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The synthesis and liquid crystal properties of some 4-*n*-nonylphenyl esters of 3-(4′-*n*-alkoxybiphenylyl)- and 3-(4′-*n*-alkoxybiphenylyl)-3-methyl-propanoic acids and their laterally fluorinated analogues

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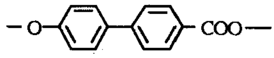
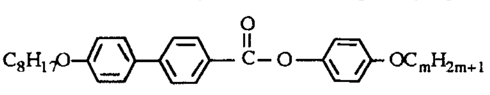
A number of 4-*n*-nonylphenyl esters and mono- and di-fluorinated 4-*n*-nonylphenyl esters derived from 3-(4′-*n*-alkoxybiphenylyl)propanoic acids (II) have been synthesized and their thermotropic liquid crystal properties assessed with a view to obtaining tilted smectic phases for possible use in ferroelectric display devices. Many of these compounds exhibit wide temperature range S_C and $S_{I/F}$ phases, but none gave the ideal phase sequence S_C–S_A–N–I mainly because the structure of these compounds was not conducive to the formation of the nematic phase. To try to alleviate this problem a series of 4-*n*-nonylphenyl esters based on 3-(4′-*n*-alkoxybiphenylyl)-3-methylpropanoic acid was prepared, where a lateral methyl group was incorporated in the *β*-position of the $-CH_2CH_2CO_2-$ linkage. Incorporation of the lateral methyl group encouraged the formation of a nematic phase at the expense of both the smectic A phase and tilted smectic phases.

1. Introduction

The nematic and smectic properties of a number of series of compounds with the central core structure



have been extensively investigated by Gray and Goodby [1] and have been shown to exhibit smectic polymorphism. Particularly interesting is the appearance of smectic C phases in 4-*n*-alkyl- and alkoxy-phenyl esters where the molecular core has been extended by the addition of, for example, an alkoxyphenyl group as in structure (I).



(I)

It would appear that an extended central core between two long alkyl or alkoxy chains encourages the formation of smectic C phases and possibly other tilted phases such as smectic I, F, and G. With this in mind, the central core has been extended [2] even

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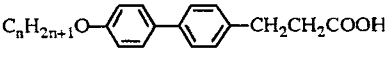
further by interposing a dimethylene group ($-CH_2CH_2-$) between the biphenylyl and carboxyl moieties in a series of esters derived from acids (II), to investigate the effect of incorporating a centrally positioned flexible group ($-CH_2CH_2-$) on the liquid–crystalline behaviour.



(II)

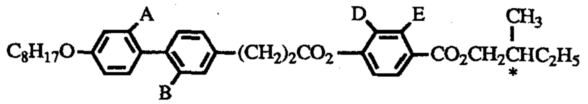
It is generally accepted that the best way to produce a ferroelectric mixture is to add a chiral material to a host mixture which exhibits a smectic C phase [3]. Mesogens exhibiting tilted phases over a wide temperature range ($<100°C$), particularly smectic C, but also I or F, are useful for ferroelectric devices since many chiral dopants are not liquid-crystalline and therefore would diminish the liquid-crystalline behaviour of the host material. The introduction of the $-CH_2CH_2-$ group did produce liquid-crystalline materials exhibiting wide S_C, S_I or S_F ranges with high S_C, S_I or S_F thermal stabilities. The introduction of the $-CH_2CH_2-$ group also yielded liquid-crystalline materials with relatively low viscosities, as shown by the fast switching times of ferroelectric S_C^* mixtures produced from mixtures incorporating chiral esters derived from the acids (II) and also non-chiral esters derived from the acids (II), doped with chiral additives.

