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New bifluorinated liquid-crystal compounds with broad mesomorphic ranges

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New bifluorinated liquid-crystal compounds with broad mesomorphic ranges

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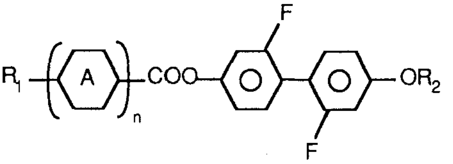
A new family of bifluorinated liquid crystal compounds of general formula



(I)

has been prepared. Their mesomorphic properties were measured. When $n = 1$ and A is cyclohexyl, phenyl, 3-bromophenyl or bicyclo[2.2.2]octane, these compounds are characterized by a wide nematic range. Some nematic mixtures with these materials were prepared and their physical properties were measured. These mixtures have a high birefringence (0·16–0·19), a negative dielectric anisotropy (−2·7), and a large value of the elastic-constant ratio K_{33}/K_{11} (1·7 at 20°C). In addition when $n = 2$ and R_2 is a chiral chain, compounds (I) show a wide chiral smectic C range, of about 100°C.

1. Introduction

In contrast with the well-known twisted or super-twisted nematic displays, the electrically controlled birefringence (E.C.B.) effect requires nematic liquid-crystal mixtures with negative dielectric anisotropy. In addition to this, E.C.B. mixtures need simultaneously a high birefringence ($\Delta n > 0{\cdot}13$) a ratio of bend/splay elastic constants K_{33}/K_{11} as large as possible, a wide nematic range and a low viscosity.

During the last ten years nematic chemistry has depended a great deal on the preparation of materials for twisted-nematic displays, that is positive dielectric anisotropy compounds. Among the materials developed, some are useful in E.C.B. mixtures to obtain some properties such as viscosity, mesomorphic range or birefringence. But materials with negative dielectric anisotropy are very limited. Nevertheless, more recently, cyclohexane derivatives with an axial cyano group have been prepared [1]. These bicyclohexyl cyano dialkyls have a large negative dielectric anisotropy, but a very low birefringence.

So, our purpose was to prepare new materials suitable for E.C.B. liquid-crystal mixtures. We were particularly interested in compounds with lateral fluorine substitution into a mesogenic system. It is known that such substitution results in a stabilization of the nematic phase [2–3]. Moreover, Scheuble and Baur [4] have shown that lateral fluorination of terminally non-polar nematic liquid crystals increases the elastic-constant ratio K_{33}/K_{11}. Because of this property and their negative dielectric anisotropy, these compounds are very interesting for our application. In particular, the doubly fluorinated BCH52FF has a high K_{33}/K_{11} ratio (1·7 at $T_R = 0{\cdot}85$)and a negative dielectric anisotropy. Unfortunately, this compound is very difficult to prepare [5].

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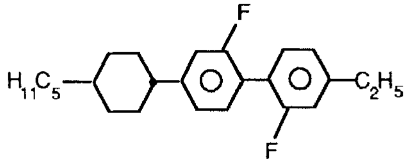
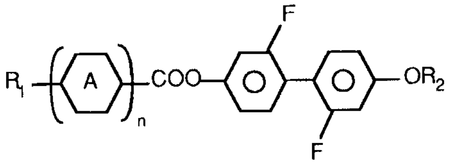
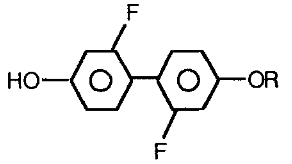


In this paper, we describe the synthesis and the mesomorphic properties of a new series of liquid-crystal compounds of formula (I) with a doubly fluorinated biphenyl core.



(I)

These esters are derived from 2,2′-difluoro-4-alkoxy-4′-hydroxybiphenyl



(II)

The physical properties of nematic mixtures prepared with these materials are also presented here.

2. Preparation of materials

The synthetic route to compounds (I) is given in scheme 1.

