Novel 2-(4-octylphenyl)pyridin-5-yl alkanoates and alkenoates: Influence of dipoles and chain conformation on smectic C formation

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Novel 2-(4-octylphenyl)pyridin-5-yl alkanoates and alkenoates: influence of dipoles and chain conformation on smectic C formation

by S. M. KELLY* and J. FÜNFSCHILLING

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A series of 2-(4-octylphenyl)pyridin-5-yl alkanoates has been synthesized and found to exhibit smectic mesomorphism including the smectic C phase. The influence on the transition temperatures of introducing a carbon–carbon double bond in the terminal alkanoyloxy (ester) chain of the alkanoates to produce the corresponding alkenoates has also been investigated. The position and configuration of the double bond has been changed systematically in order to determine the optimal configuration and conformation of the terminal chains for smectic C formation. The observed results are consistent with a linearly-extended (alternately cis and trans) conformation of the chain. The dependence of the transition temperatures on chain length was studied for one homologous series each of the alkanoates and the (E)-alk-2-enoates. The new esters are constitutional isomers of the 5-(4-octylphenyl)pyridin-2-yl alkanoates and alkenoates previously synthesized (differing only in the position of the nitrogen atom). Comparisons revealed consistently higher smectic C transition temperatures and lower ordered smectic tendencies for the new esters. The dependence of S_C formation on the position and number of dipoles associated with oxygen atoms, nitrogen atoms and carboxy groups was also investigated. Several of the new esters exhibit remarkably low viscosity values (i.e. short response times) in an optically active base mixture used for evaluation and comparison purposes.

1. Introduction

Although the 4-(5-n-alkylpyridin-2-yl)phenyl alkanoates [1] only exhibit a very narrow range (2–3°C) smectic C phase (S_C) above smectic B and F (S_B, S_F) phases, they can be used to increase the chiral smectic C transition temperature ($T_{S_C^*}$) of chiral smectic C (S_C^*) mixtures, while at the same time lowering the melting point/crystallization temperature (T_m). Esters have recently been found often to exhibit lower viscosity than that of the corresponding ethers, if the ester (carboxy) group is in a terminal rather than a central position in the molecule [2–6]. Attempts have been made to improve the properties of the 4-(5-n-alkylpyridin-2-yl)phenyl alkanoates [1] by introducing a carbon–carbon double bond in various positions and configurations into the terminal chain. In contrast to the analogous ethers, the presence of the double bond in almost any position lowered all the transition temperatures, except in the (E)-2 position and configuration. These (E)-alken-2-enoates exhibited significant increases in the nematic transition temperature, although the smectic transition temperatures were also much lower than those of the corresponding alkanoates [3]. However, the (E)-alk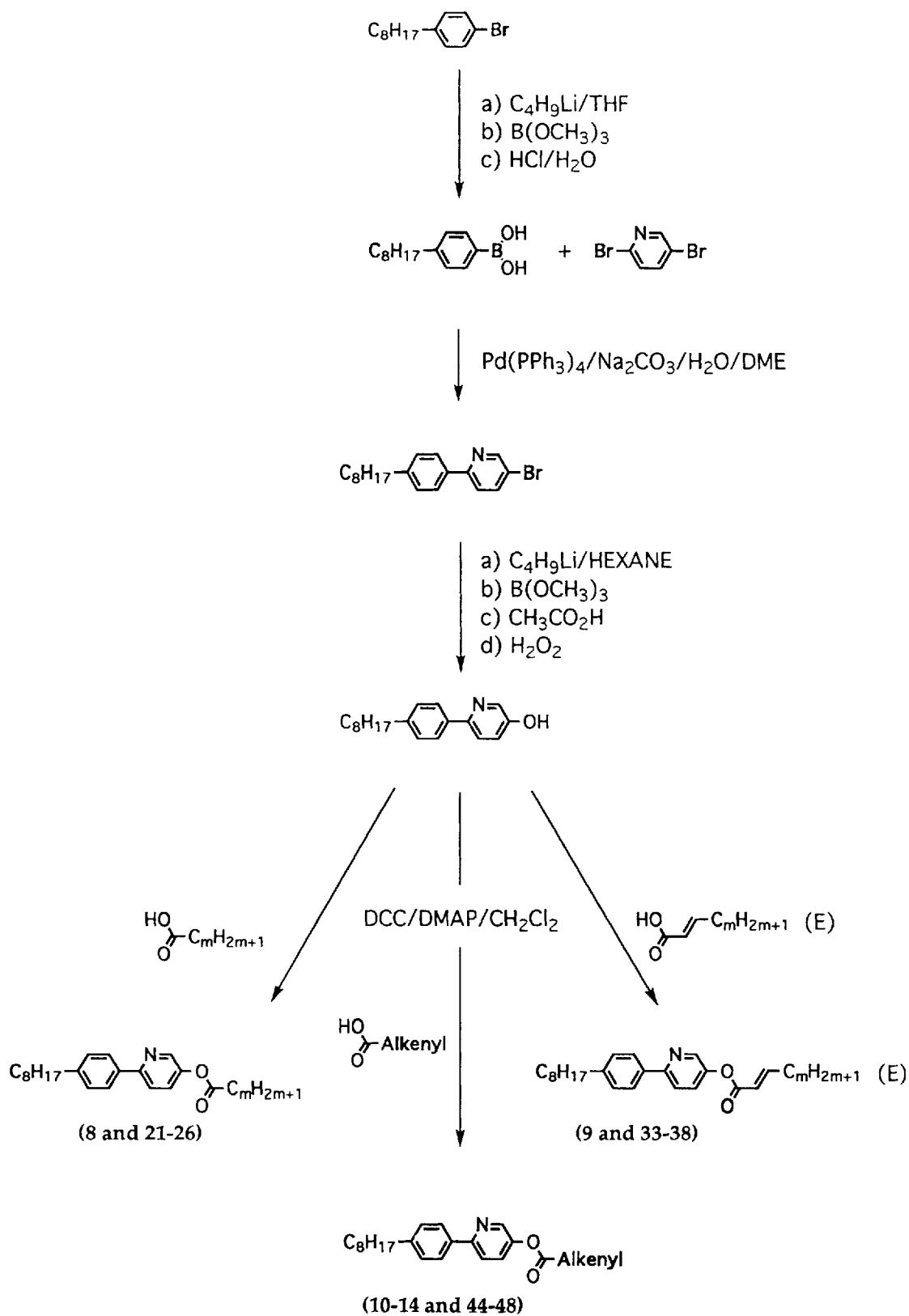-2-enoates still induce a high $T_{S_C^*}$ and a low viscosity (γ) in admixture with other S_C materials, even though the pure ester did not exhibit an S_C phase at all or only at low temperatures. This is of advantage in the development of S_C^* mixtures for electro-optic display devices based on ferroelectric effects (FLCDs) [7–11].

We now report the results of a similar investigation of the effect of a carbon–carbon double bond on the mesomorphic behaviour of the isomeric 2-(4-octylphenyl)pyridin-5-yl alkanoates with a different position of the nitrogen atom. These new alkanoates and alkenoates offer the possibility of systematically investigating the effect of the position of the dipoles due to the nitrogen and oxygen atoms, as well as the conformation of the terminal chains on the liquid crystal behaviour of a heterocyclic model system. This is of relevance to the understanding of the smectic C phase and to the development of associated theories [12–17].

2. Synthesis

The 2-(4-octylphenyl)pyridin-5-yl alkanoates (8 and 21–26) and the 2-(4-octylphenyl)pyridin-5-yl alkenoates (9–14, 33–38 and 44–48) were synthesized as depicted in reaction scheme 1. Commercially available 1-bromo-4-octylbenzene was converted in three-step one pot

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C_8H_{17}—〈 〉—Br

a) C_4H_9Li/THF
b) $B(OCH_3)_3$
c) HCl/H_2O

C_8H_{17}—〈 〉—B(OH)$_2$ + Br—〈N〉—Br

$Pd(PPh_3)_4/Na_2CO_3/H_2O/DME$

C_8H_{17}—〈 〉—〈N〉—Br

a) $C_4H_9Li/HEXANE$
b) $B(OCH_3)_3$
c) CH_3CO_2H
d) H_2O_2

C_8H_{17}—〈 〉—〈N〉—OH

$DCC/DMAP/CH_2Cl_2$

HO—CO—C_mH_{2m+1}

HO—CO—C_mH_{2m+1} (E)

HO—CO—Alkenyl

C_8H_{17}—〈 〉—〈N〉—O—CO—C_mH_{2m+1}

(8 and 21-26)

C_8H_{17}—〈 〉—〈N〉—O—CO—C_mH_{2m+1} (E)

(9 and 33-38)

