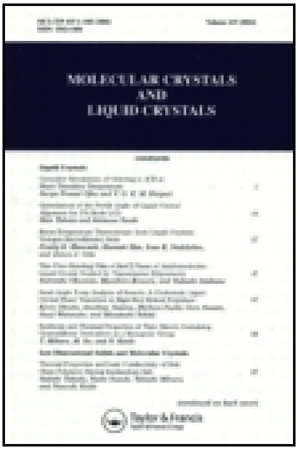

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Synthesis and Transition Temperatures of Some Branched Alkyloxycarbonylphenyl Esters of 3-(4′-n-Alkyl- and -alkoxy-biphenyl-4-yl)propanoic Acids and their Laterally Fluorinated Analogues

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Synthesis and Transition Temperatures of Some Branched Alkyloxycarbonylphenyl Esters of 3-(4′-*n*-Alkyl- and -alkoxybiphenyl-4-yl)propanoic Acids and their Laterally Fluorinated Analogues

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A number of three ring diesters based on 4′-*n*-alkoxy- and 4′-*n*-alkyl-biphenyl-4-ylpropanoic acid have been prepared to investigate the effect on the liquid crystalline behaviour of these compounds of (a) incorporation of branched (achiral) end groups, and (b) laterally positioned fluorine atoms.

Many of these diesters exhibited wide temperature range S_C and S_I phases, especially for compounds containing the 2-methylpentyl end group.

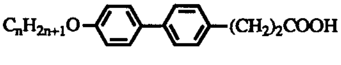
Lateral fluorination in both the 2- and 3-positions of the phenolic moiety reduced the melting point and smectic thermal stabilities of the diesters. The reduction in S_C thermal stability by incorporation of a laterally positioned fluorine atom in the 2-position was very small, giving rise to compounds with very wide S_C ranges (40–50 °C). Unexpectedly, compounds containing a laterally positioned fluorine atom in the 3-position gave a number of crystal phases.

Whether the diesters incorporated a branched terminal group or a laterally positioned fluorine atom, no nematic phase was observed.

Keywords: Fluorinated liquid crystals smectic C phase esters of 4′-n-alkoxy biphenyl-4-ylpropanoic acids esters of 4′-n-alkylbiphenyl-4-ylpropanoic acids

INTRODUCTION

Recently, we have described the synthesis and mesogenic properties of several series of 4-*n*-nonylphenyl esters derived from 3-(4′-*n*-alkoxybiphenyl-4-yl)propanoic acid (**1**), including some laterally fluorinated analogues.[1]



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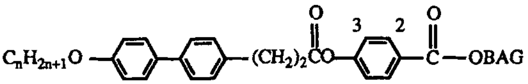
The objective of this research work was to produce compounds which would exhibit relatively low temperature tilted phases i.e., smectic *C*, *I* or *F* phases, and be suitable as host materials for ferroelectric devices. In particular, we wished to find compounds which would display, in addition to the tilted phases, narrow range nematic and smectic A phases which would assist in the alignment of the underlying tilted phases. The ideal sequence would therefore be I-N-S_A-S_C or S_{C*}.

Our previous work[1] produced a number of compounds which displayed wide temperature range smectic C phases with underlying smectic I/F phases but the required narrow range nematic and smectic A phases have thus far remained elusive. The partial success of this work encouraged us to consider other possible derivatives of the basic structure (1) in order to achieve the required sequence of nematic and smectic phases.

A common factor to all of the compounds produced previously was the use of a 4-*n*-nonylphenyl group or its 2-fluoro-or 2,3-difluoro analogue. We decided that by replacing the flexible *n*-nonyl group with a more rigid ester group e.g., racemic 2-methylbutyl, 3-methylbutyl or 2-methylpentyl ester group, nematic and smectic A phases might be more readily induced whilst retaining the tendency of this system to form tilted phases. The resultant diesters consist, therefore, of two rigid cores connected by a flexible dimethylene group with two terminal substituents containing alkyl groups, one branched (achiral), as shown in structure (**2**).



BAG = Branched Alkyl Group

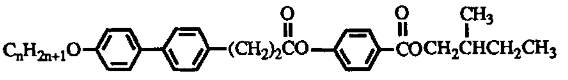
(**2**)

We also decided to produce 2- and 3-fluorophenyl analogues of some of these compounds to examine the effect of lateral fluorination on mesophase thermal stability. This would also allow comparisons to be made between these laterally fluorinated compounds and those of the *n*-nonylphenyl series previously published.[1]

RESULTS AND DISCUSSION

A. Branched (Achiral) Terminal Groups

(a) 4-(2-Methylbutyloxycarbonyl)phenyl 3-(4′-*n*-alkoxybiphenyl-4-yl) propanoates (3).