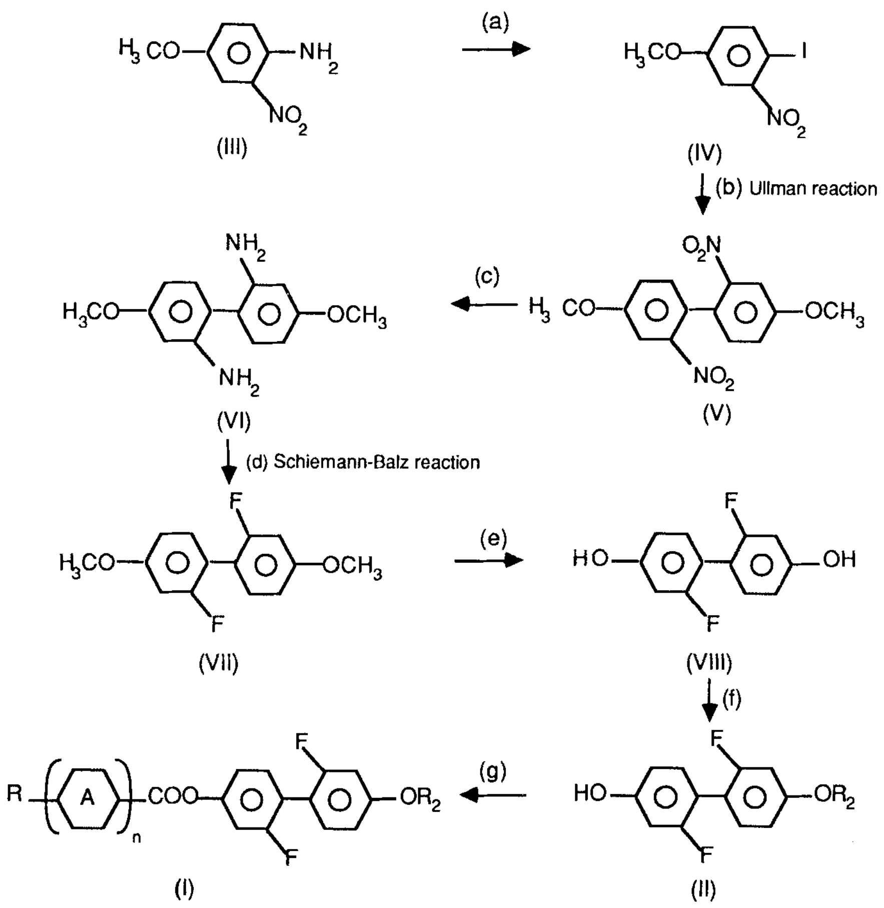
Preparation of the 2,2′-difluoro-4-alkoxy-4′-hydroxybiphenyls (*II*)

In the first step (a) 3 nitro-4-iodo-anisole (IV) is prepared by reaction of potassium iodide on a solution of diazonium salt of 3-nitro-4-amino-anisole (III). In step (b) we use the Ullmann reaction to condense two molecules of compound (IV) with copper in nitrobenzene at 220°C. Both nitro groups are reduced to amino with tin(II) chloride dihydrate in step (c). In the next step (d) amino groups are substituted by fluorine atoms by the Schiemann–Balz reaction. Compound (VII) is obtained by thermal decomposition of the bisdiazonium tetrafluoroborate salt of 2,2′-diamino-4,4′-dimethoxybiphenyl (VI). In step (e), compound (VII) is demethylated with boron tribromide in anhydrous dichloromethane. Finally, in step (f) monoalkoxylation of the biphenol (VIII) is obtained by reaction with alkyl bromide in methyl ethyl ketone with potassium carbonate.

Preparation of the carboxylic acids

4-*n*-pentylbicyclo[2.2.2]octane-1-carboxylic acid was prepared from 1-bromo-4-*n*-pentylbicyclo[2.2.2]octane, which was synthesized from methyl hexyl ketone using the method described by Gray and Kelly [6, 7].

2-Bromo-4-*n*-octyloxybenzoic acid was prepared from 3-bromo-4-hydroxybenzoic acid in three high-yield steps using the protection–deprotection method described by Dewar and Schroeder [8].



