 146.5		● 153.5	●
4		● 147.5		● 159	●
5		● 125		● 149	●
6	● 75	● 107		● 153	●
7		● 94	● 100	● 147	●
8	● 75	● 101	● 108	● 146	●
9		● 92	● 118	● 145	●
10	● 86	● 97	● 125	● 143	●
11		● 96	● 129	● 140	●
12	● 83	● 90	● 133	● 137	●

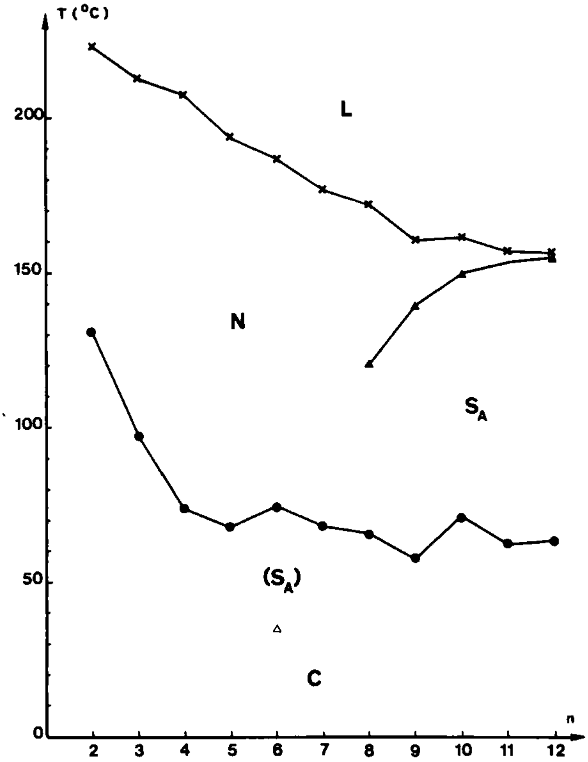


FIGURE 3 Plot of the transition temperatures *versus* *n*, the number of carbon atoms in the alkoxy chain of

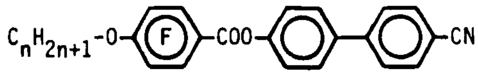
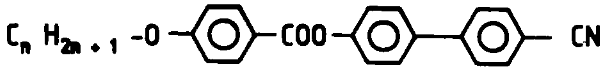


TABLE VI

Mesomorphic properties of
4-alkoxybenzoic acid 4'hydroxy-4-cyanobiphenyl esters

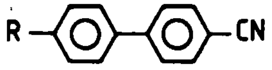


n	C	N_{re}	S_A	N	L
4(17)	● 120 7.6			● 270	●
6(18)	● 103			● 246	●
7(19)	● 89			● 246	●
8(19)	● 97	● 120	● 201	● 240	●
9(19)	● 96	● (71)	● 217	● 232	●
10(19)	● 100		● 224	● 230	●
11(19)	● 104		● 224	● 225	●
12(19)	● 102		● 224		●

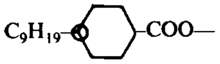
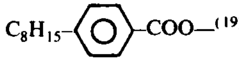
N_{re}: re-entrant nematic mesophase.

TABLE VII

Mesomorphic properties of 4-cyano-4′-substituted biphenyls (VII)



(VII)

R	Ref	C_2	C_1	N_{re}	S_A	N	L
C_7H_{15}—O—(20)	VII-1	● (47.5)	● 54 6.9			● 74	●
C_9H7_{19}—COO—(17)	VII-2		● 53.5 8.3		● 78.5	● 80	●
	VII-3		● 82.8 5.1		● 204 0.2	● 209 0.4	●
 (19)	VII-4		● 97	● 120	● 201	● 240	●

mesophase. The largest smectic A range is obtained when $n = 8$ ($\Delta T_{S_A} = 76,5°C$).

The melting points and the clearing points of these compounds are only slightly affected by the length of the alkoxy chain. When the cyano-group is replaced by the trifluoromethyl group:

- the melting points rise (except for *n* = 7);
- the stability of the mesophase decreases;
- the enthalpies of fusion are lowered (from 42% when *n* = 9 to 56% when *n* = 8).

X-ray investigations have shown that the thickness of the smectic A layer of the esters (VI) approximates to its molecular length, assuming the molecules adopt their most extended configuration. This result indicates that the mesophase is S_{A_1}. This is consistent with the rather small dipole moment of the $-CF_3$ group:[21] $\lambda(\phi - CF_3) = 2{,}54$ D.[22]

2. Dielectric properties

2-1. Quasi-static (Figure 2). We observe a large anisotropy ($\Delta\epsilon' \sim 10$) which remains constant in the smectic phase and slowly decreases as the temperatures increases in the nematic phase.