C_8H_{17}—〈 〉—〈N〉—O—CO—Alkenyl

(10-14 and 44-48)

Scheme 1.

reaction into the lithiated adduct, then the dimethyl borinate and finally the corresponding 4-octylphenyl boronic acid. A palladium mediated aryl-aryl coupling reaction [18, 19] with commercially available 2,5-dibromopyridine yielded exclusively 5-bromo-2-(4-octylphenyl)pyridine, which was then converted in four concerted steps into the corresponding 6-(4-octyl-phenyl)-3-pyridinol [6] via peroxide oxidation [20–22] of the intermediate boronic acid prepared as above. Esterification in the usual way [23] with N,N'-dicyclohexylcarbodiimide (DCC) and 4-(dimethyl-amino)pyridine (DMAP) and the appropriate commercially available alkanoic acids or alkenoic acids prepared according to literature methods [24] yielded the desired alkanoates (8 and 21–26) and alkenoates (9–14, 33–38 and 44–48). The 4-(5-octylpyridin-2-yl) phenyl hexenoates (39–43) were prepared by esterifi-cation of 4-(5-octylpyridin-2-yl)phenol [1] with known [24] or commercially available hexenoic acids as usual [23]. The biphenyl esters (54 and 62) were synthesized in four steps as shown in scheme 2. A Grignard reaction with commercially available 4-cyano-4'-octyloxybiphenyl [25] and heptyl magnesium bromide yielded 4-octanoyl-4'-octyloxybiphenyl [26]. Reduction with lithium aluminium hydride and alumi-nium chloride [27] gave 4-octyl-4'-octyloxybiphenyl, which was dealkylated as usual with boron tribromide [28]. The resultant 4'-octyl-4-hydroxybiphenyl [6] was esterified as usual [23]. The pyrimidine esters (56 and 64) were prepared in one esterification step from commercially available acids and 2-(4-octylphenyl) pyrimidin-5-ol [29].

3. Mesomorphic properties

The effect of varying the position of the nitrogen atoms (X and Y) and the position and configuration of the carbon–carbon double bond on the transition tem-peratures of two reference octanoates (1 and 8) and the corresponding octenoates (2–7 and 9–14) is shown in table 1. The two octenoate series are constitutional isomers differing only in the position of the double bond and/or the two nitrogen atoms. In accordance with previous investigations [3], the configuration at the olefinic double bond is alternately *trans* and *cis* (E and Z). The 7-octenoyloxy chain incorporating a double bond in a terminal position is neither *trans* nor *cis* due to the equivalence of the two hydrogen atoms on the end carbon atom. As the terminal chains are identical for both series, observed differences in the average values for the transition temperatures must be due to the different positions of the nitrogen atoms (i.e. pyridine rings).

The major difference between the transition temper-atures of the esters (1–7) and the esters (8–14) is that

the tendency of the latter to form S_C phases is greater than that of the former (well illustrated by comparing the two (E)-oct-2-enoates 2 and 9), although both series exhibit a variety of highly ordered smectic phases. Six homologues of the esters (8–14) possess an S_C phase at high temperatures. This tendency is confirmed by refer-ence to the data collated in table 2 and plotted against the number of methylene units (m) in the terminal alkanoyloxy chain in figures 1 and 2. Whereas the alkanoates (1 and 15–20) only exhibit highly ordered smectic phases, (S_B and S_F), one homologue (21) of the alkanoates (8 and 21–26) exhibits an N phase and all of the other homologues (8 and 21–26) also possess an S_C phase, as well as more highly ordered smectic and crystal phases (S_F and G). It is evident that without X-ray analysis it is not possible to distinguish with any degree of certainty between the fluid smectic F and I mesophases (S_F and S_I). A schlieren texture was observed on cooling a schlieren texture of the preceding S_C phase for the S_F phase and a mosaic texture for the S_I phase. The same problem exists for the crystal G phase, which was also identified by microscopy. Another highly ordered mesophase (S_3) could not be identified with any certainty.

The effect of introducing a *trans*-carbon–carbon double bond into the alkanoates (1 and 15–20) to produce the (E)-alk-2-enoates (2, 27–32 and 9, 33–38) is shown by the thermal data collated in table 3 and plotted against the number of methylene units (m) in the terminal alkenoyloxy chain in figures 3 and 4. The tendency to form ordered smectic phases is lower and to promote S_C and N phase formation higher. T_{S_C} is higher for the 2-(4-octylphenyl)pyridin-5-yl (E)-alk-2-enoates (9 and 33–38) than for the 4-(2-octylpyridin-5-yl)phenyl (E)-alk-2-enoates (2 and 27–32), while T_C is more or less the same, and T_m is sometimes considerably lower for each homologue.

Therefore for all three ester series investigated, the order of increasing T_{S_C} and the tendency for S_C formation is as follows:


The data collated in table 4 reveal the effect on the transition temperatures of changing the configuration and thus the conformation of the hexenoyloxy chain of the hexenoates (18, 27 and 39–43) and (24, 33 and 44–48) by modifying the configuration (E/Z) of the double bonds at different positions in the chain. The major difference between the data for the two sets of esters is the tendency of the hexenoates (18, 27 and 39–43) to form the orthogonal S_B phase and that of the
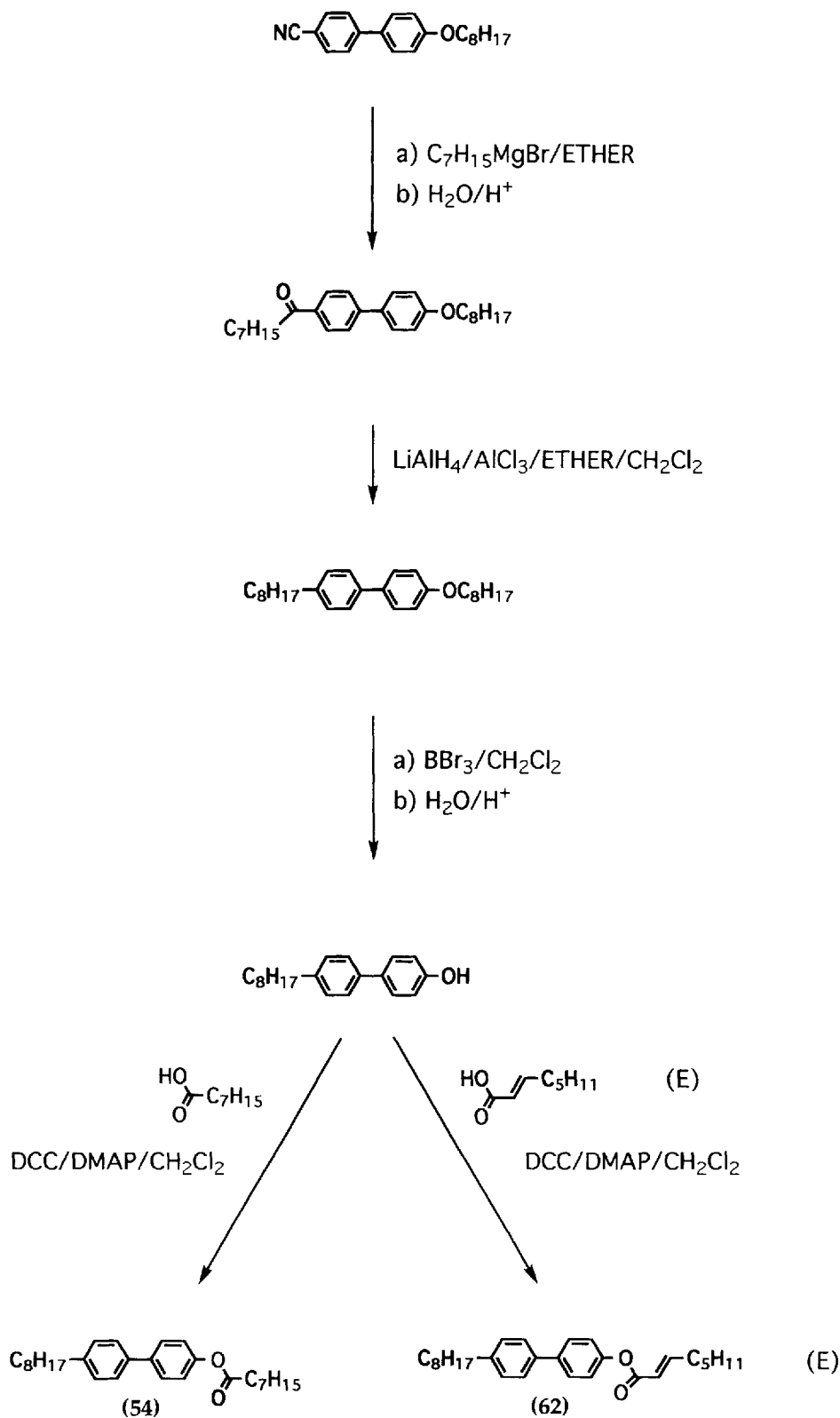
Scheme 2.