Through our previous work on laterally substituted fluoroterphenyls [4], the incorporation of a lateral fluoro-substituent is known to be conducive to the formation of tilted smectic (S_C/S_I) phases. It was also demonstrated that the position of the lateral fluoro-substituent was critically important in relation to the smectic tendency of these novel systems. From earlier results [2] on a range of esters (III), some prepared from the acid (II) with $n=8$ (results expressed in graphical form in figure 1), the best location for the fluorine atom to induce tilted smectic phases would appear to be in the phenolic moiety. This information and the use of a long alkyl chain in the 4 position of the phenolic group led us to synthesize three series of esters (compounds V, VI and VII) having one or two lateral fluorines in the 4-nonylphenyl part of the esters of the acid (II) with $n=$ a range of integers. For comparison, the parent non-fluorinated esters (4-*n*-nonylphenyl esters of the acids (II)), i.e. the compounds (IV), were also prepared. The intention was that the combination of the long terminal alkyl chains and the fluoro-substituent(s) would enhance the formation of tilted smectic phases and also diminish the likelihood of the formation of crystal smectic phases. The negative dielectric anisotropy of these materials would also enhance AC stabilization in ferroelectric display devices. In the five homologous series investigated only one (see § 2.1) gave a nematic phase. In order to induce the formation of a nematic phase but without seriously affecting the ability of these compounds to form tilted smectic phases, the structure of the compounds in § 2.3 were modified in a very novel way, in that a lateral methyl group was attached to the C-atom in the $CH_2CH_2CO_2-$ linking groups adjacent to the biphenylyl group.

2. Results and discussion

2.1. *Effect of incorporation of a laterally positioned fluoro-substituent*

In the esters (III) there are a number of sites of lateral fluorination i.e. in either the biphenylyl or phenyl moieties and the results from the earlier work [2] reviewing this situation are illustrated graphically in figure 1. This clearly shows that a lateral fluoro-substituent in the phenyl moiety is more conducive to the formation of tilted smectic (S_C/S_I) phases than lateral fluorination in the biphenylyl moiety (S_A phase only).



(III)

A, B, D, or E = hydrogen or fluorine.

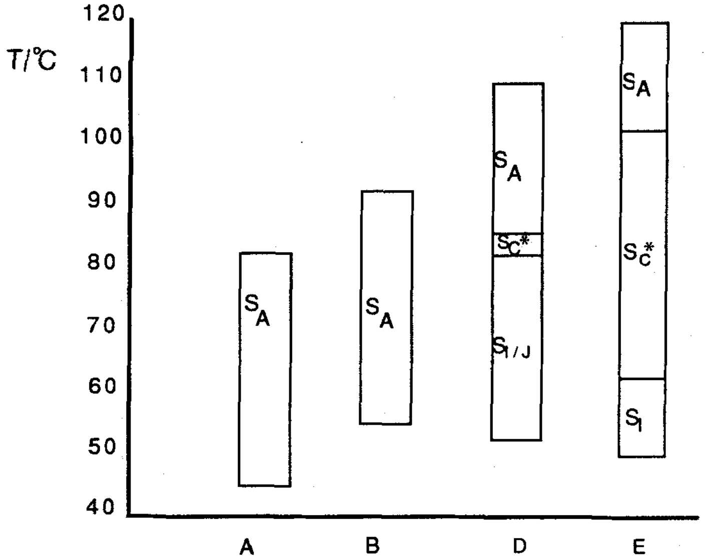
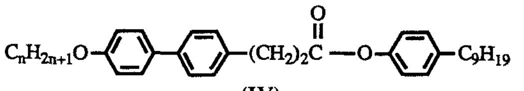


Figure 1. The effect of fluoro monosubstitution of the biphenylyl ring (A or B) or the phenyl ring (D or E) on smectic polymorphism in the compounds (III).

With these facts established, three series of fluorinated nonylphenyl esters of the 3-(4-alkoxybiphenylyl)propanoic acids were prepared in order to investigate the effect of the number and position of the fluoro-substituents on the formation and thermal stability of the tilted smectic phases.

2.2. *4-n-Nonylphenyl esters of 3-(4′-n-alkoxybiphenylyl)propanoic acids (IV)*



(IV)

A parent series consisting of four compounds was prepared (see structure (IV), $n=4$, 6, 8 and 10) and the transition temperatures are given in table 1. Each of the four homologues exhibits a relatively high melting point (90–105°C) and each melts to form a crystal B phase. The lower two homologues ($n=4$ and 6) show smectic A phases before clearing to isotropic liquids at about 130°C. For the other two homologues ($n=8$ and 10), a smectic C phase, the only tilted smectic phase shown in the series, appears above the crystal B phase. A smectic A phase appears above the smectic C phase in the octyloxy ($n=8$) homologue, but is absent in the decyloxy ($n=10$) homologue. The length of the alkoxy chain apparently influences the type of mesophase formed, the longer chains ($n=8$ and 10) favouring the formation of a smectic C phase. However mesophase thermal stability seems little affected by the length of the chain since each of the four compounds clears at about 130°C.