(**3**)

Six compounds were made in this series ($n = 6$ to 11) and the transition temperatures for these compounds are shown in Table 1.

TABLE 1

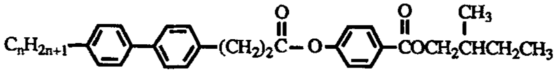
Transition Temperatures (°C) for Compounds of Structure (**3**).

n	T_{K-S_E}	T_{K-S_I}	T_{K-S_C}	$T_{S_K-S_I}$	$T_{S_E-S_B}$	$T_{S_I-S_C}$	$T_{S_B-S_A}$	$T_{S_C-S_A}$	T_{S_A-I}
6	54.0	–	–	–	58.5	–	100.0	–	130.5
7	–	55.0	–	–	–	90.5	–	100.0	127.0
8	–	59.0	–	(43.0)	–	90.5	–	107.5	127.0
9	–	67.0	–	–	–	83.0	–	108.0	126.0
10	–	75.0	–	–	–	82.0	–	112.0	125.0
11	–	–	79.0	–	–	–	–	112.0	123.0

( ) Indicates a monotropic phase transition

The lowest homologue of this series ($n = 6$) shows an orthogonal phase (smectic B) preceded by a smectic A phase but exhibits no tilted phases. The remaining homologues ($n = 7$–11), however, display polymesomorphism consisting mainly of tilted phases, namely smectic I and smectic C. These higher homologues show wide temperature range smectic I phases on melting which narrow considerably on ascending the homologues series until they are squeezed out completely in the highest homologue ($n = 11$). This narrowing effect is reinforced by a progressive widening of the temperature range of the smectic C phase. In each case the smectic C phase is followed by a narrow range smectic A phase but no nematic phases are observed in any of the homologues. The clearing point temperature reduces slowly as the homologues series is ascended (130.5 to 123.0°C).

(b) 4-(2-Methylbutyloxycarbonyl)phenyl 3-(4′-*n*-alkylbiphenyl-4-yl) propanoates (4).



(4)

Three compounds were made in this series ($n = 7, 9$ and 11) and their transition temperatures are shown in Table 2.

Replacement of the alkoxy chain by an alkyl chain has a pronounced effect on mesophase thermal stability when the results shown in Table 2 are compared with those of Table 1. Both melting and clearing points are much lower for the alkylbiphenyl compounds with large reductions in mesophase transition temperatures (see figure 1). Generally, both alkoxy- and alkyl-biphenyl compounds show similar liquid crystalline behaviour, i.e., they exhibit S_I, S_C and S_A phases. The octyloxybiphenyl compound exhibits a wide range S_I phase with a relatively narrow S_C phase, a situation which is

TABLE 2

Transition Temperatures (°C) for Compounds of Structure (**4**)

n	$T_{K-S_{I/F}}$	T_{K-S_B}	$T_{S_{I/F}-S_C}$	$T_{S_B-S_A}$	$T_{S_C-S_A}$	T_{S_A-I}
7	–	50.0	–	79.0	–	95.5
9	35.0	–	71.5	–	74.5	94.5
11	39.0	–	68.0	–	76.5	94.5

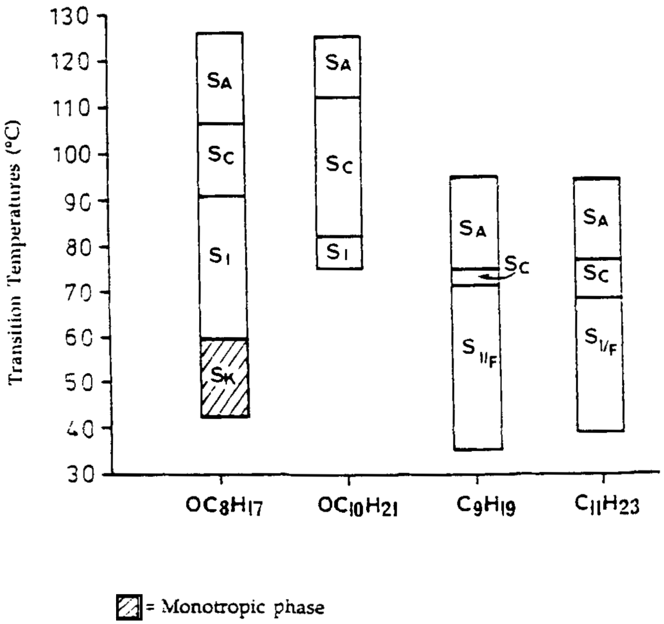
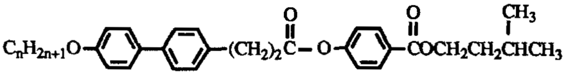