Table 1. Transition temperatures for the 4-(5-octylpyridin-2-yl)phenyl octanoate (**1**) and ocenoates (**2–7**) and the 2-(4-octylphenyl)pyridin-5-yl octanoate (**8**) and octenoates (**9–14**).

$$C_8H_{17} - \underset{}{\bigcirc} \overset{=X}{\underset{Y=}{}} \bigcirc - OR$$
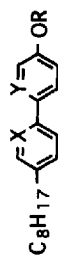
Ester	R	X	Y	Cr–S/N/°C	S_F–S_B/S_3/S_C/I/°C	S_3–S_C/I/°C	S_B–I/°C	S_C–N/I/°C	N–I/°C	Reference
1		N	CH	60	80	—	—	—	—	[1]
2	(E)	N	CH	62	—	—	—	$(46)^a$	83	[3]
3	(Z)	N	CH	56	—	59	—	—	—	[3]
4	(E)	N	CH	52	—	—	76	—	—	[3]
5	(Z)	N	CH	44	—	59	—	—	—	[3]
6	(E)	N	CH	48	51	—	73	—	—	[3]
7		N	CH	49	70	—	—	—	—	[3]
8		CH	N	41	77	—	—	85	—	
9	(E)	CH	N	39	—	—	—	51	82	
10	(Z)	CH	N	43	—	46	—	47	—	
11	(E)	CH	N	43	69	—	—	76	—	
12	(Z)	CH	N	15	32	52	—	—	—	
13	(E)	CH	N	62	—	—	—	77	—	
14		CH	N	43	69	—	—	75	—	

^{a}Represents a monotropic transition temperature.

Table 2. Transition temperatures for the 4-(5-octylpyridin-2-yl)phenyl alkanoates (1 and 15–20) and the 2-(4-octylphenyl)pyridin-5-yl alkanoates (8 and 21–26)

$$C_8H_{17}\text{—}\langle\!\!\!=\!\!X\rangle\text{—}\langle Y\!=\rangle\text{—}O\text{—}\overset{O}{\underset{O}{\|}}\text{—}C_mH_{2m+1}$$
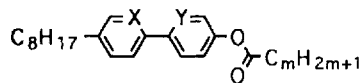
Ester	m	X	Y	Cr–G/S_F/S_B/S_C/°C	G–S_F/°C	S_F–S_C/I/°C	S_B–I/°C	S_C–N/I/°C	N–I/°C	Reference
15	5	N	CH	57	—	—	76	—	—	[1]
16	6	N	CH	57	—	77	—	—	—	[1]
1	7	N	CH	60	—	80	—	—	—	[1]
17	8	N	CH	61	—	81	—	—	—	[1]
18	9	N	CH	61	—	83	—	—	—	[1]
19	10	N	CH	42	—	83	—	—	—	[1]
20	11	N	CH	51	—	83	—	—	—	[1]
21	5	CH	N	64	—	—	—	69	70	
22	6	CH	N	61	—	—	—	77	—	
8	7	CH	N	41	—	77	—	85	–	
23	8	CH	N	58	(46)[a]	85	—	88	—	
24	9	CH	N	36	60	92	—	—	—	
25	10	CH	N	13	66	93	—	—	—	
26	11	CH	N	26	43	96	—	—	—	

[a]Represents a monotropic transition temperature.
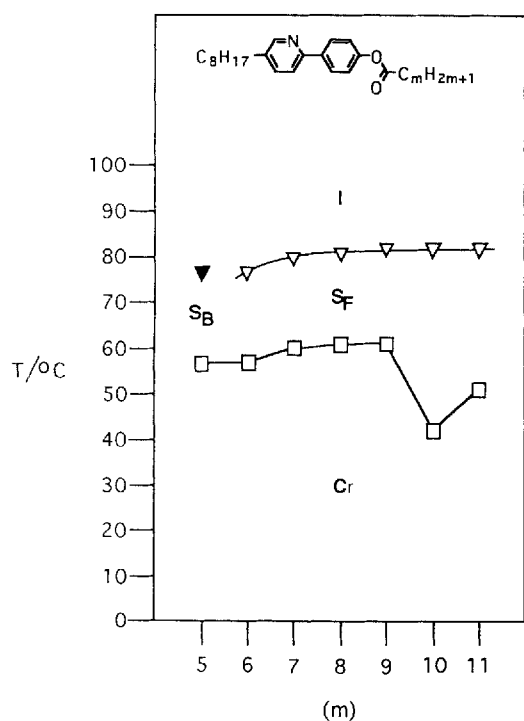

Figure 1. Plot of the transition temperatures against the number of carbon atoms (m) in the terminal chain after the carboxy group of the esters (1, 15–20).
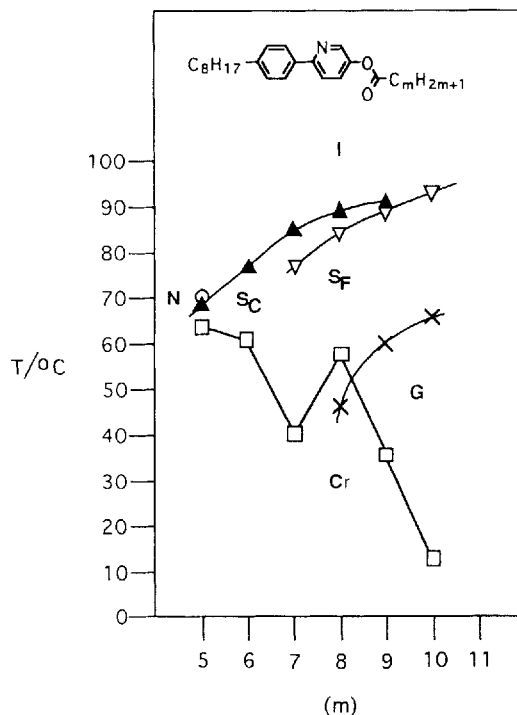

Figure 2. Plot of the transition temperatures against the number of carbon atoms (m) in the terminal chain after the carboxy group of the esters (8, 21–26).

hexenoates (24, 33 and 44–48) to form the tilted S_C phase. Both (E)-hex-2-enoates exhibit an N phase. However, there is a clear odd–even effect in T_C for both ester series. These results are consistent with an alternat-

ing cis/trans linear conformation of the hexenoyloxy chain [30].

The effect of systematically introducing additional lateral dipoles into the model 4-octyloxy- and 4-(E)-

Table 3. Transition temperatures for the 4-(5-octylpyridin-2-yl)phenyl (*E*)-alk-2-enoates (**2** and **27–32**) and the 2-(4-octylphenyl) pyridin-5-yl (*E*)-alk-2-enoates (**9**, and **33–38**)

$$C_8H_{17} - \underset{X}{\overset{Y}{\bigcirc}} - \underset{O}{\overset{O}{\bigcirc}} \hspace{-0.5em} \diagup C_mH_{2m+1} \quad (E)$$
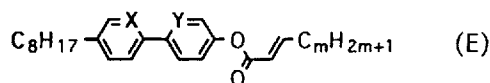
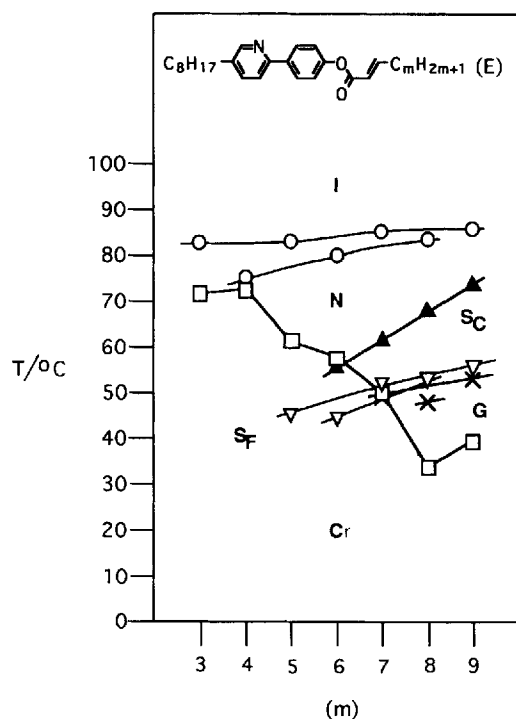| Ester	*m*	*X*	*Y*	Cr–G/S$_I$/S$_C$/N/°C	G–S$_F$/°C	S$_F$–S$_C$/N/°C	S$_C$–N/°C	N–I/°C	Reference
27	3	N	CH	72	—	—	—	83	[3]
28	4	N	CH	73	—	—	—	75	[3]
2	5	N	CH	62	—	(46)[a]	—	83	[3]
29	6	N	CH	57	—	(45)[a]	(56)[a]	80	[3]
30	7	N	CH	50	51	53	63	85	[3]
31	8	N	CH	34	48	53	68	83	[3]
32	9	N	CH	39	53	56	74	86	[3]
33	3	CH	N	46	—	—	—	77	
34	4	CH	N	49	—	—	—	71	
9	5	CH	N	39	—	—	51	85	
35	6	CH	N	31	—	—	59	78	
36	7	CH	N	58	—	—	72	86	
37	8	CH	N	16	—	53	83	87	
38	9	CH	N	23	—	64	91	—	

[a]Represents a monotropic transition temperature.