Table 1. Transition temperatures for compounds of structure (IV).

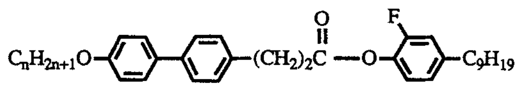
n	T_{CS_B}/°C	$T_{S_BS_C}$/°C	$T_{S_BS_A}$/°C	$T_{S_CS_A}$/°C	T_{S_AI}/°C	T_{S_CI}/°C
4	104·5	—	119·5	—	129·5	—
6	93·0	—	120·0	—	130·5	—
8	92·0	122·5	—	126·5	130·5	—
10	92·5	121·0	—	—	—	129·5

Table 2. Transition temperatures for compounds of structure (V).

n	T_{CS_C}/°C	T_{CS_I}/°C	T_{CS_B}/°C	$T_{S_IS_C}$/°C	$T_{S_BS_C}$/°C	T_{S_CN}/°C	T_{S_CI}/°C	T_{NI}/°C
4	72·5	—	—	—	—	(71·0)	—	103·0
5	70·0	—	—	—	—	81·5	—	99·0
6	—	—	64·0	—	64·5	96·0	—	103·5
7	—	49·0	—	66·0	—	96·0	—	103·5
8	—	—	58·0	—	74·0	—	105·5	—
9	—	58·5	—	76·0	—	—	105·5	—
10	—	—	55·5	—	82·0	—	107·5	—

( ) Indicates a monotropic phase transition.

2.3. *2-Fluoro-4-n-nonylphenyl esters of 3-(4′-n-alkoxybiphenylyl)propanoic acids (V)*



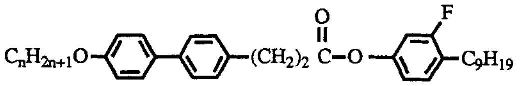
(V)

A series of seven compounds was prepared ($n = 4$ to 10). Transition temperatures for these compounds are given in table 2. When compared with the non-fluorinated parent compounds (IV), the data for which are shown in table 1, it is immediately apparent that both melting and clearing points are much lower in the laterally fluorinated compounds; the fluoro-substituent broadens the molecule, probably exerts a steric twisting effect, and increases the separation of the molecular long axes, diminishing liquid crystal thermal stability. The lateral fluorination also encourages the formation of tilted phases and even in the *n*-butoxy compound, a monotropic S_C phase is observed. The S_C phase is observed enantiotropically in all of the other homologues. In the lower four homologues ($n = 4$, 5, 6 and 7) nematic phases are observed above the smectic C phase, but do not appear from $n = 8$ onwards where the smectic C is the first mesophase formed on cooling from the isotropic liquid. The lower homologues of the esters (IV) exhibit, by contrast, a S_A phase on cooling from the isotropic liquid. Perhaps the most interesting feature of this series is the appearance of a smectic I phase for the odd numbered homologues, $n = 7$ and 9, alternating with the crystal B phase found in the even numbered homologues, $n = 6$, 8 and 10. The tilted smectic I phase appears to be favoured by the odd-numbered alkoxy chains, whereas even alkoxy chains generate orthogonal crystal B phases, despite the presence of a lateral fluoro-substituent.

