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Laterally fluorinated phenyl biphenylcarboxylates; versatile components for ferroelectric smectic C mixtures

M. Chambers[a]; R. Clemitson[a]; D. Coates[a]; S. Greenfield[a]; J. A. Jenner[a]; I. C. Sage[a]
[a] B.D.H. Limited, Poole, Dorset, England

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Laterally fluorinated phenyl biphenylcarboxylates; versatile components for ferroelectric smectic C mixtures

by M. CHAMBERS, R. CLEMITSON, D. COATES, S. GREENFIELD, J. A. JENNER and I. C. SAGE

B.D.H. Limited Broom Road, Poole, Dorset BH12 4NN, England

Twenty-six fluoro-substituted 4-*n*-alkyl- and 4-*n*-alkoxyphenyl 4′-*n*-alkyl- and 4′-*n*-alkoxybiphenyl-4-carboxylates are reported. The number and position of the fluoro groups influences the liquid crystal phase sequence and has a dramatic effect on the liquid crystal transition temperatures. Some compounds have low melting points and a very wide smectic C phase, whereas other compounds exhibit a very wide smectic A phase. Compounds containing a 2,3-difluorophenyl group provide useful materials which have a large negative dielectric anisotropy.

1. Introduction

Since the discovery, by Meyer *et al.* [1] in 1975, that the chiral smectic C phase is ferroelectric there has been an increasing interest in materials which exhibit a smectic C phase. Several recent publications have shown how an appropriately branched terminal alkyl chain [2] and/or lateral substitution [3] can affect both the liquid crystal phase sequence and the thermal stability of the smectic C phase as well as other liquid crystal phases. Some years ago a range of 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkoxy- and 4-alkylbiphenyl-4′-carboxylates were reported [4] which exhibit smectic C phases with a moderate temperature range. By altering the position and number of fluoro groups in such molecules, many new and interesting compounds have now been prepared. The physical properties of these new compounds are very varied; thus, a range of useful components for commercial ferroelectric smectic C mixtures have been discovered.

2. Compounds with one fluoro group

In table 1 the transition temperatures of the monofluoro substituted 4-*n*-alkyl- and 4-*n*-alkoxyphenyl 4-*n*-alkoxy- and 4′-*n*-alkylbiphenyl-4-carboxylates are listed. It can be seen clearly that the lowest melting compounds occur when the 2-fluorophenol group is present. As previously predicted [3], the 3-fluoro compounds have a higher smectic C thermal stability and a much increased smectic A thermal stability; indeed, the nematic phase present in the 2-fluoro compounds (**1**–**5** and **7**), has been eliminated by the increased thermal stability of the smectic A phase in compound **6**.

When a fluoro group is between the two phenyl rings of the biphenyl acid, (compound **10**), the smectic C thermal stability is a little lower than when the fluoro group is in the 3-position of the phenol ring (compound **8**), but when the fluoro group in the acid points away from the main core, the smectic C thermal stability increases significantly (compound **11**).

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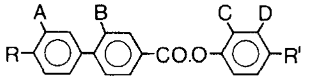
Table 1. Transition temperatures (in °C) for a variety of monofluoro phenyl biphenylcarboxylates.