FIGURE 1

reversed in the decyloxybiphenyl compound which has a wide range S_C phase and a relatively short range S_I phase. The octyloxybiphenyl compound also shows a crystal K phase. A similar situation is shown by the alkylbiphenyl compounds in which the nonyl homologue has the widest S_I range but the undecyl homologue has the widest S_C range. It is also apparent from results given in Figure 1 that the alkoxybiphenyl compounds are more inclined to give wide range S_C phases whereas the corresponding alkyl homologues are more predisposed to wide range S_I phases.

(c) 4-(3-Methylbutyloxycarbonyl)phenyl 3-(4′-*n*-alkoxybiphenyl-4-yl) propanoates (5).



(5)

Five compounds were synthesised ($n = 6$ to 10) and their transition temperatures are shown in Table 3.

These compounds show high melting points and high clearing points across the whole series and display smectic polymesomorphism within a relatively narrow temperature range (about 45°C). Tilted, narrow temperature range smectic F and smectic C phases are seen from $n = 8$ onwards and for each member of the series,

TABLE 3

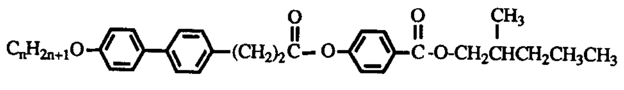
Transition Temperatures (°C) for Compounds of Structure (5)

n	T_{K-S_B}	T_{K-S_F}	$T_{S_F-S_C}$	$T_{S_F-S_B}$	$T_{S_B-S_A}$	$T_{S_C-S_A}$	T_{S_A-I}
6	89.0	–	–	–	117.0	–	136.0
7	89.0	–	–	(86.0)	108.5	–	133.0
8	–	90.0	109.0	–	–	113.0	133.0
9	–	96.0	103.0	–	–	119.0	130.5
10	–	89.0	101.0	–	–	121.0	129.0

( ) Indicates a monotropic phase transition

a smectic A phase appears on cooling from the isotropic liquid. However, none of the compounds exhibits a nematic phase.

(d) 4-(2-Methylpentyloxycarbonyl)phenyl 3-(4′-*n*-alkoxybiphenyl-4-yl) propanoates (6).



(6)

In order to reduce the melting and clearing points of compounds of structure (5), we next produced a small series of homologues similar in structure to those previously described (5) (Table 3) but with each containing a 2-methylpentyl terminal ester group in place of the 3-methylbutyl ester group. By bringing the lateral methyl group closer to the ester group, we hoped that this adjustment in structure would decrease the high mps found for compounds of structure (5) and also induce the required sequence of phases. Results for this series are given in Table 4.

A comparison of the heptyloxy, nonyloxy and decyloxy homologues of compounds of structure (3), (5) and (6), is shown in Figure 2. This clearly shows that the increased chain length in the 2-methylpentyl series (6) gives compounds of lower melting points and wider temperature S_C and S_I ranges.

If one is seeking useful materials exhibiting tilted smectic phases then the position of the lateral methyl group in the branched alkyl group is very important. In the 3-methylbutyl series (5), not only do we observe a rapid increase (~ 40°C) in the melting point when compared to the 2-methylbutyl series (3), but also a sharp decrease in the temperature range of the S_C phase for the individual homologues, i.e., about 50% reduction. The phase behaviour, the thermal stabilities and temperature ranges of the smectic phases for compounds in series (3) and (6) were very similar, with compounds in series (3) giving the highest melting points. Comparison of the thermal data for

TABLE 4

Transition Temperatures (°C) for Compounds of Structure (6)

n	T_{K-S_I}	$T_{S_I-S_C}$	$T_{S_C-S_A}$	T_{S_A-I}
7	49.0	84.0	95.0	125.0
9	56.0	77.0	105.0	124.0
10	64.0	75.5	111.0	123.5