Each of the homologues $n = 6$–10 shows a fairly wide (30°C) smectic C range. Microscopically this consists of a woolly grainy schlieren texture, buff coloured at the upper end of the temperature band but becoming blue on cooling. As the temperature is reduced, the angle of tilt observed by X-ray diffraction increases, but apparently not smoothly as an occasional ripple effect crossing from one side of the field of view to the other appears to indicate a release of stress in the molecular packing. In the homologues $n = 7$ and 9, the transition to a smectic I phase is shown by loss of the woolly grainy effect giving a optically clearer schlieren texture which is, however, typically difficult to bring to sharp focus. This sequence is similar to that shown by Gray and Goodby [5] for the smectic C to smectic I sequence observed for 4-(2'-methylbutyl)phenyl 4'-*n*-octyloxybiphenyl-4-carboxylate.

Examination of table 2 also shows the complete absence of the smectic A phase. This is regrettable since a narrow smectic A and a narrow nematic phase range above a smectic C phase are generally required to assist alignment in ferroelectric devices. However by carefully formulating smectic C host mixtures from these compounds and materials that do exhibit smectic A phases, useful smectic C host mixtures exhibiting the required phase sequence, $I \rightarrow N \rightarrow S_A \rightarrow S_C$, could be produced.

2.4. *3-Fluoro-4-nonylphenyl esters of 3-(4'-n-alkoxybiphenylyl)propanoic acids (VI)*

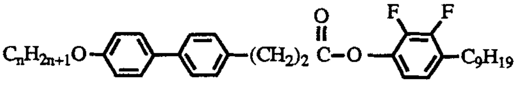


(VI)

Three compounds (VI) were prepared ($n = 6$, 8 and 10) and transition temperatures for this series are given in table 3. Each of these compounds gives a higher clearing point than its isomer (V); the values are in the region 15–20°C higher than those found for the 2-fluorophenyl esters listed in table 2. The decreases in clearing temperatures from those of the parent non-fluorinated esters (IV) are indeed small. This reflects the minimal effects of lateral fluoro-substitution when no steric effect occurs, and indicates that the larger reduction in clearing temperatures from the esters (IV) to the esters (V) are probably due to the twisting effect about the O-ring bond.

None of the compounds (VI) shows a nematic phase, but smectic A phases are observed in all three compounds. Narrow temperature range smectic C phases were observed for two of the compounds ($n = 8$ and 10), but only the higher homologue ($n = 10$) gave a hexatic (S_I or S_F) tilted phase. The other two compounds ($n = 6$ and 8) exhibited only orthogonal crystal B phases below the smectic C phase. Compounds (IV), therefore, show significant differences from their 2-fluoro isomers (V), which in addition to having lower clearing temperatures, show much wider smectic C phases, particularly for the higher homologues. Smectic A phases, however, are entirely absent in the 2-fluorophenyl series (V), but do appear in two compounds of the 3-fluorophenyl series (VI). Neither series of compounds (IV) nor (VI) shows nematic phases.

2.5. *2,3-Difluoro-4-nonylphenyl esters of 3-(4'-n-alkoxybiphenylyl)propanoic acids (VII)*



(VII)

Four compounds (VII) were prepared in this series ($n = 4$, 6, 8 and 10) and transition temperatures for these compounds are given in table 4. Comparison of the thermal data

Table 3. Transition temperatures for compounds of structure (VI).

n	$T_{CS_{I/F}}$/°C	T_{CS_B}/°C	$T_{S_{I/F}S_C}$/°C	$T_{S_BS_A}$/°C	$T_{S_BS_C}$/°C	$T_{S_CS_A}$/°C	T_{S_AI}/°C
6	—	74·0	—	119·0	—	—	129·5
8	—	70·5	—	—	89·0	98·0	122·0
10	75·5	—	86·5	—	—	116·5	120·0

Table 4. Transition temperatures for compounds of structure (VII).

n	T_{CS_B}/°C	T_{CS_C}/°C	$T_{S_ES_B}$/°C	$T_{S_BS_C}$/°C	$T_{S_{I/F}S_C}$/°C	$T_{S_BS_A}$/°C	$T_{S_CS_A}$/°C	T_{S_CI}/°C	T_{S_AI}/°C
4	74·0	—	(67·0)	—	—	77·0	—	—	106·0
6	—	66·0	—	(64·5)	—	—	89·0	—	106·0
8	—	65·0	—	—	(58·0)	—	—	109·0	—
10	—	71·0	—	—	(62·0)	—	—	109·0	—