(a) 1) $NaNO_2$; HCl (0°C)
2) KI

(b) Cu, $PhNO_2$

(c) $SnCl_2$, $2H_2O$; HCl, EtOH

(d) (1) $NaNO_2$; HCl (0°C)
(2) $NaBF_4$; H_2O
(3) heating

(e) BBr_3; CH_2Cl_2

(f) R_2Br; $H_3CCOC_2H_5$; K_2CO_3

(g) R-(-Ⓐ-)$_n$-COCl (IX), pyridine

Scheme 1.

4′-*n*-alkoxybiphenyl-4-carboxylic acids were prepared from 4′-hydroxybiphenyl-4-carboxylic acid using the same method [8].

Preparation of the esters (*I*)

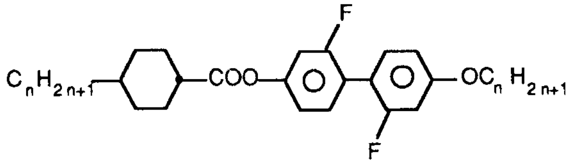
All of the esters (I) were prepared using fairly standard procedures. They were synthesised using an acid-chloride method.

3. Results and discussion

*Properties of the esters of 2,2′-difluoro-4-*n*-alkoxy-4′-hydroxybiphenyls*

The mesomorphic properties and the transition enthalpies of compounds (I), with R_2 an *n*-alkyl chain are listed in tables 1, 2 and 3. No major differences appear on

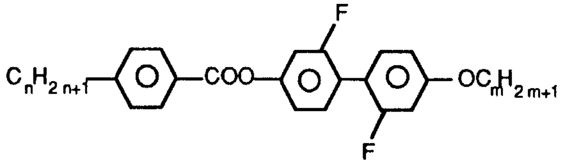
Table 1. Transition temperatures and transition enthalpies of 2,2′-difluoro-4-(4-*n*-alkylcyclohexylcarbonyloxy)4′-*n*-alkoxybiphenyls.



CHFnm

		Transition temperature/°C		ΔH/kJ mol^{-1}		N range/°C
n	*m*	C–N	N–I	C–N	N–I	
3	3	57	158	16·33	1·21	101
3	4	41	157	12·14	1·34	116
4	3	62	152	19·26	0·80	90
4	4	51	149	21·27	0·92	98
5	2	74	170	20·98	0·92	96
5	3	66	157	34·37	1·84	91
5	4	65	155	36·30	1·55	90

Table 2. Transition temperatures and transition enthalpies of 2,2′-difluoro-4-(4-*n*-alkylbenzoyloxy)4′-*n*-alkoxybiphenyls.



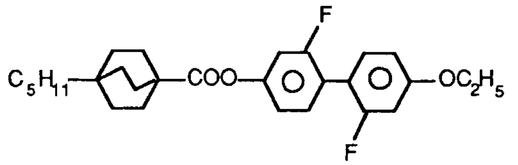
PFnm

		Transition temperature/°C		ΔH/kJ mol^{-1}		N range/°C
n	*m*	C–N	N–I	C–N	N–I	
5	3	83	138	22·15	1·00	55
6	2	74·5	142·5	27·47	1·00	68
6	3	74	127	27·00	0·96	53
6	4	55	131	22·69	1·13	76
6	5	55	123	19·68	0·96	68

varying the carboxylate groups or the chain length: all compounds have the same mesomorphic sequence, with only a wide nematic phase. In table 1 esters of 4-*n*-alkylcyclohexylcarboxylic acids, CHF*nm*, show a wide nematic range of about 100°C. For esters of 4-*n*-alkoxybenzoic acids, PF*nm* (table 2) the nematic range is shorter. In table 3, we can see that the bicyclo[2.2.2]octane carboxylate group of BCOF52 increases the transition temperatures and stabilizes the nematic phase. This is due to the steric hindrance of the bicyclo[2.2.2]octane group. We observe the same effect with the ester of 4-*n*-butoxybenzoic acid, PF402. Finally, a lateral bromine atom on a *n*-alkoxybenzoate group as in compound PBrF804 seems to decrease the nematic range and the transition temperatures.