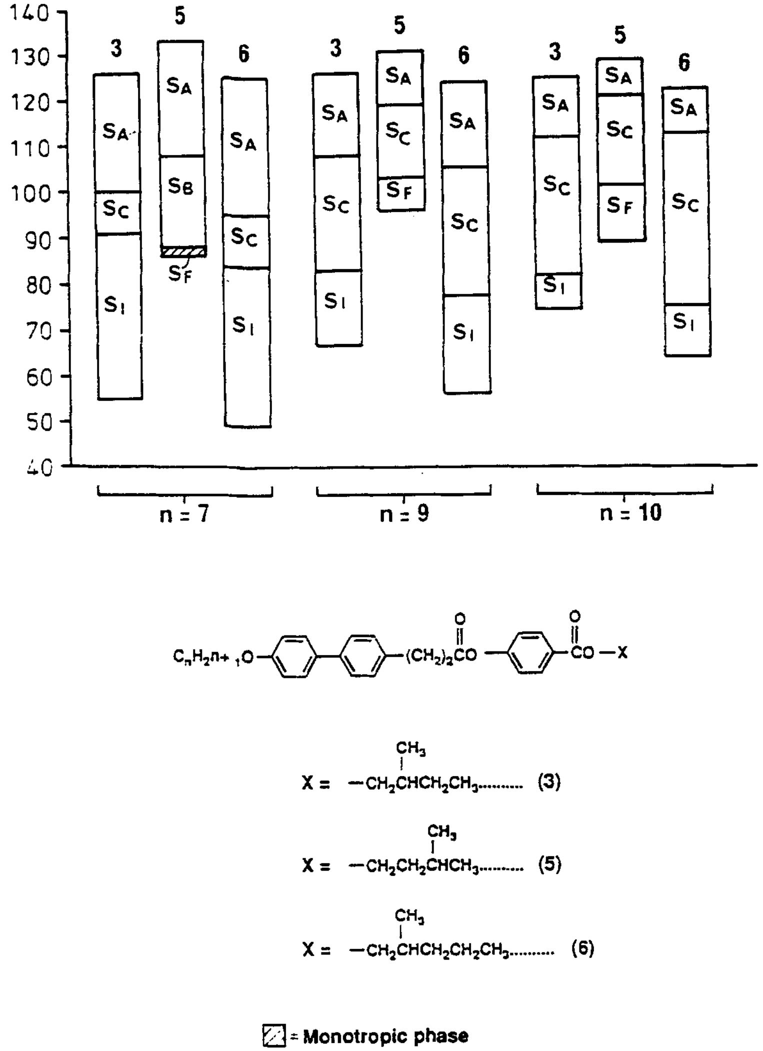
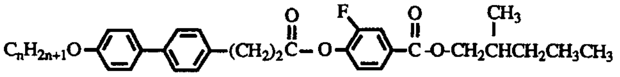


FIGURE 2

compounds in series (**5**) and series (**6**) with those from series (**3**) clearly shows that the position of the lateral methyl group on the alkyl chain has had a more dramatic effect on the liquid crystalline behaviour of these compounds than simply extending the alkyl chain length. By increasing the size of the alkoxy group of the compounds in series (**3**) and (**6**), the smectic I temperature range narrows as the smectic C temperature range increases e.g., when $n = 7$, S_I range = 35°, S_C range = 10°, but when $n = 10$, S_I range = 7° and the S_C range = 30°. No nematic phases were observed for compounds in series (**5**) or (**6**).

B. Lateral Fluorination

(a) 4-(2-Methylpentyloxycarbonyl)-3-fluorophenyl 3-(4′-*n*-alkoxybiphenyl-4-yl) propanoates (7).



(7)

Since the 2-methylpentyl terminal group had produced the desired effect of reducing the melting points and widening the temperature ranges of the tilted phases, the option of using lateral fluorination as a means of reducing even further the thermal stability of the non-tilted smectic phases[2–4] was considered. As shown in our previous work,[1] fluorination of the phenyl ring reduced the smectic thermal stability of the system. With this in mind, a series of 3-fluorophenyl analogues of compound (6) was produced. A series consisting of 5 compounds ($n = 6$–10) was prepared and the results are shown in Table 5.

These results, when compared with the non-fluorinated analogues shown in Table 4, show only a slight reduction in clearing points (15–20°C). All members of this series of compounds display smectic polymesomorphism but only the higher homologues ($n = 8$) showed tilted phases.

The effect of lateral fluorination on transition temperatures and phase type exhibited by compounds of structure (7) can best be illustrated by making direct comparisons with their non-fluorinated analogues (6). Figure 3 shows such a comparison using the homologues, $n = 7$ (C_7H_{15}) and $n = 10$ ($C_{10}H_{21}$). Although lateral fluorination depresses both melting and clearing points in the lower homologues it also, surprisingly, suppresses the formation of smectic tilted phases, with an orthogonal smectic B phase replacing the tilted smectic I and smectic C phases found in the non-fluorinated compound.