2-2. Dynamic (Figure 1). The frequency dependence of the permittivities is rather classical. In the parallel direction, we observe a strong Debye-type absorption connected with the molecular reorientation around a short axis ("flip-flop" mechanism).

In the perpendicular direction, the absorption observed is strongly distributed. The absorption in the isotropic phase is very close to a Debye mechanism. Figure 4 shows the variation of the critical fre-

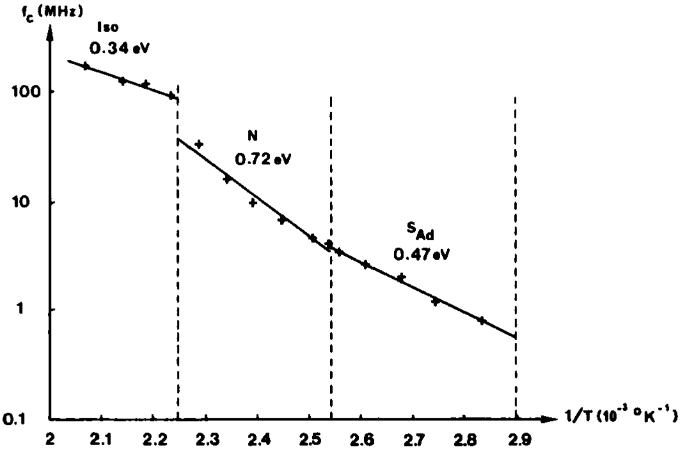


FIGURE 4 Variation of f_c versus $1/T$ for the ester (I) with $n = 8$.

quencies of the relaxation domains of the "flip-flop" mechanism *versus* the inverse temperature. The same variation is also given in the isotropic phase. Assuming an Arrhenius dependence of the critical frequency ($f_c \sim e^{-W/RT}$), one can obtain the activation energies of the various mechanisms. We obtain

$$W_N \gg W_{S_A} > W_{ISO}$$

These results indicate that the S_A phase is probably a partially bilayer structure S_{Ad}.[23]

Preliminary results obtained with the esters (VI) show a tendency to homeotropic alignment of the samples. This is consistent with the optical microscopy observations.

APPLICATIONS

The material used in laser addressed and matrix addressed smectic A storage displays is a mixture of cyanobiphenyl derivatives exhibiting a smectic A mesophase at room temperature and a short nematic range. For this purpose 4-cyano-4′-octylbiphenyl (8 CB) and 4-cyano-4′-decylbiphenyl (10 CB) are two attractive compounds. For example, the mixture M-1 of 8 CB (58%) and 10 CB (42%) shows the following phase transitions.[27]

$$C\ 5\ S_A\ 40\ N\ 43\ ISO$$

Some applications require a lower melting point and a higher clearing point of the materials. This may be done by adding a third component to a 8 CB–10 CB mixture. So, assuming ideal behaviour of the ternary system, we calculated the eutectic composition of 8 CB, 10 CB and esters (I).

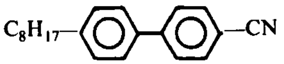
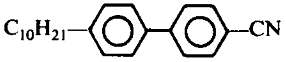
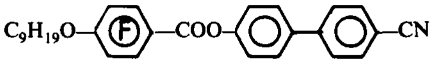
The widest mesomorphic range was obtained when $n = 9$ (mixture M-2). In Table VIII, the thermodynamic data obtained by means of differential scanning calorimetry for an experimental M-2 mixture is reported. M-2 is smectic A from −4, 5°C to 45°C; performances of this mixture are therefore better than those of mixture M-1.

Ternary mixtures with 8 CB, 10 CB and esters (VI) provided only smectic A materials.

Nematic compounds (esters (I) with $n \leqslant 5$) exhibiting a wide mesomorphic temperature range are possible interesting additives to nematic display mixtures.

TABLE VIII

Thermodynamic data of mixture M-2

Compounds	Molar Fraction
	66.50
	22.40
	11.10

Range C – 4.5 S_A 45 N 53 ISO

EXPERIMENTAL SECTION

Physical measurements and purity of compounds

Thermal analysis data were obtained using a 990 Du Pont thermal analyser.

Contact method was performed using an orthoplan Leitz microscope equipped with a Mettler FP5 heating and cooling stage.

X-ray diffraction experiments were carried out with a high resolution Guinier camera equipped with a heating stage ($\lambda = 1{,}7889$ Å).

The purity of all compounds was checked by thin layer chromatography and their structures were confirmed by infrared spectroscopy (using a 283 B Perkin–Elmer infrared spectrophotometer) and by proton NMR spectroscopy (using a WP 80 SY Bruker spectrometer).