Figure 3. Plot of the transition temperatures against the number of carbon atoms (*m*) in the terminal chain after the double bond of the esters (**2, 27–32**).
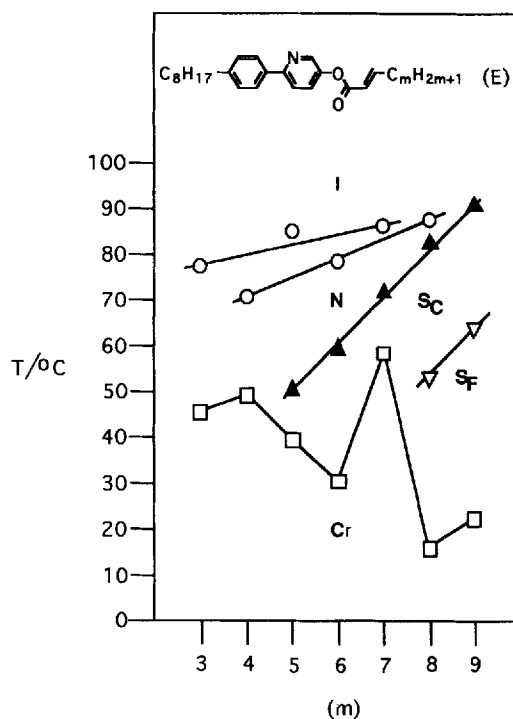

Figure 4. Plot of the transition temperatures against the number of carbon atoms (*m*) in the terminal chain after the double bond of the esters (**9, 33–38**).

octen-1-yloxy-4'-octylbiphenyls (ethers **49** and **57**) and 4-octanoyloxy- and 4(*E*)-octen-1-oyloxy)-4'-octyl-biphenyls esters **54** and **62**) is illustrated in the tables 5 and 6. The smectic phases of the weakly polar biphenyls
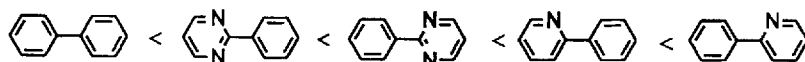
are all orthogonal (S$_B$ and S$_E$), whereas the pyridines and pyrimidines incorporating the nitrogen hetero-atom exhibit tilted phases, as expected on the basis of current theories of the smectic C phase [12–17]. The ethers

Table 4. Transition temperatures for the 4-(5-octylpyridin-2-yl)phenyl hexenoates (**18, 27** and **39–43**) and the 2-(4-octylphenyl) pyridin-5-yl hexenoates (**24, 33** and **44–48**)

$$C_8H_{17} - \underset{X}{\bigcirc} - \underset{Y}{\bigcirc} - OR$$
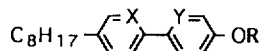
Ester	R	X	Y	Cr–S$_F$/S$_B$/S$_C$/N/I/°C	S$_F$–S$_C$/I/°C	S$_B$–I/°C	S$_C$–N/I/°C	N–I/°C	Reference
18	Hexanoyl	N	CH	61	—	76		—	[1]
27	(E)-Hex-2-enoyl	N	CH	72	—	—	—	83	[3]
39	(E)-Hex-3-enoyl	N	CH	80	(60)[a]	–	—	—	
40	(Z)-Hex-3-enoyl	N	CH	70	—	(67)[a]	—	—	
41	(E)-Hex-4-enoyl	N	CH	69	—	74	—	—	
42	(Z)-Hex-4-enoyl	N	CH	64	—	(62)[a]	—	—	
43	5-Hexenoyl	N	CH	51	—	69	—	—	
24	Hexanoyl	CH	N	64	—	—	69	70	
33	(E)-Hex-2-enoyl	CH	N	46	—	—	—	77	
44	(E)-Hex-3-enoyl	CH	N	66	—	—	(50)	—	
45	(Z)-Hex-3-enoyl	CH	N	54	(51)	—	—	—	
46	(E)-Hex-4-enoyl	CH	N	66	—	—	(61)	74	
47	(Z)-Hex-4-enoyl	CH	N	48	—	—	(46)		
48	5-Hexenoyl	CH	N	42	54	—	58		

[a]Represents a monotropic transition temperature.

generally exhibit a greater tendency to form the S$_C$ phase at higher temperatures than the corresponding esters. This is also valid for the pyridines compared to the corresponding pyrimidines (ethers or esters). This may be due to the effect of the lateral dipole associated with the pyridine ring with one nitrogen atom. The lateral component of the two nitrogen atoms in the pyrimidines should be almost compensated. The ability of an (E)-alk-2-enoyloxy chain to induce the N phase at the cost of smectic mesophases is clearly shown in tables 5 and 6 by comparing the thermal data for the octanoates (**1, 8** and **54–56**) and the (E)-oct-2-enoates (**2, 9** and **62–64**). Hence, the order of increasing T_{S_C} and S$_C$ temperature range is generally as follows:

$$\bigcirc\!\!-\!\!\bigcirc < \underset{N}{\overset{N}{\bigcirc}}\!\!-\!\!\bigcirc < \bigcirc\!\!-\!\!\underset{N}{\overset{N}{\bigcirc}} < \underset{N}{\overset{N}{\bigcirc}}\!\!-\!\!\bigcirc < \bigcirc\!\!-\!\!\overset{N}{\bigcirc}$$

4. Physical properties in mixtures

In order to investigate the suitability of the esters (**1–38**) as non-optically active components of chiral smectic C mixtures for electro-optic display device applications based on ferroelectric effects (SSFLCDs, [7, 8] DHFLCDs [9] and SBFLCDs [10, 11]) a fixed amount (15 wt%) was dissolved in a standard chiral smectic C mixture (SCO 1014; Cr/S$_X$–S$_C^*$ = −7·6°C, S$_C^*$ –S$_A$ = 60·6°C, S$_A$–N* = 67·7°C and N*–I = 74·6°C; see §5). The transition temperatures (S$_C^*$–S$_A$, S$_A$–N* and N*–I) the spontaneous polarizations (P_s) and the observed switching times (τ) of the resulting mixtures were determined under standard conditions

(τ:10 V$_{pp}$μ^{-1} square wave, time to maximum current, at 25°C; P_s: 10 Hz, 10 V$_{pp}$μ^{-1}, triangle).

There is an odd–even effect for the transition temperatures and τ for both series of mixtures shown in figures 5 and 6. The values for those mixtures containing esters with a cis double or terminal bond (double bond position 2, 4, 6) are lower than those for the mixtures incorporating esters with a trans double bond (double bond position 1, 3, 5), reflecting the trends in the transition temperatures of the pure compounds. As the spontaneous polarization of all the mixtures is similar (implying a similar tilt angle θ), this indicates a lower viscosity (γ) for the cis-substituted esters as P_o is constant. The values for $T_{S_C^*}$, P_s and τ of the mixtures containing the esters

(**8–14**)—see figure 6, are somewhat higher than those of the mixtures containing the esters (**1–7**)-see figure 5.