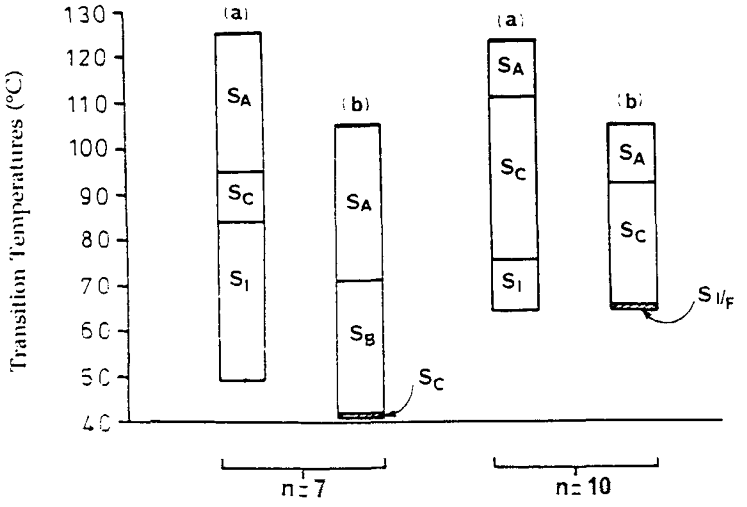
In the higher homologues ($n = 10$) the fluorinated compound does exhibit tilted smectic phases. It consists of a very narrow temperature range smectic I phase below a wider range smectic C phase. In both series of compounds a smectic A phase appears on cooling from the isotropic liquid, but no nematic phase was observed in any of these compounds.

TABLE 5

Transition Temperatures (°C) for Compounds of Structure (7)

n	T_{K-S_B}	$T_{K-S_{I/F}}$	$T_{S_C-S_B}$	$T_{S_{I/F}-S_C}$	$T_{S_{I/F}-S_A}$	$T_{S_C-S_A}$	T_{S_B-A}	T_{S_A-I}
6	58.0	–	(57.5)	–	–	–	83.0	107.0
7	42.0	–	(41.0)	–	–	–	71.0	105.0
8	–	44.0	–	–	75.0	–	–	108.0
9	–	49.0	–	66.0	–	83.0	–	106.0
10	–	64.0	–	65.0	–	92.0	–	105.0

( ) Indicates a monotropic phase transition



(a) Non-fluorinated compound (6)

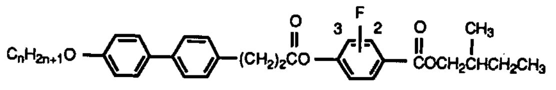
(b) Laterally fluorinated compound (7)

▨ Monotropic phase

FIGURE 3

(b) 4-(2-Methylbutyloxycarbonyl)-2- and -3-fluoro-phenyl 3-(4′-*n*-alkoxybiphenyl-4-yl)propanoates (9) and (10).

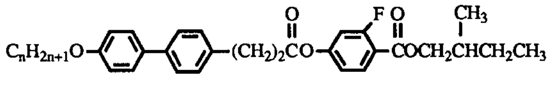
To investigate the effect of lateral fluorination at the 2- and 3- positions in the phenyl ring on the liquid crystalline behaviour of diesters based on 3-(4′-*n*-alkoxybiphenylyl) propanoic acid, the following diesters of structure (**8**) were prepared. Their transition temperatures are given in Tables 6 and 7.



(**8**)

For the diesters of structure (**9**), the 2 F-series, five compounds were prepared ($n = 7$, 9 to 12) and the homologues, except for $n = 12$, exhibited a monotropic S_I phase. All the homologues gave the same phase sequence from the isotropic liquid, i.e., I and S_A to S_C to S_I, showing very wide S_C temperature ranges, e.g., $n = 10$, S_C temperature range is 50°; $n = 11$, S_C temperature range is 53°. However, no nematic phase was exhibited by the compounds from the 2F-series.