( ) Indicates a monotropic phase transition.

for the 2,3-difluoro series with results found for the 3-fluoro series (see table 3) shows that the 2,3-difluoro compounds have much lower clearing points than the 3-fluoro compounds; as would be expected, the values are somewhat similar to those found for the 2-fluoro compounds (see table 2). The higher homologues of the 2,3-difluoro series ($n=8$ and 10) show smectic C phases of wide temperature range (50°C) and these appear from the isotropic liquid on cooling. Monotropic smectic I or smectic F phases, as yet uncertain which, are observed on further cooling in each case. Therefore, these two homologues exhibit only tilted smectic phases, but unfortunately neither shows the required narrow temperature range nematic and smectic A phases needed for good host materials for ferroelectric devices, although the addition of chiral dopants may induce such phases.

The lower two homologues ($n=4$ and 6) show monotropic crystal E and crystal B phases, respectively. Smectic A phases are observed in both cases but nematic phases are absent in both compounds. Only the higher homologue of this pair ($n=6$) shows a tilted phase (smectic C), but this is of narrow temperature range and is preceded by an orthogonal crystal B phase.

Comparison of the 3-fluoro compounds (VI) and the 2,3-difluoro compounds (VII) shows few similarities in polymorphism. Indeed, greater similarities exist, as would be anticipated, between the 2-fluoro (V) and 2,3-difluoro esters, particularly in respect of their clearing points and wide smectic C ranges. The polymorphism of the 3-fluoro compounds is akin to that for the non-fluorinated esters (IV), with the higher homologues ($n=8$ and 10) having high clearing points and narrow range smectic phases. These results must be due to the fact that a fluoro substituent placed in the 2-position of the phenyl group exercises a dominant effect through its steric interactions with the oxygen of the carbonyl group of the ester function.

A graphical comparison of the octyloxy and decyloxy homologues of the 3 series of laterally fluorinated compounds with the corresponding non-fluorinated parent homologues is given in figure 2. From this we note that the introduction of the 3-fluoro substituent in the 2-fluoro series giving the 2,3-difluoro-esters slightly enhances the S_C clearing temperatures, a further example of space filling by a substituent which does not increase the molecular breadth.

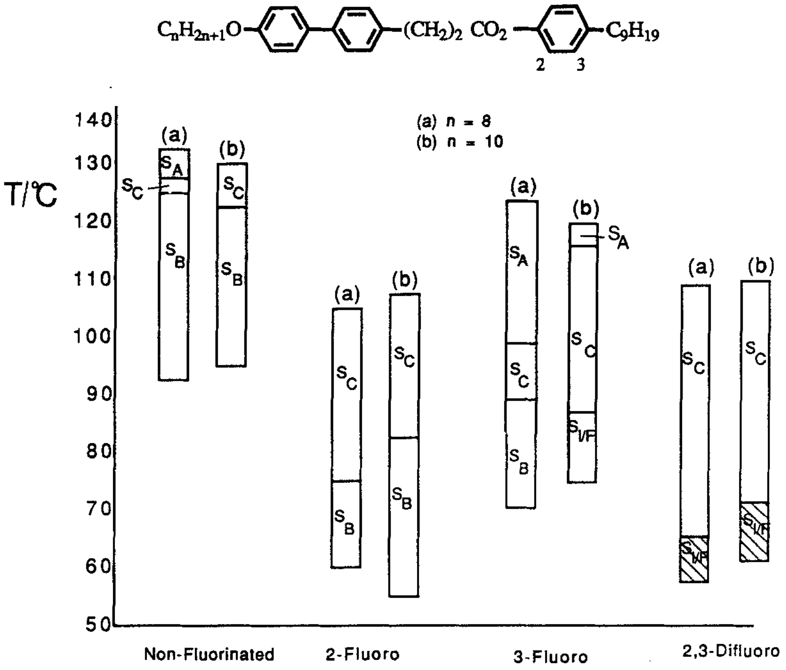
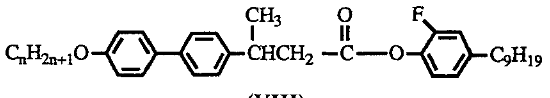


Figure 2. The effect of fluoro substitution on smectic polymorphism.