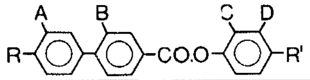
Compound	*R*	*R'*	*A*	*B*	*C*	*D*	C–S_C	S_I–S_C	S_C–S_A/N	S_A–N/I	N–I
1	$C_8H_{17}O$	C_5H_{11}	H	H	F	H	49	[30]	121	128	164·4
2	$C_8H_{17}O$	C_6H_{13}	H	H	F	H	56	59	128	136	156
3	$C_8H_{17}O$	C_7H_{15}	H	H	F	H	48	[29]	122	128	166
4	C_8H_{17}	C_5H_{11}	H	H	F	H	63	[35]	78·0	86·5	134·7
5	$C_{10}H_{21}$	C_8H_{17}	H	H	F	H	63·2	[54·2]	100·6	112·1	122·3
6	$C_8H_{17}O$	C_7H_{15}	H	H	H	F	87	-	128·9	181	-
7	$C_8H_{17}O$	$C_8H_{17}O$	H	H	F	H	68·2	-	136·7	-	171·8
8	$C_8H_{17}O$	$C_8H_{17}O$	H	H	H	F	85	-	149·3	192·4	-
9	C_8H_{17}	$C_8H_{17}O$	H	H	H	F	75	-	106·9	162·5	-
10	$C_8H_{17}O$	$C_8H_{17}O$	H	F	H	H	87	-	140·5	-	164
11	$C_8H_{17}O$	$C_8H_{17}O$	F	H	H	H	93	-	167·5	182·4	-
12	$C_8H_{17}O$	C_8H_{17}	F	H	H	H	85	-	139·5	163	-

3. Compounds with two fluoro groups

In table 2 we present the data for the difluoro 4-alkyl- and 4-alkoxyphenyl-4'-alkoxy- and 4'-alkylbiphenyl-4-carboxylates. Again, the lowest melting point compounds result when the phenol contains a 2-fluoro group (compounds **15** and **16**). In these compounds the smectic C thermal stability is dramatically affected by the position of the fluoro group in the acid. A large number of compounds of type **15** have been synthesized [5] and the low melting, wide range smectic C phase is common in this series. These compounds are also interesting since, unlike the monofluoro compounds **1–5**, they do not exhibit a higher order smectic phase. The wide smectic C phase, low melting point and lack of higher order smectic phases make compounds of type **15** particularly useful in ferroelectric smectic C mixtures. Not only do the 2-fluorophenyl compounds have lower melting points than the 3-fluorophenyl analogues, they also exhibit smectic C to nematic transitions. In contrast, the 3-fluorophenyl analogues exhibit a smectic A phase of high thermal stability in which the nematic phase has been suppressed.

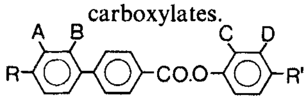
A range of esters having a 2,3-difluorophenyl ring have also been synthesized; some examples of these compounds are given in table 3. The various phase thermal stabilities are not greatly affected by the position of the two fluorines.

Table 2. Transition temperatures (in °C) for some difluoro phenyl biphenylcarboxylates.



Compound	*R*	*R'*	*A*	*B*	*C*	*D*	C–S_C	S_C–S_A/N	S_A–I	N–I
13	$C_8H_{17}O$	C_7H_{15}	F	H	H	F	65	119	165·2	-
14	$C_8H_{17}O$	$C_8H_{17}O$	F	H	H	F	97	147	180	-
15	$C_8H_{17}O$	C_7H_{15}	F	H	F	H	34	115	-	138
16	$C_8H_{17}O$	C_8H_{17}	H	F	F	H	47	53	-	123
17	$C_8H_{17}O$	C_8H_{17}	H	F	H	F	81·5	127·8	156·2	-

Table 3. Transition temperatures (in °C) for 2,3-difluoro derivatives of some phenyl biphenylcarboxylates.



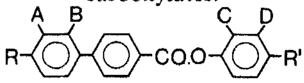
Compound	*R*	*R'*	*A*	*B*	*C*	*D*	C–S_C	S_C–S_A	S_A–N	N–I
18	$C_8H_{17}O$	$C_8H_{17}O$	F	F	H	H	83·8	151·7	154·9	165·4
19	$C_8H_{17}O$	C_8H_{17}	F	F	H	H	83·6	121·0	139·0	144·6
20	$C_8H_{17}O$	$C_7H_{15}O$	H	H	F	F	94·0	156·9	166·2	174·7
21	C_8H_{17}	$C_7H_{15}O$	H	H	F	F	86·0	125·2	131·2	145·5

All of the 2,3-difluoro compounds have high melting points and exhibit both smectic A and nematic phases. The smectic C thermal stability is similar to that of the best monofluoro compounds; compare compounds **11** and **20**.