TABLE 6



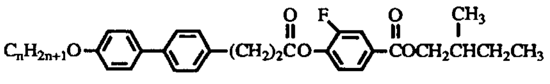
(9)

Transition Temperatures (°C) for Compounds of Structure (9)

n	T_{K-S_C}	$T_{S_I-S_C}$	$T_{S_C-S_A}$	T_{S_A-I}
7	61.0	(58.5)	98.5	120.5
9	58.0	(57.0)	106.0	119.0
10	59.0	(56.0)	106.0	117.0
11	58.0	(49.5)	102.5	116.0
12	58.0	–	103.0	116.0

( ) Indicates monotropic phase transition

TABLE 7



(10)

Transition Temperatures (°C) for Compounds of Structure (10)

n	T_{K-S_E}	T_{K-S_I}	$T_{S_K-S_I}$	$T_{S_E-S_B}$	$T_{S_I-S_C}$	$T_{S_B-S_A}$	$T_{S_C-S_A}$	T_{S_A-I}
6	39.0	–	–	66.5	–	93.0	–	112.5
7	37.5	–	–	59.0	–	83.5	–	109.0
9	–	53.0	(49.0)	–	75.5	–	94.5	109.5
10	–	58.0	–	–	75.0	–	98.5	109.5

( ) Indicates monotropic phase transition

The liquid crystalline behaviour of the compounds of structure (**10**), the 3F-series, is in sharp contrast to the previous compounds in that the earlier members of the 3F-series exhibit crystal phases, i.e., when $n = 6$ and 7, compounds exhibit crystal B and E phases, when $n = 9$, this compound exhibited a crystal K phase. The first two members of the 3F-series show only orthogonal smectic phases (crystal B and E, and smectic A), and tilted smectic phases S_I and S_C appear suddenly for the third member of the series ($n = 9$) with the rapid disappearance of the crystal phases. The appearance of crystal phases in the 3F-series is unusual since it is generally accepted that lateral fluorination in mesogens depresses the formation of smectic phases, especially the formation of crystal phases, and this is exemplified by the liquid crystalline behaviour found for the 2F-series. The significant difference in the liquid crystalline behaviour of the two series of compounds must be due to the position of the fluorine atom. The unusual smectic behaviour of the 3F-series could be due to the fact that the lateral fluorine atom is pointing inwards towards an ester group. Since the ester group is attached to the aromatic ring through the phenolic oxygen, there is very little or no steric interference between the C═O of the ester group and the lateral fluorine atom, thus increasing the chance that the structure of the 3F-series of compounds could be relatively planar. In the case of the 2F-series, without the presence of a lateral fluorine atom, the C═O of the second ester group would be co-planar with the aromatic ring due to the overlap of the p-orbitals. However, the presence of a lateral fluorine atom in

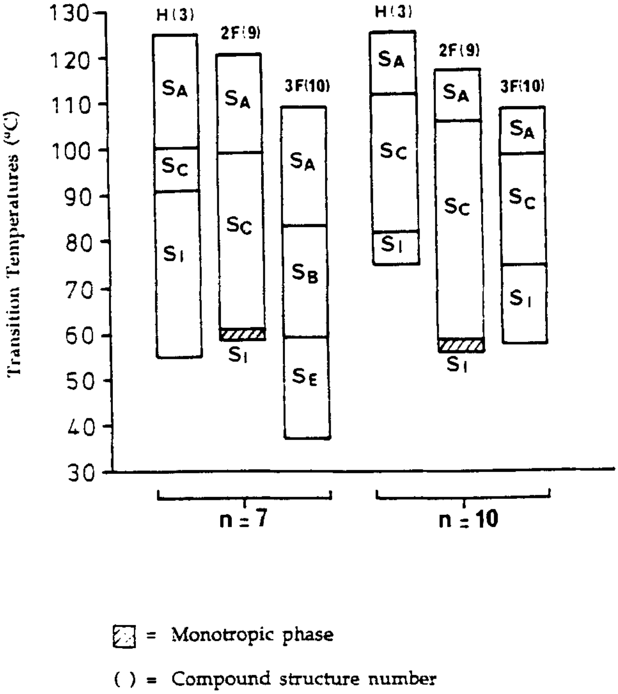


FIGURE 4

the 2F-series sterically hinders the co-planar relationship of the C=O of the ester group with the aromatic ring, causing the C=O to twist out of plane. This out-of-plane twisting between the C=O of the ester group and the aromatic ring decreases the packing efficiency of the molecules and is therefore detrimental to the formation of the more ordered crystal phases.

A comparison of the 2F- and 3F-series of compounds with their non-fluorinated analogue (3) is given in Figure 4. Clearly the incorporation of a lateral fluorine atom into the 2-position of the benzene ring has decreased the smectic thermal stability of both the S_A and S_C phases, but the decrease for the thermal stability of the S_C phase is very small (about 1–2°). In the case of the 3F-series the laterally positioned fluorine atom has markedly reduced the thermal stability of the tilted S_C and S_I phases, and only the higher homologues ($n = 9$ and 10) exhibited tilted phases.