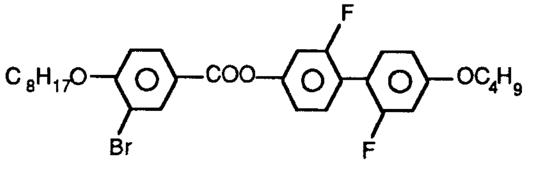
In table 4 we give the mesomorphic properties and the transition temperatures of compounds (I) containing a chiral chain derived from the (*S*)-(+)-2-methylbutyl group. Compounds CHF45* and PF85* can be compared with the series listed in

Table 3. Transition temperatures and transition enthalpies of 2,2′-difluoro-4-(4-*n*-pentylbicycol[2.2.2]octane-1-carbonyloxy)-4′-ethoxybiphenyl.



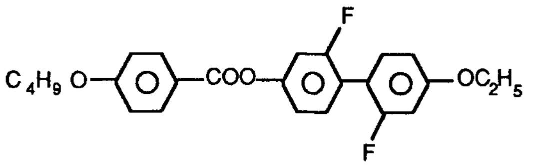
BCOF52

2,2′-difluoro-4-(4-*n*-octyloxy-3-bromobenzoyloxy)-4′-butoxybiphenyl



PBrF804

2,2′-difluoro-4-(4-*n*-butoxybenzoyloxy)-4-ethoxybiphenyl



PF402

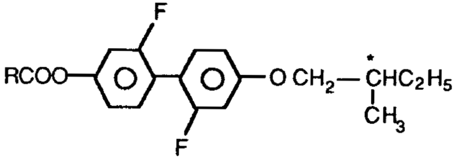
	Transition temperature/°C		ΔH/kJ mol^{-1}		N range/°C
Compounds	C–N	N–I	C–N	C–I	
BCOF52	102	205·5	15·66	0·84	103·5
PBrF804	59	115	41·70	1·09	56
PF402	124	193	30·35	1·51	69

tables 1 and 2 respectively. We can see a reduction of the chiral nematic phase with a decrease of the clearing point. Table 5 gives the mesomorphic properties of the non-fluorinated PF45* [9]. We notice that the lateral bifluorinated core of PF45* induces a clear disappearance of the chiral smectic C phase. With compound PF1005* an undetermined smectic phase appears, owing to the chain length of the *n*-alkoxy group. Finally we have investigated two esters derived from 4′-*n*-alkoxybiphenyl-4-carboxylic acids: BF705* and BF805*. We can see the appearance of a large chiral smectic C phase of about 100°C and a shorter smectic A phase. As expected, the transition temperatures are rather high, more particularly the clearing point. The lateral bifluorinated core of BF805* involves an important decrease of the C-S_C^* transition temperature in comparison with the non-fluorinated compound (table 5) [9]. Moreover, the chiral smectic C range is clearly stabilized.

Eutectic mixtures

Two nematic eutectic mixtures, MF, have been investigated, using CHF*nm* or PF*nm* compounds. The composition and transition temperatures have been

Table 4. Transition temperatures and transition enthalpies of esters derived from 2,2′-difluoro-4-hydroxy-4′-[(*S*)-(+)-2-methylbutyloxy]biphenyl.



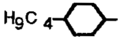
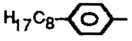
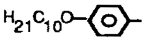
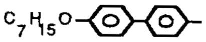
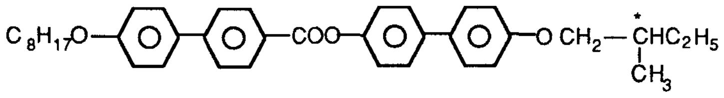
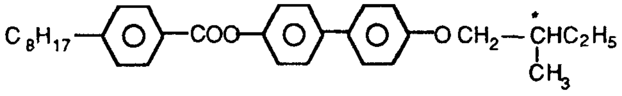
Compounds	R	Transition temperature/°C (ΔH kJ mol^{-1})					N*range/°C	S_C^* range/°C
		C–S_X^*	S_X–S_C^*	S_C^*–S_A	S_A–N*	N*–I		
CHF45*					36(19·26)	100(0·25)	64	0
PF85*					55(20·10)	81(0·54)	26	0
PF1005*		62(20·10)			71(0·7)	110(0·54)	31	0
BF705*			93(23·03)	184(–)	193(–)	> 220(–)	> 27	91
BF805*			94·5(10·84)	188(–)	192(–)	> 220(–)	> 28	93·5