4. Compounds with three fluoro groups

Table 4 presents the transition temperature data for some representative esters having three fluoro groups. It is immediately noticeable that the melting points are much lower for these compounds than for the 2,3-difluorophenyl compounds shown in table 3. Compounds **23** and **24**, which incorporate a 2-fluorophenol, again exhibit an S_C–N transition whereas the 3-fluorophenol compound exhibits an S_C–S_A transition. These moderately low melting compounds also exhibit a useful smectic C phase temperature range. Compound **25** is interesting in that it is low melting and exhibits an enormously wide (101°C) smectic A phase; this material is potentially very useful to induce smectic A phases.

Table 4. Transition temperatures (in °C) for some trifluoro derivatives of phenyl biphenylcarboxylates.



Compound	*R*	*R'*	*A*	*B*	*C*	*D*	C–S_C	S_C–S_A/N	S_A–N S_A–I	N–I
22	$C_8H_{17}O$	$C_7H_{15}O$	F	H	F	F	60	150	155	157
23	$C_8H_{17}O$	C_8H_{17}	F	F	F	H	45	84·5	–	120·7
24	$C_8H_{17}O$	$C_8H_{17}O$	F	F	F	H	56·7	103	–	141·6
25	$C_8H_{17}O$	$C_7H_{15}O$	F	F	H	F	44·7	[41]	146	–
26	$C_8H_{17}O$	$C_8H_{17}O$	F	F	H	F	83·6	116	162·9	–

5. Dielectric anisotropy

The dielectric anisotropy of compounds **1**, **15** and **22** have been measured in the nematic phase of a non-polar nematic host (a binary eutectic mixture of 1-(4-alkylcyclohexyl)-2-[4'-(2-fluoro-4-alkylbiphenyl)] ethanes using a frequency of 1 kHz at 20°C. These results are shown in table 5. As the number of fluoro groups in the molecule is increased, the dielectric anisotropy becomes more negative; this is particularly marked in the 2,3-difluorophenyl compounds. Therefore, the dielectric anisotropy of a smectic C ferroelectric mixture can be readily adjusted by appropriately incorporating these components.

Table 5. Extrapolated dielectric permittivities, measured at 1 kHz and 20°C, for various fluoro substituted phenyl biphenylcarboxylates. The compounds were dissolved in a non-polar nematic host.

Compound	Dielectric anisotropy, $\Delta\varepsilon$
1	−0·047
15	−1·93
22	−3·84

6. Mixture formulation

All of the compounds reported are miscible with each other and the smectic C phases mix in an almost ideal manner. The tilt angle of all the compounds measured is about 20–23° at 20°C. The birefringence in the smectic C phase is approximately 0·18. Viable ferroelectric smectic C mixtures with a birefringence of 0·18 are therefore readily obtained, and mixtures of lower birefringence can be produced by using other low birefringence components which will be reported later. The difluoro compounds of type **15** provide a wide temperature range smectic C phase of significant negative dielectric anisotropy, whereas the 2,3-difluorophenyl compounds provide some very negative components with modest melting points. Compound **25** provides a compound of high negative dielectric anisotropy which exhibits a very wide smectic A phase; it is ideal for inducing a smectic A phase in ferroelectric mixtures.

These components have been incorporated into commercial ferroelectric smectic C mixtures which have a response time of less than 30 μs at 30°C when subjected to a field of 10 V μm^{-1} [6].

7. Experimental

(*a*) *4-Alkyl-2-fluorophenols*

2-Fluoroanisole was acylated [7] using the appropriate alkanoyl chloride and aluminium chloride in dichloromethane. The product was reduced by Huang–Minlon reduction [7] to the 4-alkyl-2-fluoroanisole, which was demethylated using hydrobromic acid and acetic acid to produce the required phenol.