2.6. *2-Fluoro-4-n-nonylphenyl esters of 2-(4'-n-alkoxybiphenylyl)-3-methylpropanoic acids (VIII)*



$$C_nH_{2n+1}O-C_6H_4-C_6H_4-CH(CH_3)CH_2-C(=O)-O-C_6H_3F-C_9H_{19}$$

(VIII)

A series of six homologues ($n=4$, 6–10) was prepared and the results from this investigation are given in table 5. Each of the six homologues shows a low melting point (44·0–54·0°C) with smectic and nematic polymorphism over a relatively narrow temperature range (10–20°C). Melting points are considerably lower than those of the corresponding homologues of the alkoxybiphenylylpropanoic esters given in § 2.3. There is a low temperature crystal phase in the compound where $n=10$, but tilted smectic C phases appear in three of the six homologues ($n=8$–10) but only within a narrow temperature range (10–15°C).

The structural modification of the biphenylyl to phenyl linkage ($-CH_2CH_2CO_2-$ to $-CH(CH_3)CH_2CO_2-$) has suppressed the formation of smectic B and I phases seen in the unmodified compounds (V) in §2.3, but has induced the formation of nematic phases in compounds where $n=4$–9. This phase is, however, absent for the compound where $n=10$. Figure 3 illustrates these changes by comparing (a) the unmodified (V) and (b) the modified (VIII) compounds where $n=6$ and 9. Figure 3 illustrates the extent to which lateral methylation in the linkage group has reduced mesophase thermal stability by reducing clearing points by 40–50°C when compared with the corresponding non-laterally methylated compounds (V). In the lower homologue ($n=6$) only a

Table 5. Transition temperatures for compounds of structure (VIII).

n	$T_{CS_{cryst}}$/°C	T_{CS_C}/°C	T_{CN}/°C	$T_{S_IS_C}$/°C	T_{S_CN}/°C	T_{S_CI}/°C	T_{NI}/°C
4	—	—	54·0	—	—	—	64·5
6	—	—	44·0	—	—	—	64·0
7	—	—	49·0	—	—	—	65·5
8	—	52·0	—	—	60·0	—	70·0
9	—	51·0	—	—	64·5	—	67·5
10	61·0	—	—	62·5	—	72·0	—

S_{cryst} = Unidentified smectic phase.

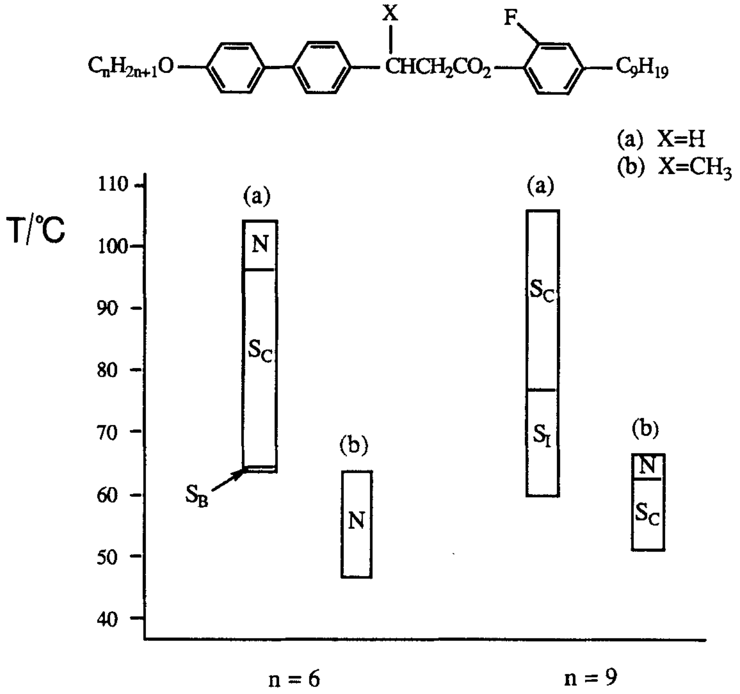


Figure 3. The effect of incorporating a lateral methyl group into the linkage on the formation of smectic and nematic phases.

nematic phase is seen but this is partially replaced by a tilted smectic C phase in the higher homologue (*n* = 9). None of these compounds displays a smectic A phase, which in combination with a narrow temperature nematic phase is generally required to produce mixtures which could be useful for ferroelectric devices.