The fluorine atom in the 2-position of the benzene ring (the 2F-series) is, therefore, conducive to the formation of tilted smectic (S_I/S_C) phases, a fact which is only apparent for the higher homologues of the 3F-series.

CONCLUSIONS

A systematic investigation has now been completed into the effect of (a) incorporation of branched (achiral) end groups and (b) lateral fluorination, on the liquid crystalline behaviour of diesters based on 4′-*n*-alkyl- and -alkoxy-biphenyl-4-ylpropanoic acid. The following conclusions can be drawn from this study.

Branched (Achiral) Terminal Groups

(a) Compounds incorporating the 2-methylbutyl and 2-methylpentyl terminal groups produce compounds that exhibit the same phase sequence (I to S_A to S_C to S_I), with the compounds incorporating the 2-methylpentyl terminal group giving the lower melting points and widest S_C and S_I ranges (35°).

(b) The incorporation of the 3-methylbutyl terminal group substantially raises the melting point of these compounds and gives much narrower S_C ranges (15–20°).

(c) Comparison of the liquid crystalline behaviour of compounds containing the terminal groups 2-methylbutyl, 2-methylpentyl and 3-methylbutyl clearly show that the position of the lateral methyl group on the terminal group had a more dramatic effect on the liquid crystalline behaviour of these compounds than simply extending the alkyl chain length by one carbon atom.

(d) The effect of changing the alkoxy end group to an alkyl end group reduced both the melting point and transition temperatures of the compounds, as demonstrated for the 2-methylbutyl series (**3**) and (**4**).

Lateral Fluorination

(a) The effect of lateral fluorination in both the 2- and 3-positions of the benzene ring reduces the melting points and smectic thermal stabilities of the diesters.

(b) In the case of the 2F-series, the reduction in S_C thermal stability by the laterally positioned fluorine atom was very small (2–3°C), giving rise to compounds with very wide S_C ranges (40–50°C).

(c) The lower members of the 3F-series exhibited a number of crystal phases which is unusual for compounds incorporating a laterally positioned fluorine atom.

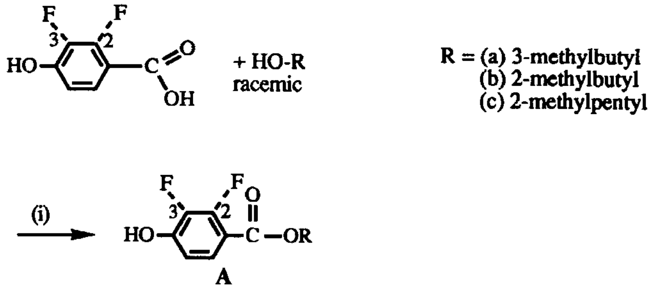
Whether the diesters incorporated a branched terminal group or a laterally positioned fluorine atom, no nematic phase was observed for these compounds.

Experimental Section

The compounds described in this paper were prepared by using the following synthetic schemes.

The biphenyl-4-ylpropanoic acids **D** were prepared by the use of a Heck[2] reaction. Coupling of methyl acrylate to 4-bromo-4′-hydroxybiphenyl via a palladium catalyst in the presence of *o*-tolylphosphine produced the α,β-unsaturated ester **B**. Ester **C** was obtained by catalytic hydrogenation using 5% palladium-charcoal and hydrogen. Alkylation with an appropriate *n*-alkyl bromide in the presence of potassium carbonate using butanone as the solvent followed by hydrolysis of the ester group gave acid **D**.

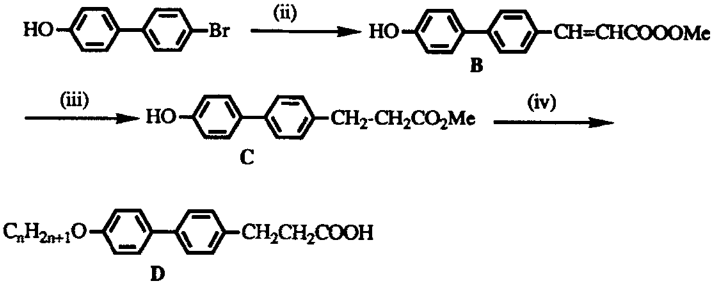
The alkylbiphenyl-4-ylcarboxylic acid **E** was treated with borane-THF to form alkylbiphenylylmethanol **F**. This was brominated using phosphorous tribromide in benzene to form compound **G** which was then reacted with diethyl malonate and