Table 5. Transition temperatures of non-fluorinated BF805* and PF85* compounds.



$$C \xrightarrow{142°C} S_C^* \xrightarrow{229°C} S_A \xrightarrow{251°C} N^* \xrightarrow{281°C} I$$



$$C \xrightarrow{85.5°C} S_C^* \xrightarrow{105°C} N^* \xrightarrow{151.5°C} I$$

determined by applying the Schröder–Van Laar equation. The composition and physical properties of mixture MF3 mixture MF6′ are as follows.

Mixture MF3

composition: 21 per cent of PF65,
16·5 per cent of PF64,
22 per cent of CHF44,
19·5 per cent of CHF43,
21 per cent of CHF33,

nematic range < -10 to $\sim 138{\cdot}2$°C;

dielectric constants: $\varepsilon_\perp = 6{\cdot}2$ at 20°C, 1 kHz,
$\Delta\varepsilon = -2{\cdot}7$;

birefringence and elastic-constant ratio:

T °C	T_R	Δn (633 nm)	K_{33}/K_{11}
20	0·71	0·1744	1·76
40	0·76	0·1643	1·609
60	0·81	0·1575	1·59

Mixture MF6′

composition 54 per cent of I22,
19 per cent of CHF33,
13 per cent of CHF43,
15 per cent of CHF44;

nematic range < -10 to ~ 102°C;

dielectric constants: $\varepsilon_\perp = 4{\cdot}1$ at 20°C, 1 kHz,
$\Delta\varepsilon = -1{\cdot}0$;

birefringence: $\Delta n = 0{\cdot}148$ (633 nm) at 20°C;

elastic-constant ratio: $K_{33}/K_{11} = 1{\cdot}62$ at 20°C.

The nematic mixture MF3 has a high birefringence of about 0·17 and a large negative dielectric constant. However, the most interesting property of MF3 is the high ratio of bend and splay elastic constants K_{33}/K_{11} (1·76 at 20°C). This result is certainly due to a low K_{11} values, which represents weak intermolecular interactions in the nematic phase. If molecules are not planar, their packing is poor. This is achieved with compounds derived from 2,2′-difluorobiphenyl. Nevertheless, this mixture is not usable for E.C.B. applications. As a matter of fact, we did not suceed in obtaining a homeotropic orientation of MF3 with standard methods, i.e. on silica surfaces treated with *n*-octadecyltriethoxysilane (O.D.S.E.) or *n*-octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride (D.M.O.A.P.). Strong lateral dipoles, due to both fluorine atoms, increase the K_{33}/K_{11} ratio. This effect is so important that the homeotropic alignment of the molecules near the silylated surfaces of the cell is not energetically stable. Therefore the birefringence values have been obtained by a non-linear least-squares fit, which is performed in order to find the elastic constants. No measurement of the viscosity has been performed, but it must be rather high.

In mixture MF6′ there is only 37 per cent of CHF*nm* compounds. The aim was to lower the effect of the new bifluorinated materials on the homeotropic orientation. The rest of the mixture is composed of 1-(4-ethylcyclohexyl)-2-(2′-fluoro-4′-ethyl-4-biphenyl)ethane (I22), which is characterized by a wide nematic range (6–60°C), an elastic-constant ratio K_{33}/K_{11} of 1·2 at 20°C, a birefringence of 0·143 at 20°C and a negative dielectric anisotropy close to zero. Moreover I22 is very easy to align homeotropically. In comparison with MF3, we can see a decrease in all the physical parameters. However, the elastic-constant ratio K_{33}/K_{11} is also high (1·62). Homeotropic orientation of MF6′ is possible, but alignment is better on surfaces treated with D.M.O.A.P. than with O.D.S.E. Nevertheless, E.C.B. displays using the MF6′ mixture show that the homeotropic tilt of the molecules near the surface is too high. This fact is associated with a non-optimized sharpness of the electro-optic *V*/*T* curve.