$T_{S_C^*}$ of the mixtures incorporating both series of alkanoates (**1, 15–20** and **8, 21–26**) increases with the number (m) of methylene units in the terminal alkanoyloxy chain—see figures 7 and 8, respectively. However, whereas τ of the mixtures containing the alkanoates (**1** and **15–20**)—see figure 7, increases with increasing chain length, those of the mixtures containing the alkanoates (**8** and **21–26**)—see figure 8, decrease. As P_s values for both series are similar, this implies that the viscosity of the alkanoates shows a dissimilar chain-length dependency. Thus the alkanoates (**8** and **21–26**) with

Table 5. Transition temperatures for the octyloxy-substituted ethers (**49–53**) and octanoyloxy-substituted esters (**1**, **8**, and **54–56**).

$$C_8H_{17}-CORE-O_{\diagdown}{}_W\diagdown{}^{C_5H_{11}}$$

Ether/Ester	CORE	W	Cr–S/°C	E–S_B/I/°C	S_F–S_C/I/°C	S_B–I/°C	S_C–S_A/I/°C	S_A–N/I/°C	N–I/°C	Reference
49		CH$_2$	57	86	—	—	—	—	—	[6]
50		CH$_2$	38	—	62	—	82	—	—	[31]
51		CH$_2$	24	—	65	—	81	87	—	[6]
52		CH$_2$	34	—	—	—	56	64	70	[24]
53		CH$_2$	39	—	—	—	58	84	—	[29]
54		CO	65	83	—	91	—	—	—	
1		CO	60	—	80	—	—	—	—	[1]
8		CO	41	—	77	—	85	—	—	
55		CO	52	—	—	—	53	55	57	[3]
56		CO	80	—	—	—	—	(75)	—	

Table 6. Transition temperatures for the (E)-alkenyloxy-substituted ethers (57–61) and (E)-alkenoyloxy-substituted esters (2, 9 and 62–64).

$$C_8H_{17}-CORE-O\diagdown_W\diagup\diagup^{C_mH_{2m+1}}$$

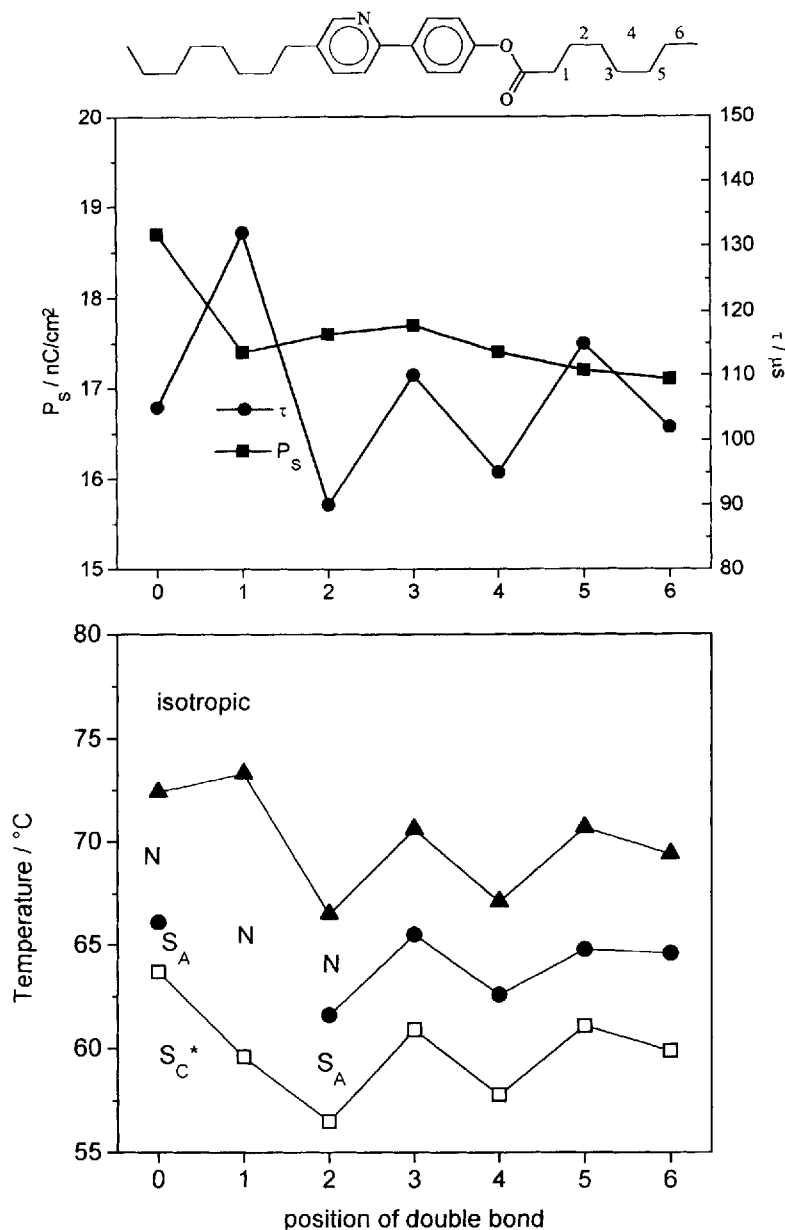| Ether/Ester	CORE	W	Cr–S/N/°C	S_T–S_C/°C	E–S_B/I/°C	S_B–N/°C	S_C–S_A/N/I/°C	S_A–I/°C	N–I/°C	Reference
57	(structure)	CH_2	75	—	93	—	—	—	—	[6]
58	(structure)	CH_2	43	75	—	—	85	—	—	[31]
59	(structure)	CH_2	25	72	—	—	84	—	—	[6]
60	(structure)	CH_2	24	—	—	—	56	—	68	[24]
61	(structure)	CH_2	56	—	—	—	70	84	—	[29]
62	(structure)	CO	36	—	59	66	—	—	75	[3]
2	(structure)	CO	62	—	—	—	(46)	—	83	[3]
9	(structure)	CO	39	—	—	—	51	—	82	
63	(structure)	CO	46	—	—	—	—	—	75	[3]
64	(structure)	CO	74	—	—	—	—	—	81	[3]

Figure 5. Plot of the spontaneous polarizations (P_s), the switching times (τ) and the transition temperatures of the mixtures containing 15 wt % of the esters (1–7) and 85 wt % of the chiral smectic C mixture SCO 1014 versus the position of the carbon–carbon double bond in the octenoyloxy chain; 0 indicates no double bond in the chain.

long chains combine a high $T_{S_C^*}$ with a short τ and high P_s—see figure 8.

The mixtures containing the alkenoates (2, 27–32 and 9, 33–38)—see figures 9 and 10, exhibit similar trends in $T_{S_C^*}$, P_s and τ as the mixtures containing the analogous alkanoates (1, 15–20 and 8, 21–26)—see figures 7 and 8. However, the absolute values for these parameters are often significantly higher. It is interesting to note that most of the mixtures containing the alkenoates do not exhibit an S_A phase.

5. Experimental

The configuration of the carbon–carbon double bond in the alkenyloxy chain of the new esters (8–14, 33–48,

62 and 64) was confirmed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy (the *trans*-olefinic coupling constants ≈ 12–18 Hz are larger than those of the corresponding *cis*-olefinic coupling constants ≈ 7–11 Hz) and by infrared spectroscopy (the *trans*-absorption bands are narrow and exact ≈ 970–960 cm^{-1}, while the *cis*-absorption bands are observed at distinctly different wave lengths ≈ 730–675 cm^{-1}). Traces of undesired isomers formed during the preparation of the various alkenoic acids required as reaction intermediates, or present in commercially available starting materials, could be removed by recrystallization of the desired end product (see the experimental section). The structural and isomeric purity was determined by differential ther-
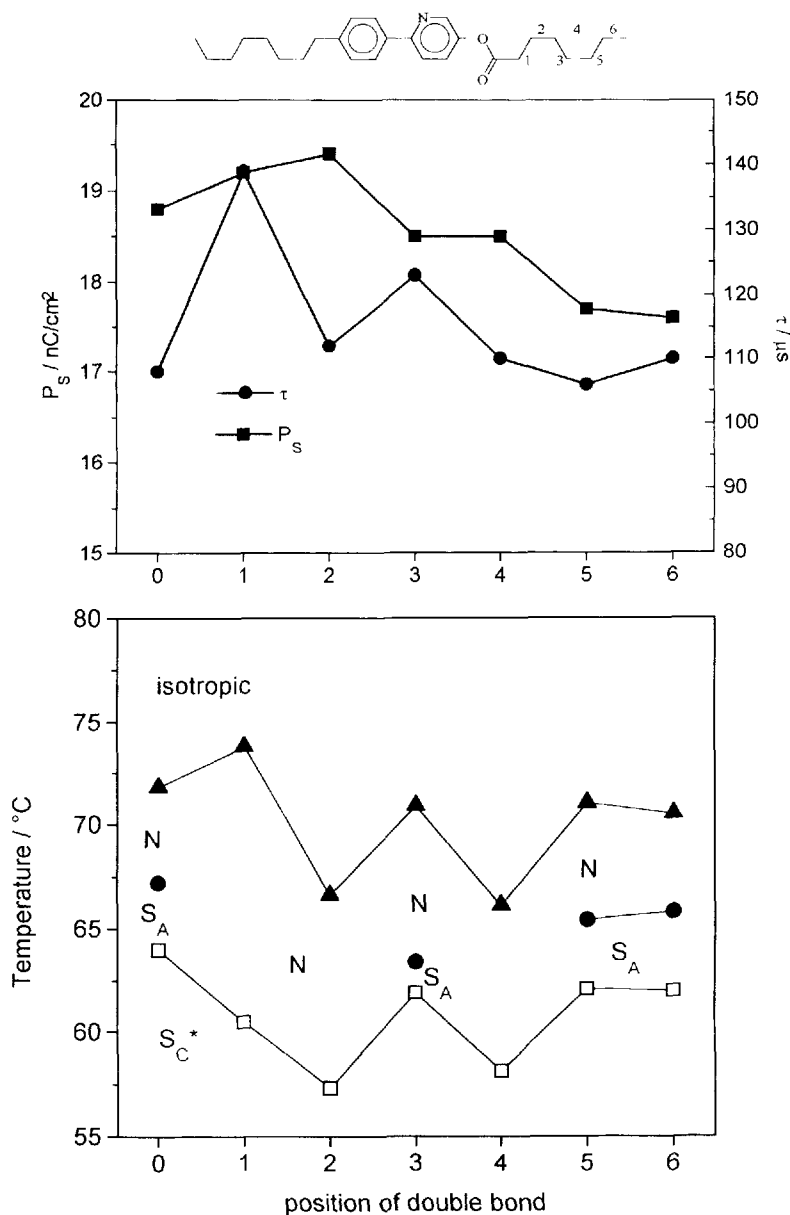
Figure 6. Plot of the spontaneous polarizations (P_s), the switching times (τ) and the transition temperatures of the mixtures containing 15 wt % of the esters (8–14) and 85 wt % of the chiral smectic C mixture SCO 1014 versus the position of the carbon–carbon double bond in the octenoyloxy chain; 0 indicates no double bond in the chain.