R = (a) 3-methylbutyl
(b) 2-methylbutyl
(c) 2-methylpentyl

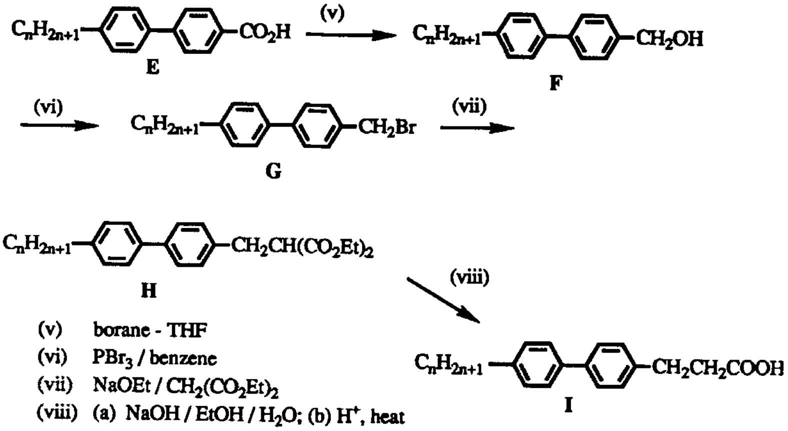
(i) conc H_2SO_4, toluene

SCHEME 1



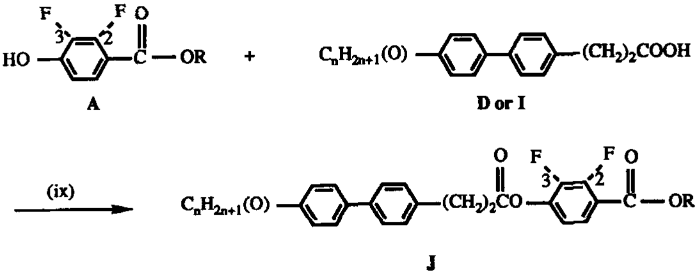
(ii) CH_2=$CHCO_2CH_3$, Et_3N, (o-tolyl)$_3$P, Pd(II) acetate
(iii) H_2/Pd/C
(iv) (a) $C_nH_{2n+1}Br$ / K_2CO_3 / butanone; (b) NaOH / EtOH / H_2O; (C) H^+

SCHEME 2



(v) borane - THF
(vi) PBr_3 / benzene
(vii) NaOEt / $CH_2(CO_2Et)_2$
(viii) (a) NaOH / EtOH / H_2O; (b) H^+, heat

SCHEME 3



(ix) dicyclohexylcarbodiimide (DCC), 4-(*N*-pyrrolidino)pyridine.

R = (a) 3-methylbutyl.
(b) 2-methylbutyl.
(c) 2-methylpentyl.

SCHEME 4

sodium ethoxide to form diester **H**. Hydrolysis and decarboxylation gave the required acid I.

Esterification of the alkyl 4-hydroxybenzoate **A** with biphenylylpropanoic acids **D** or **I** using dicyclohexylcarbodiimide (DCC) and 4-(*N*-pyrrolidino)pyridine formed the target compounds **J**.

Purification of each final compound was achieved by using column chromatography on silica gel (60–120 mesh) and eluting with a 5:1 mixture of petroleum fraction (bp 60–80°C) and ethyl acetate. Successive recrystallisations from petroleum fraction (bp 40–60°C) gave products of one spot purity when examined by thin layer chromatography.

The degree of purity was also determined by the use of reverse-phase high performance liquid chromatography. This was achieved on a Partisil ODS-2 column using methanol as the eluent. Detection of the eluting products was *via* a Kratos SF 7697 u/v detector (254 nm). The degree of purity in each case was found to be $> 99.5\%$.

Structural elucidation of all of the target compounds and intermediates was achieved using a combination of proton nuclear magnetic resonance spectroscopy (Jeol JNM-GX 270 MHz spectrophotometer), infrared spectrometry (Perkin-Elmer 783 IR spectrophotometer) and mass spectral analysis (Finnigan 1020 GC-MS). Predicted structures were confirmed in each case.

Phase assignments and the corresponding transition temperatures of the target molecules were determined by thermal optical microscopy using an Olympus BH 2 microscope fitted with crossed polarisers and equipped with a Mettler FP 52 microfurnace and FP 5 control unit. Differential scanning calorimetry (DSC) was used to determine both transition temperatures and associated enthalpy changes. This was achieved by using a Perkin-Elmer DSC 7 calorimeter calibrated against an indium standard.

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