3. Conclusions

(1) Lateral fluorination in the 2- or 3-position and 2,3-difluorination are all conducive to the formation of tilted smectic phases (S_C/$S_{I/F}$).

(2) 2-Fluoro and 2,3-difluoro compounds have similar melting points and S_C thermal stabilities.

(3) 2-Fluoro and 2,3-difluoro compounds have lower melting points and mesophase thermal stabilities than the 3-fluoro compounds.

(4) For the 2-fluoro compounds the lateral position of the fluoro-substituent encourages the formation of the S_C phase, whereas for the 3-fluoro compounds, the fluoro substituent is more conducive to the formation of both the S_A and the S_C phase. In both cases, except for the decyloxy homologue in the 3-fluoro series, there is always an underlying crystal S_B phase or a S_I phase.

(5) For the 2,3-difluoro series of compounds, there is no underlying crystal S_B phase, but instead a $S_{I/F}$ phase. This coupled with the fact that these compounds show wide range S_C phases, demonstrates quite clearly the importance of lateral fluorination. 2,3-Difluoro esters may therefore be useful as S_C host materials for ferroelectric devices, particularly if mixed with suitable dopant molecules to produce the usually required sequence $S_C \rightarrow S_A \rightarrow N \rightarrow I$, essential for the alignment of ferroelectic materials.

(6) In the 2-fluoro series, an alternation of phase type was observed with the even members (even number of carbon atoms in the alkoxy chain) giving crystal S_B phases and the odd members S_I phases.

(7) Incorporation of a methyl group into the β position of the $-CH_2CH_2CO_2-$ linkage (compound VIII) has had the following effects on polymorphism and mesophase thermal stability when compared with the unmodified compounds (V).

  (*a*) Melting and clearing points are considerably lowered due to the broadening effect of the laterally positioned methyl group.

  (*b*) Smectic polymorphism is mostly confined to a narrow temperature range smectic C phase.

  (*c*) Smectic I, F and crystal B phases, which are prominent in the unmodified compounds (V), are suppressed in the modified series (VIII).

  (*d*) There is a greater tendency to form nematic phases in the modified series (VIII) but these are not accompanied by smectic A phases.

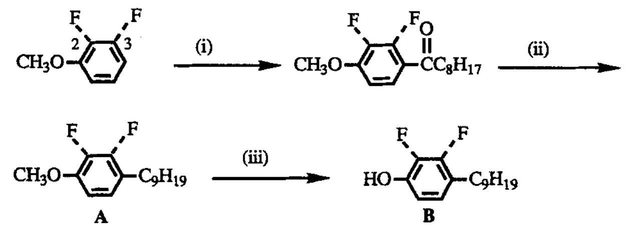
4. Experimental

The structures of all of the target compounds and intermediates were confirmed by a combination of ^1H NMR (Jeol JNM-GX 270 MHz spectrometer), infrared spectroscopy (Perkin–Elmer 783 IR spectrophotometer) and mass spectral analysis (Finnigan 1020 GCMS).

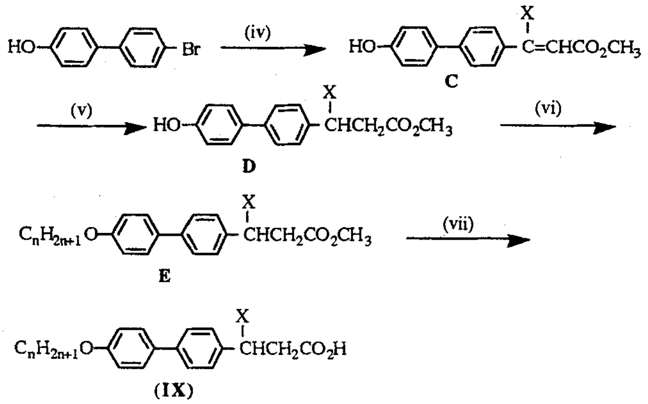
Phase assignments and the corresponding transition temperatures of the target molecules were determined by the examination of defect textures by thermal optical microscopy, using an Olympus BH-2 microscope fitted with crossed polarisers and equipped with a Mettler FP 52 microfurnace and FPS control unit. In some cases the phase assignment obtained by thermal optical microscopy was confirmed by X-ray diffraction (University of Bristol). Scanning calorimetry 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.