mal analysis (DTA) and capillary gas chromatography (GC), where necessary using liquid crystal packed columns.

The transition temperatures of the esters prepared and recorded in tables 1–6 were determined by optical microscopy using a Leitz Ortholux II POL BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All the monotropic phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. The transition temperatures were also determined using a Mettler DTA TA 2000.

The purity of the compounds was determined by thin

layer chromatography (TLC), (GC) and DTA. A Perkin Elmer 8310 capillary gas chromatograph and GP-100 graphics printer were used. 4 cm × 8 cm precoated TLC plates, SiO_2 SIL G/UV$_{254}$, layer thickness 0·25 mm (Machery-Nagel, Düren, Germany) were utilized.

Column chromatography was carried out using silica gel 60 (230–400 mesh ASTM). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were carried out under N_2 unless water was present as a reagent or solvent. All temperatures were measured externally unless otherwise stated. The ^{1}H-NMR spectra were recorded at 60 MHz (Varian T-60), 80 MHz (Bruker WP-80) or 250 MHz
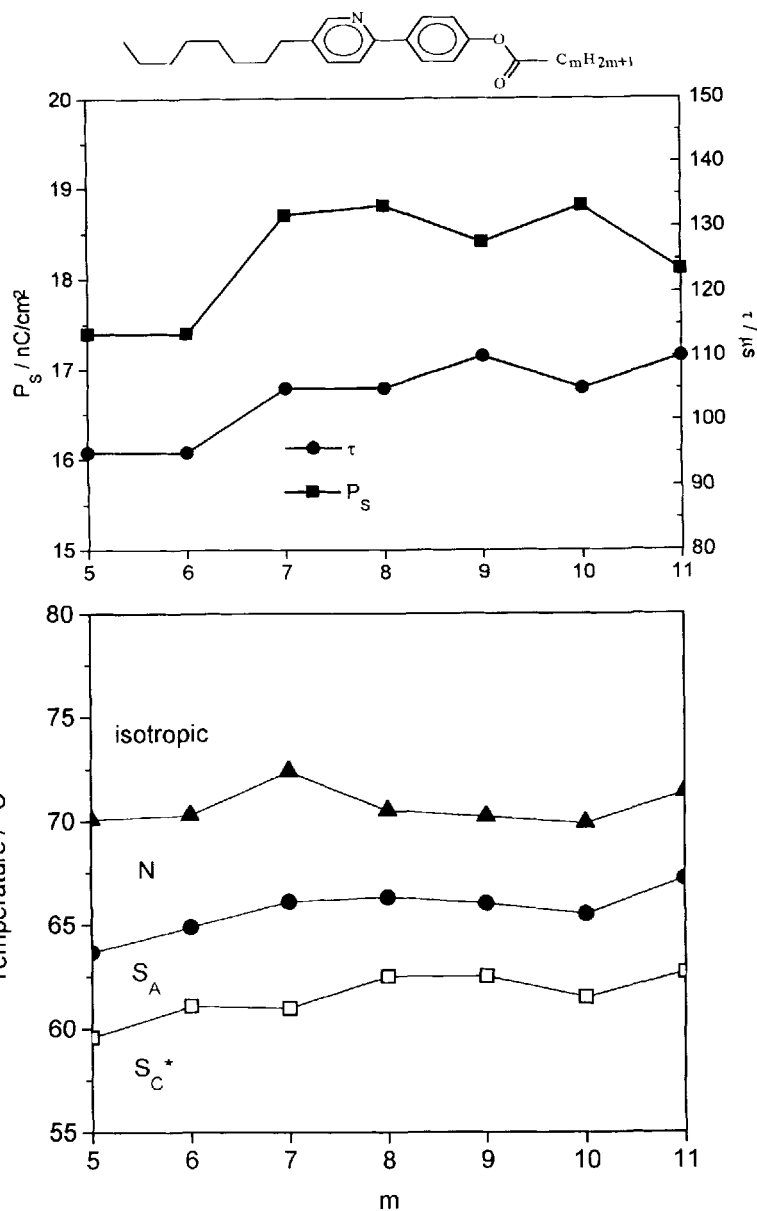
Figure 7. Plot of the spontaneous polarizations (P_s), the switching times (τ) and the transition temperatures of the mixtures containing 15 wt % of the esters (1, 15–20) and 85 wt % of the chiral smectic C mixture SCO 1014 versus the number of carbon atoms (m) in the terminal chain after the carboxy group.

(Bruker HX-250). Tetramethylsilane was used as the internal standard. Mass spectra were recorded on an MS9 (AEZ Manchester) spectrometer.

The chiral smectic C mixture SCO 1014 consists of 4-[*trans*-4-([(R)-2-fluorohexanoyl]oxy)cyclohexyl]-phenyl 2,3-difluoro-4-(octyloxy)benzoate (16 wt %), 2-[4-(hexyloxy)phenyl]-5-nonylpyrimidine (24 wt %), 2-[4-(nonyloxy)phenyl]-5-nonylpyrimidine (24 wt %), 2-[4-(nonyloxy)phenyl]-5-heptylpyrimidine (12 wt %), 2-[4-(hexyloxy)phenyl]-5-octylpyrimidine (12 wt %) and 2-[4-(decyloxy)phenyl]-5-octylpyrimidine (12 wt %).

The determination of the physical properties of the chiral mixtures containing the new esters was carried out as previously described [2, 30].

5.1. 2-(4-Octylphenyl)pyridin-5-yl hexanoate (21)