Synthesis

4-n nonylbenzoic acid. This acid was prepared by Friedel–Craft's acetylation of nonylbenzene,[24] followed by hyprobromite oxidation of the 4-*n*-nonylacetophenone to the corresponding acid.[25]

Trans 4-noncylcyclohexanecarboxylic acid. Yield: 55,5%; mesomorphic properties: C 34 S_B 92 ISO (This result agrees with data obtained by Billard *et al.*[26] and Gray *et al.*[27]

4-cyano-4′-hydroxybiphenyl. This phenol was prepared by the method of Dubois *et al.*[28] The starting material was commercially available 4 hydroxybiphenyl.

4-alkoxyperfluorobenzoic acids. A solution of the sodium alkanoate in alkanol was prepared by heating at 60°C, 4,6 g (0,2 mole) of sodium with 350 ml of the appropriate alkanol. When all the sodium has reacted, a solution of 21,2 g (0,1 mole) of perfluorobenzoic acid in the appropriate alkanol was quickly added to the solution. The reaction mixture was stirred efficiently and heated under reflux (when $n \leqslant 3$), at 60° ± 2°C (when $n > 3$)—for 44 hours (when $n \leqslant 8$) or for 4 days (when $n \geqslant 9$). The cooled mixture was poured into 800 ml of water, acidified to pH = 2 with 5M HCl, and the crude product isolated by ether extraction. The alkanol was removed by vacuum distillation. Purification was effected by crystallisation from hexane at −18°C.

n	2	3	4	5	6	7	8	9	10	11	12
Yield %	43	17	59	42	34	28	27	18	20,5	10,7	12

4 methoxy 4′bromobiphenyl. 4-hydroxy-4′-bromobiphenyl was methylated by a well known method.[10] The yield was 87%, m.p. 144.5°C.

4-methoxy-4′-trifluoromethylbiphenyl. 4 methoxy-4′bromobiphenyl (11,23 g) was dissolved in DMF (100 ml) in a stainless steel autoclave, and precipited copper powder[29] (30 g) was added. The autoclave was cooled to −40°C in an acetone—dry-ice bath. Then liquefied ICF_3 was quickly added. The reaction mixture was then shaken at 150°C for 20 hours. After cooling, the autoclave was opened and the reaction mixture was taken up in $CHCl_3$ and poured into H_2O (300 ml). Inorganic materials were filtered off, washed with $CHCl_3$ and the washings combined with the filtrate. The organic layer was separated by decantation, washed with water and dried over $MgSO_4$. The solvent was removed under vacuum. The crude product (10,5 g) was purified by chromatography on a silica gel column which was eluted with benzene, followed by crystallisations from methanol. The yield was 40%, m.p. 120.5°C. IR: $-CF_3$, 1340 cm^{-1}(s) 1130 cm^{-1}(s).

4 hydroxy-4′trifluoromethylbiphenyl. To 2,28 g (9,05 mmole) of 4-methoxy-4′-trifluoromethylbiphenyl was added 25 ml of $CHCl_3$ and then 2,32 g (9,21 m.mole) of trimethylsilyl iodide. The solution was stored and maintained at room temperature for 5 days and then treated with 5 ml of methanol for 1 hour. The mixture was decolourised by washing with a solution of sodium bisulfite. The organic layer was separated by decantation, washed with water and dried over $MgSO_4$. The solvents were removed by rotary evaporation. The phenol was purified by liquid chromatography (eluant benzene then dichloromethane). The yield was 79%, m.p. 144,5°C.

CONCLUSIONS

We have prepared a variety of fluorinated liquid crystal materials and compared their mesomorphic properties with those found for non-fluorinated analogues. In the 4-alkoxyperfluorobenzoic acid series and the 4-alkoxyperfluorobenzoic acid-4'hydroxy-4-cyanobiphenyl ester series, the introduction of a perfluorinated 1-4-phenylene ring leads to compounds having lower melting points and decreased mesomorphic stability.

When we compare perfluorobenzoate derivatives with a trifluoromethyl group (esters VI) and perfluorobenzoate derivatives with a cyano-group (esters I), we conclude that for the esters (VI), the melting points are higher and the mesophase stability lower. Other trifluoromethylated liquid crystal materials exhibit only smectic mesophases with the molecules arranged perpendicular to the layers.

Esters (I) provide positive liquid crystal materials with a broad nematic temperature range when $n \leqslant 5$, and with a wide smectic A_d temperature range, followed by a nematic mesophase, when $n \geqslant 8$. Esters (VI) are only smectic A_1, these existing over a wide temperature range. All these compounds are additives of interest for display mixtures. For example mixture M-2 shows the following phase transitions

$$C - 4.5\ S_A\ 45\ N\ 53\ ISO$$

This behaviour is better than that so far obtained with commercial mixtures.

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