The synthetic routes used to produce the parent nonfluorinated esters and the mono- and di-fluoro-4-nonylphenyl esters of the 3-(4-alkoxybiphenylyl)propanoic acids are discussed in schemes 1–3.

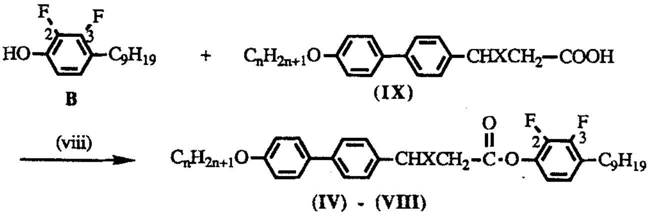
The mono- and di-fluoro-4-nonylphenols were prepared by Friedel–Crafts acylation of the appropriate fluoroanisole followed by reduction of the aryl ketone using



Scheme 1. (i) $C_8H_{17}COCl$, $AlCl_3$, $PhNO_2$. (ii) Et_3SiH, CF_3COOH^2. (iii) BBr_3 (1·0 M solution in dichloromethane).



Scheme 2. (iv) $H_2C{=}CHCO_2CH_3$, (when $X{=}H$) or $H(CH_3)C{=}CHCO_2CH_3$ (when $X{=}CH_3$), Et_3N, (*o*-tolyl)$_3$P, Pd (II) acetate, CH_3CN. (v) H_2/Pd/C, THF. (vi) RBr, K_2CO_3 butanone. (vii) NaOH, H_2O, EtOH. $X{=}H$ or CH_3.



Scheme 3. (viii) DCC, 4-pyrrolidinopyridine, CH_2Cl_2. $X{=}H$ or CH_3.

triethylsilane in trifluoroacetic acid [6] to form mono- and di-fluoro-4-nonylanisoles (A). Alkyl-aryl ether cleavage using boron tribromide (1·0 M) in dichloromethane gave the mono- and di-fluoro-4-nonylphenols (B).

Biphenylylpropanoic acids (IX) were prepared firstly via a Heck [7] reaction in which methyl acrylate or methyl crotonate was coupled to 4-bromo-4′-hydroxybiphenyl in the presence of tri-*o*-tolylphosphine with palladium (II) acetate as the catalyst, to form the unsaturated ester (C). Catalytic hydrogenation using 5 per cent palladium-charcoal produced ester D. Alkylation using the appropriate *n*-alkyl bromide and potassium carbonate in butanone gave the alkoxybiphenylyl ester E. Finally ester hydrolysis using sodium hydroxide in water and ethanol gave the acid (IX). Esterification of the phenols B with the acids (IX) was carried out using dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinopyridine as the catalyst to form the target compounds (VIII).

Each of the final compounds (IV)–(VIII) was purified by column chromatography using silica gel (60–120 mesh) and petroleum fraction (bp 40–60°C)/ethyl acetate mixture 9 : 1) as the eluent. Successive recrystallizations from acetonitrile gave products of one-spot purity when examined by thin-layer chromatography (silica gel, petroleum fraction (bp 40–60°C)/ethyl acetate (9 : 1)). The degree of purity was also determined by using reverse-phase high performance liquid chromatography. This was carried out on a Partisil 005-2 column using a mixture of methanol/chloroform (4 : 1) as the eluent. The purity of the products was found to be >99·5 per cent.

4-*n*-Nonylphenol, which was obtained from Merck Ltd, Poole, Dorset, was esterified with acids prepared as in scheme 2, by the procedure given in scheme 3.

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