4. Summary

New laterally bifluorinated compounds have been synthesized. As expected, these materials have a wide nematic range and a large negative dielectric anisotropy. In addition, nematic mixtures prepared with some of these compounds are mainly interesting with regard to their elastic-constant ratio K_{33}/K_{11} for E.C.B. applications. Nevertheless, homeotropic alignment is difficult to obtain with these mixtures. The problem stems from the laterally bifluorinated compounds. These materials are interesting as dopants (about 20 per cent) to improve the K_{33}/K_{11} ratio and the dielectric anisotropy of E.C.B. liquid-crystal mixtures.

We have shown that lateral bifluorination can induce a stabilization of the chiral smectic C phase and a decrease of the melting point when we increase the length of the core of a chiral compound of formula (I).

5. Experimental

*2,2′-difluoro-4-*n*-alkoxy-4′-hydroxybiphenyls (II)*

3-Nitro-4-iodoanisole (IV)

A suspension of 3-nitro-4-aminoanisole (III) (72·3 g) in concentrated hydrochloric acid (210 ml) was stirred at 0°C and ice (140 g) was added. A solution of sodium nitrite (32·2 g) in water (133 ml) was added slowly. After 15 min at 5°C, the mixture was filtered and poured on a solution of potassium iodide (294 g) in water (800 ml). The solid obtained was washed with a solution of sodium sulphite (5 per cent), then with water and was finally dried. The product was purified by distillation under reduced pressure (90 g). Yield 75 per cent; b.p. 173°C (0·9 mmHg); m.p. 61°C.

2,2'-Dinitro-4,4'-dimethoxybiphenyl (V)

A solution of (IV) (50 g) in nitrobenzene (50 ml) was heated at 190°C, and then copper powder (45 g) was poured in during 15 mn. The mixture was strongly stirred and heated for 0·5 h more at 210°C. Toluene was then added and the suspension was filtered. The solvents were distilled under reduced pressure. The solid obtained was purified by several recrystallizations in methanol (16·5 g). Yield 60 per cent; m.p. 132°C.

2,2'-Diamino-4,4'-dimethoxybiphenyl (VI)

A suspension of (V) (10 g) and tin(II) chloride dihydrate (74·2 g) in ethanol (130 ml) was stirred vigorously. Concentrated hydrochloric acid (20 ml) was added very slowly. The homogeneous solution was stirred for 2 h more and was cooled with ice and poured into a sodium hydroxide solution (2 M). The suspension obtained was filtered, and washed with water. The solid was dissolved in diethyl ether, washed again with water and dried. The solvent was removed and the product was purified by recrystallization in ethanol (6·85 g). Yield 85 per cent; m.p. 108–109°C; I.R. 3350 and 3440 cm^{-1} (NH_2).

2,2'-Difluoro-4,4'-dimethoxybiphenyl (VII)

A suspension of (VI) (6·8 g) in concentrated hydrochloric acid (8 ml) and dioxan (8 ml) was stirred at 0°C. A solution of sodium nitrite (4·5 g) in water (12 ml) was added slowly. Just after, a solution of sodium tetrafluoroborate (13·4 g) in water (30 ml) was added, drop by drop, at 0°C. The precipitate obtained was filtered, washed with cold water and dried under vacuum at room temperature. The perfectly dried powder (11·3 g) was then poured into a large three-necked flask (250 ml). Decomposition of the salt occurs at around 120°C with gas evolution of boron trifluoride and nitrogen. It was therefore necessary at the beginning to decompose the reagent by heating with an I.R. lamp. As soon as the decomposition occurred (prominent white fumes) heating was stopped, owing to the very exothermic reaction. As soon as the gas evolution stopped, the heating was continued. Finally, a black viscous liquid was obtained. The liquid was then stirred and heated in an oil bath at 140°C until no more fumes evolved. The black product obtained was chromatographed on silica gel using a chloroform/carbon tetrachloride mixture (35/65). The solid was purified by recrystallization in ethanol (3·5 g). Yield 50 per cent; m.p. 75°C.