A solution of N,N'-dicyclohexylcarbodiimide (0·16 g, 0·8 mmol) in dichloromethane (10 cm³) was added slowly to a solution of 6-(4-octylphenyl)-3-pyridinol (0·20 g, 0·7 mmol), hexanoic acid (0·10 g, 0·7 nmol), 4-(dimethylamino)pyridine (0·04 g) and dichloromethane (25 cm³) at 0°C. The reaction mixture was stirred overnight at room temperature filtered and then evaporated. The residue was purified by column chromatography on silica gel using a 3:1 cyclohexane/ethyl acetate mixture as eluent and then recrystallized from ethanol to yield the desired ester (yield 0·26 g, 96 per cent). ¹H NMR (CDCl₃): 0·88–0·94 (6H, overlapping peaks), 1·27 (14H, overlapping peaks), 1·56 (2H, overlapping peaks), 1·82
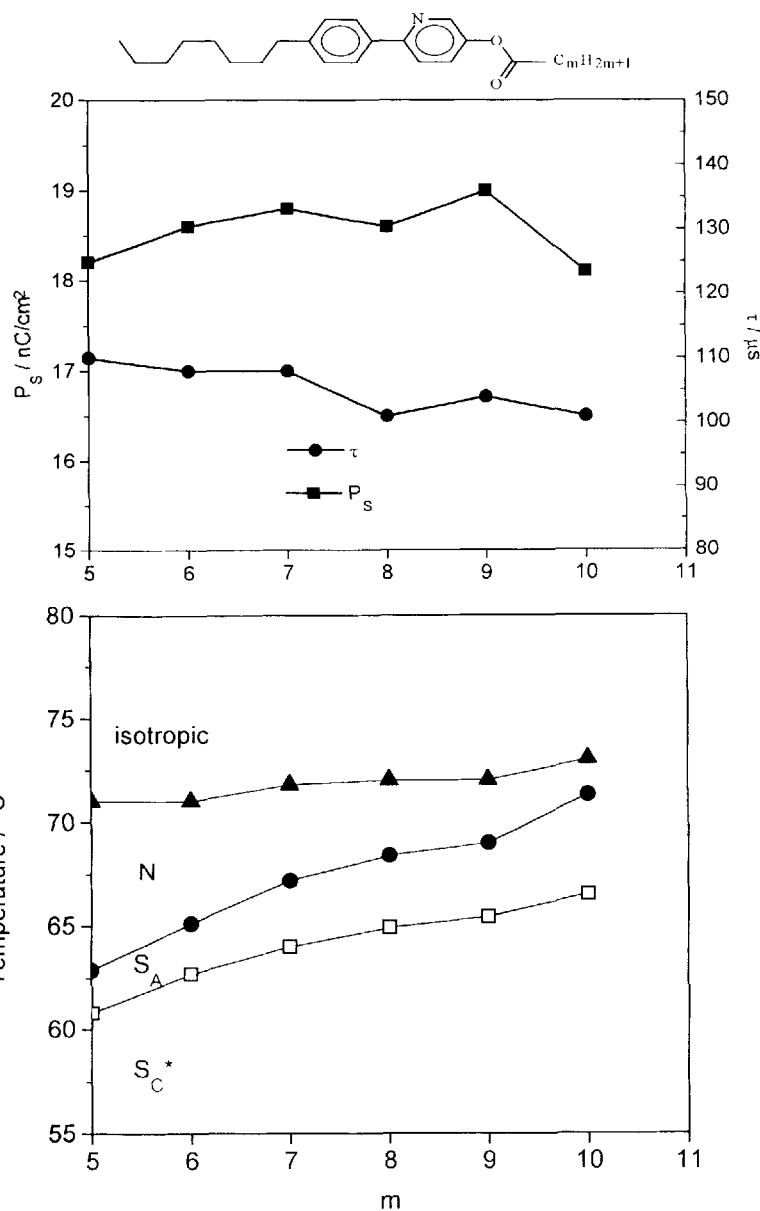
Figure 8. Plot of the spontaneous polarizations (P_s), the switching times (τ) and the transition temperatures of the mixtures containing 15 wt% of the esters (**8**, **21–26**) and 85 wt% of the chiral smectic C mixture SCO 1014 versus the number of carbon atoms (m) in the terminal chain after the carboxy group.

(2H, q), 2·58–2·64 (4H, t), 7·26–7·29 (2H, overlapping peaks), 7·50–7·54 (1H, d), 7·70–7·74 (1H, d), 7·85–7·88 (2H, d), 8·44–8·46 (1H, s). IR (KBr)v_{max}: 2922, 2852, 1752, 1602, 1470, 1213, 824 cm^{-1}. m/z: 381 (M$^+$), 283 (C$_{19}$H$_{25}$NO$^+$). The transition temperatures of this ester (**21**) and similar esters (**8, 21–26, 54** and **56**), prepared using this general method, are recorded in tables 1, 2 and 4–6.

5.2. 2-(4-Octylphenyl)pyridin-5-yl (E)-hex-2-enoate (**33**)

The reaction was carried out, worked up and the product purified as above for **24** to yield the desired ester (yield 0·16 g, 60 per cent). ^{1}H NMR (CDCl$_3$): 0·88 (3H, t), 0·97–1·03 (3H, t), 1·27 (10H, overlapping peaks),

1·56–1·59 (4H, overlapping peaks), 2·31 (2H, q), 2·65 (2H, t), 6·08 (1H, d), 7·26–7·29 (3H, overlapping peaks), 7·58 (1H, d), 7·70–7·74 (1H, d), 7·85–7·88 (2H, d), 8·48 (1H, s). IR (KBr)v_{max}: 2924, 2850, 1786, 1640, 1473, 1214, 829 cm^{-1}. m/z: 379 (M$^+$), 283 (C$_{19}$H$_{25}$NO$^+$). The transition temperatures of this ester (**33**) and similar esters (**9, 33–38, 62** and **64**), prepared using this general method, are recorded in tables 1, 2 and 4–6.

5.3. 2-(4-Octylphenyl)pyridin-5-yl (E)-hex-3-enoate (**44**)

The reaction was carried out, worked up and the product purified as above for **24** to yield the desired ester (yield 0·12 g, 42 per cent). ^{1}H NMR (CDCl$_3$): 0·88
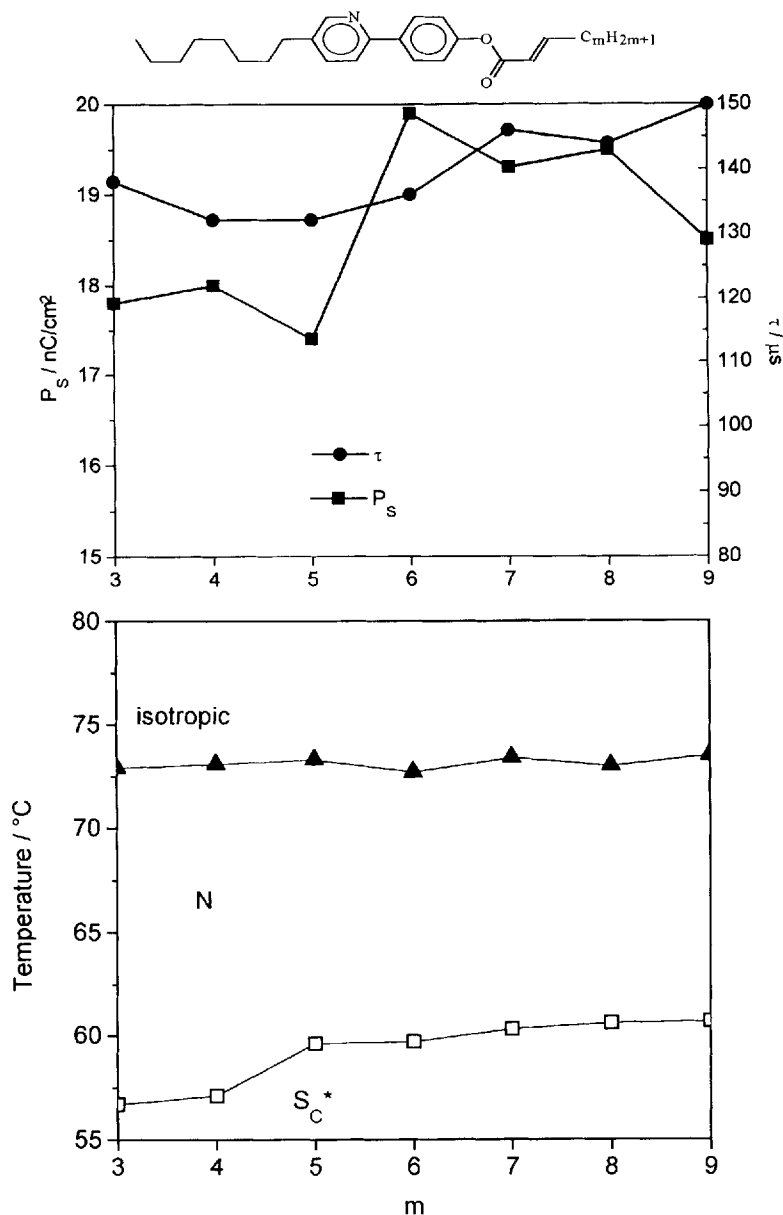
Figure 9. Plot of the spontaneous polarizations (P_s), the switching times (τ) and the transition temperatures of the mixtures containing 15 wt % of the esters (**2, 27–32**) and 85 wt % of the chiral smectic C mixture SCO 1014 versus the number of carbon atoms (m) in the terminal cahin after the double bond.

(3H, t), 1·00–1·06 (3H, t), 1·27 (10H, overlapping peaks), 1·56 (2H, overlapping peaks), 2·11 (2H, overlapping peaks), 2·65 (2H, t), 3·31–3·34 (2H, t), 5·65 (2H, overlapping peaks), 7·26–7·29 (2H, d), 7·53–7·55 (1H, d), 7·70–7·74 (1H, d), 7·85–7·88 (2H, d), 8·43–8·46 (1H, s). IR (KBr)ν_{max}: 2925, 2852, 1754, 1605, 1562, 1474, 1220, 838 cm^{-1}. m/z: 379 (M$^+$), 283 (C$_{19}$H$_{25}$NO$^+$). The transition temperatures of this ester (**44**) are recorded in table 4.