(*b*) *4-Alkyl-3-fluorophenols*

1-Bromo-3-fluoro-4-iodobenzene was coupled [8] with an appropriate terminal acetylene ($Pd(PPh_3)Cl_2$ catalyst) to give the corresponding 4-bromo-2-fluorophenylacetylene, which on hydrogenation [7] over Pd/charcoal gave the 4-alkyl-3-fluoro-1-bromobenzene. Conversion to the phenol was accomplished by formation of the Grignard reagent followed by treatment [9] with trimethylborate/hydrogen peroxide.

(*c*) *4-Alkoxy-2-fluorophenols*

4-Bromo-2-fluorophenol was benzylated [7] using benzyl chloride and potassium carbonate in butanone. The product was converted to the Grignard reagent, cooled to −10°C and treated [9] with trimethylborate to produce a boronic acid which was then oxidized to the phenol. The 3-fluoro-4-benzyloxyphenol was then alkylated [7], using an alkyl bromide and the benzyl group was removed by hydrogenolysis [10] to produce the required phenol.

(*d*) *4-Alkoxy-3-fluorophenols*

4-Bromo-2-fluorophenol was alkylated [7] using an alkyl bromide and potassium carbonate in butanone. The bromo group was then converted to the Grignard reagent in tetrahydrofuran, cooled to − 10°C and converted to a phenol via the boronic acid intermediate.

(*e*) *4-Alkoxy-2,3-difluorophenol*

2,3-Difluorobenzene was lithiated [11] using butyl lithium at − 70°C and converted to the boronic acid at − 70°C, using trimethyl borate. Oxidation [9] of the boronic acid gave 2,3-difluorophenol which was alkylated [7], using an alkyl bromide, potassium carbonate and butanone. A repeat lithiation, boronation and oxidation gave the required product.

(*f*) *4-Alkoxy-3-fluorobiphenyl-4′-carboxylic acid*

4-Alkoxy-3-fluorobromobenzene was converted to the Grignard reagent and then to the boronic acid at − 70°C, using trimethyl borate. This was then coupled [12] with methyl 4-bromobenzoate, using palladium tetrakis triphenylphosphine in toluene and sodium carbonate solution to produce methyl 4-alkoxy-3-bromobiphenyl-4′-carboxylate which, upon alkaline hydrolysis [7], gave the required carboxylic acid.

(*g*) *4-Alkoxy-2′-fluorobiphenyl-4′-carboxylic acid*

4-Bromo-2-fluorobiphenyl was acylated with acetyl chloride and then treated with *m*-chloroperbenzoic acid (Baeyer–Villager oxidation) [13] followed by alkaline hydrolysis to give 2′-fluoro-4′-bromo-4-hydroxybiphenyl. Cyanation of the bromo compound, using cuprous cyanide, gave the corresponding cyano compound. Alkylation of the hydroxyl group with and appropriate alkyl bromide followed by hydrolysis of the cyano group using acetic acid/sulphonic acid gave the biphenyl acid.

(*h*) *4-Alkyl-2,3-difluorobiphenyl-4′-carboxylic acid*

4-Alkoxy-2,3-difluorobenzene was lithiated [11] at − 70°C using butyl lithium and converted to the boronic acid using trimethyl borate at − 70°C. This was then coupled [12] with methyl 4-bromobenzoate using palladium tetrakis triphenylphosphine, the product was demethylated [7], using alkaline hydrolysis, to the required acid.

(*i*) *Esterification*

The appropriate phenol (0·01 M) was added to a solution of acid (0·011 M) and trifluoroacetic anhydride (0·012 M) in dry dichloromethane at room temperature. After stirring the mixture for 4 h it was washed successively with water and dilute sodium carbonate solution. The product was purified by column chromatography and crystallized until greater than 99·5% pure by H.P.L.C.

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