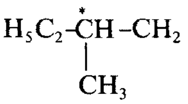
2,2'-Difluoro-4,4'-dihydroxybiphenyl (VIII)

A solution of boron tribromide (21·3 g) in anhydrous dichloromethane (30 ml) was added, drop by drop, to a solution of (VII) (3·5 g) in dichloromethane (100 ml). The solution was stirred overnight at room temperature. Water (40 ml) was poured in carefully and dichloromethane was removed. The product was extracted with diethyl ether. The solution was washed with water, dried, and the solvent was removed. The solid obtained was purified by recrystallization in a chloroform/diethyl ether mixture (2·5 g). Yield 80 per cent; m.p. > 210°C (sublimation).

*2,2'-Difluoro-4-*n*-alkoxy-4'-hydroxybiphenyls (II)*

A suspension of (VIII) (1g) and potassium carbonate (4 g) in methyl ethyl ketone (250 ml) was stirred vigorously. A solution of alkyl bromide (1 equivalent) in methyl ethyl ketone was added slowly and the mixture was heated under reflux for 20 h. The solution was poured into cold water and the product was extracted with chloroform. The solution was washed with water and dried, the solvent was removed, and the product was purified by chromatography on silica gel using a chloroform/diethylether mixture (95/5). The final product was recrystallized in a pentane–diethyl ether mixture.

2,2'-Difluoro-4-alkoxy-4'-hydroxybiphenyls

Alkyl group	Yield/per cent	m.p./°C
C_2H_5	40	106–107
C_3H_7	35	95·96
C_4H_9	35	103–104
C_5H_{11}	31	106–107
 $H_5C_2\text{-}\overset{*}{C}H(CH_3)\text{-}CH_2$	30	113–114

The (*S*)-(+)-2-methylbutyl bromide was obtained from (*S*)-(+)-2-methylbutanol using the method described by Gray and McDonnell [10].

Carboxylic acids

*4-*n*-Pentylbicyclo[2.2.2]octane-1-carboxylic acid* [6, 7]
m.p. 160°C; I.R. 1690 cm^{-1} (acidic CO).

*4-*n*-Octyloxy-3-bromobenzoic acid* [9]
m.p. 109·5–110°C; I.R. 1670–1690 cm^{-1} (acidic CO).

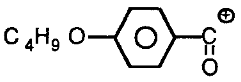
*4'-*n*-alkoxybiphenyl-4-carboxylic acids* [8]
I.R. 1680–1690 cm^{-1} (acidic CO).
Mesomorphic properties
$R = C_7H_{15}$: C → S_C at 194°C; S_C→ N at 251°C; N → I > 251°C (265·5°C [8])
$R = C_8H_{17}$: C → S_C at 183°C; S_C → N at 254°C; N → I > 254°C (264·5°C [8])

Preparation of the esters

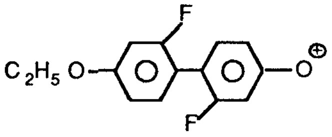
2,2'-Difluoro-4-ethoxy-4'-(4-butoxybenzoyloxy)biphenyl

To 4-butoxybenzoic acid, an excess of thionyl chloride was added and the mixture was heated under reflux for 3 h. The hot solution was then evaporated to dryness and the resulting acid chloride (V) was distilled under vacuum. The acid chloride (410 mg) was dissolved in pyridine (5 ml). This solution was added to a cooled mixture of 2,2'-difluoro-4-ethoxy-4'-hydroxy-biphenyl (400 mg) and pyridine (20 ml). The mixture was then stirred for 1 day. The solution was evaporated to dryness. The residue was dissolved in chloroform and the pure ester was obtained using a silica-gel column and chloroform as eluant. It was recrystallized from methanol. Yield 80 per cent; I.R. 1720 cm^{-1} (ester CO).

m/e 177



m/e 249



All the other esters of the series were prepared in the same way.

Techniques

The transition temperature and enthalpies were determined using a Setaram D.S.C. 101 differential-scanning calorimeter. Transition temperatures were also determined by optical microscopy using an Olympus BH-2 polarization microscope and a Mettler FP-52 hot stage.

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