5.4. 2-(4-Octylphenyl)pyridin-5-yl (Z)-hex-3-enoate (45)

The reaction was carried out, worked up and the product purified as above for **24** to yield the desired ester (yield 0·08 g, 30 per cent). ^{1}H NMR (CDCl$_3$): 0·88

(3H, t), 1·01–1·06 (3H, t), 1·27 (10H, overlapping peaks), 1·56 (2H, overlapping peaks), 2·14 (2H, overlapping peaks), 2·65 (2H, t), 3·37–3·40 (2H, t), 7·26–7·29 (2H, d), 7·54–7·55 (1H, d), 7·70–7·74 (1H, d), 7·85–7·88 (2H, d), 8·46 (1H, s). IR (KBr)ν_{max}: 2925, 2852, 1759, 1605, 1590, 1474, 1218, 838 cm^{-1}. m/z: 379 (M$^+$), 283 (C$_{19}$H$_{25}$NO$^+$). The transition temperatures of this ester (**45**) and the similar ester (**10**), prepared using this general method, are recorded in tables 1 and 4.

5.5. 2-(4-Octylphenyl)pyridin-5-yl (E)-hex-4-enoate (46)

The reaction was carried out, worked up and the product purified as above for **24** to yield the desired ester (yield 0·10 g, 75 per cent). ^{1}H NMR (CDCl$_3$): 0·88
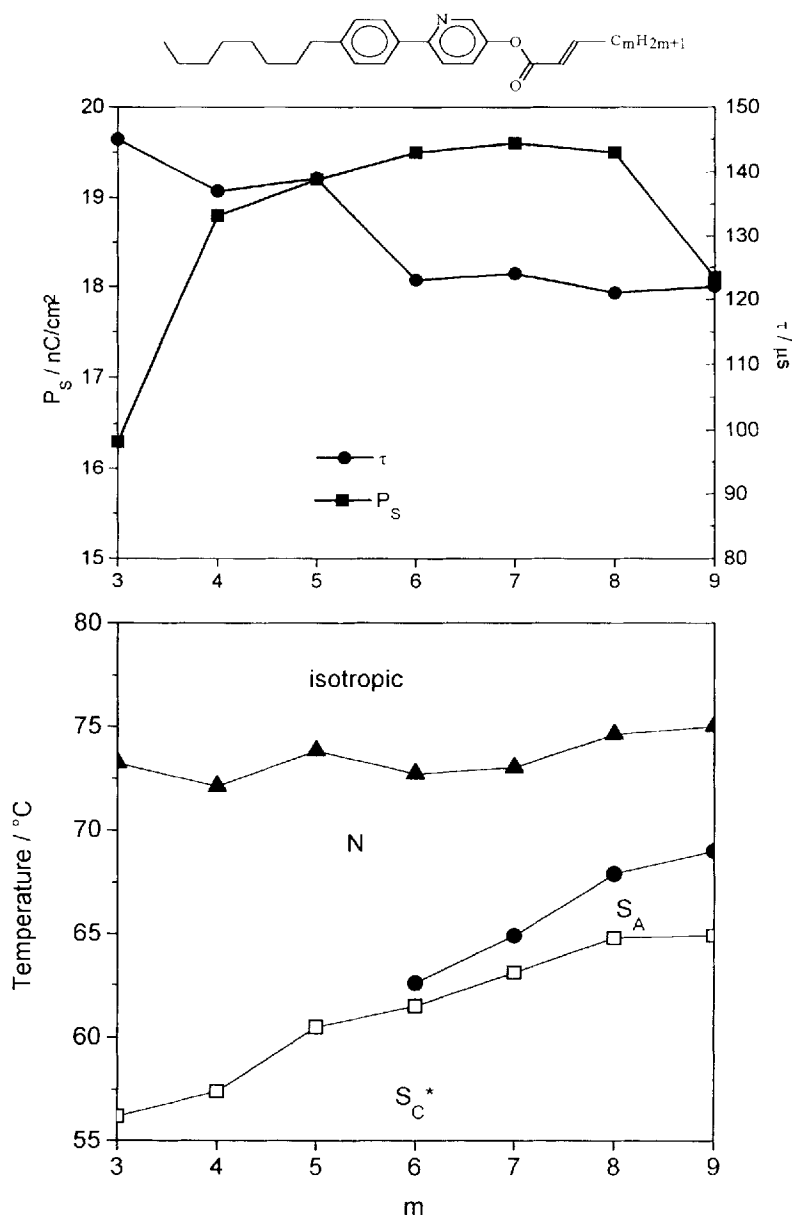
Figure 10. Plot of the spontaneous polarizations (P_s), the switching times (τ) and the transition temperatures of the mixtures containing 15 wt% of the esters (9, 33–38) and 85 wt % of the chiral smectic C mixture SCO 1014 versus the number of carbon atoms (m) in the terminal chain after the double bond.

(3H, overlapping peaks), 1·27 (10H, overlapping peaks), 1·68–1·70 (5H, overlapping peaks), 2·50 (2H, q), 2·64–2·67 (4H, overlapping peaks), 5·55 (2H, overlapping peaks), 7·26–7·29 (2H, overlapping peaks), 7·51–7·53 (1H, d), 7·70–7·74 (1H, d), 7·85–7·88 (2H, d), 8·43 (1H, s). IR $(KBr)\nu_{max}$: 2924, 2853, 1756, 1602, 1474, 1217, 965, 844 cm^{-1}. m/z: 379 (M$^+$), 283 (C$_{19}$H$_{25}$NO$^+$). The transition temperatures of this ester (46) are recorded in table 4.

5.6. *2-(4-Octylphenyl)pyridin-5-yl (Z)-hex-4-enoate* (47)
   The reaction was carried out, worked up and the ester purified as above for 24 to yield the desired ester (yield 0·08 g, 30 per cent). ^{1}H NMR (CDCl$_3$): 0·88 (3H, t), 1·27

(10H, overlapping peaks), 1·56–1·70 (5H, overlapping peaks), 2·50 (2H, q), 2·64–2·67 (4H, overlapping peaks), 2·50 (2H, q), 2·64–2·67 (4H, overlapping peaks), 5·50 (2H, overlapping peaks), 7·26–7·29 (2H, d), 7·53 (1H, d), 7·70–7·74 (1H, d), 7·85–7·88 (2H, d), 8·44 (1H, s). IR $(KBr)\nu_{max}$: 2926, 2853, 1758, 1610, 1563, 1473, 1217, 835 cm^{-1}. m/z: 379 (M$^+$), 283 (C$_{19}$H$_{25}$NO$^+$). The transition temperatures of this ester (47) are recorded in table 4.

5.7. *2-(4-Octylphenyl)pyridin-5-yl hex-5-enoate* (48)
   The reaction was carried out, worked up and the ester purified as above for 24 to yield the desired ester (yield 0·12 g, 45 per cent). ^{1}H NMR (CDCl$_3$): 0·88 (3H, t), 1·27

(10H, overlapping peaks), 1·56 (2H, overlapping peaks), 1·88–1·92 (2H, q), 2·19 (2H, overlapping peaks), 2·60–2·66 (4H, q), 5·08 (2H, overlapping peaks), 5·80 (1H, overlapping peaks), 7·26–7·29 (2H, overlapping peaks), 7·53 (1H, d), 7·70–7·74 (1H, d), 7·85–7·88 (2H, d), 8·44–8·46 (1H, s). IR (KBr)ν_{max}: 2923, 2852, 1754, 1642, 1610, 1474, 1214, 834 cm^{-1}. *m/z*: 379 (M$^+$), 283 (C$_{19}$H$_{25}$NO$^+$). The transition temperatures of this ester (**48**) and the similar ester (**14**), prepared using this general method, are recorded in tables 1 and 4.

6. Conclusions

New series of 2-(4-octylphenyl)pyridin-5-yl alkanoates and alkenoates have been synthesized and found to possess tilted smectic phases at high temperatures for two-ring compounds. The transition temperatures are often higher than those of the constitutional isomers 4-(5-octylpyridin-2-yl)phenyl alkanoates and alkenoates. The effect of introducing one or two nitrogen atoms into various positions of a biphenyl model system has been investigated. One nitrogen atom (i.e. in a pyridine ring) leads to the highest T_{S_C} values. This is consistent with standard theories of the S_C phase. The 2-(4-octyl-phenyl)pyridin-5-yl alkanoates and alkenoates often exhibit higher $T_{S_C^*}$ and shorter response times in S_C^* mixtures for FLCDs than those of the corresponding 4-(5-octylpyridin-2-yl)phenyl alkanoates and alkenoates.

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