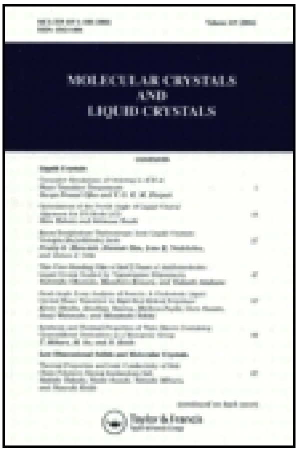

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Synthesis, Transition Temperatures and Some Physical Properties of Some Low-Melting Smectic C Materials

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SYNTHESIS, TRANSITION TEMPERATURES AND SOME PHYSICAL PROPERTIES OF SOME LOW-MELTING SMECTIC C MATERIALS.

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Abstract As part of a systematic study of the factors affecting the smectic C phase, a dipole (ie., an oxygen atom) was introduced into the middle of one of the (non-polarisable) alkyl chains of a model phenylpyrimidine. A carbon-carbon double bond has also been introduced and the position and nature (E/Z) of the double bond was varied systematically and the resultant effect on the transition temperatures and several other physical properties of relevance to ferroelectric liquid crystal displays (FLCDs) studied. The new phenylpyrimidines exhibit nematic, smectic C and sometimes highly ordered smectic phases for long chain lengths. The effect of the oxygen atom in a central position in the chain is often to reduce the melting point (T_m) more than all the other transition temperatures (eg., below room temperature). This often results in a widening of the smectic C temperature range compared to the corresponding compounds without an oxygen atom in the middle of the chain. Of the alkenyl substituted compounds the ethers with a *trans* double bond in the 2-position [(E)-2-] exhibit the highest T_{Sc} values and lowest smectic A transition temperatures. The ethers with a double bond in a terminal position of the alkenyloxy chain exhibit the widest smectic C mesophase ranges (up to 60°C). Of the esters only the (E)-alk-2-enoates exhibit mesomorphic properties.

INTRODUCTION

Most models[1-6] of the smectic C phase postulate that terminal outboard dipoles next to a polarisable molecular core promote smectic C formation. As part of a systematic study[7-15] of the factors affecting the smectic C phase, dipoles such as oxygen atoms and carboxy (ester) groups have recently been introduced systematically into various positions of two-ring phenylpyrimidines and a model cyclohexyl-phenyl-pyrimidine.[7-9] An ester group in a terminal position on the (aromatic) benzene ring of the two-ring phenylpyrimidines was found to strongly support smectic C behaviour. Surprisingly, the viscosity was shown to be lower for the esters than for the corresponding ethers. Additionally, dipoles in the form of oxygen atoms or carboxy (ester) groups were found to destabilise the smectic C phase. In order to further investigate this effect a dipole (ie., an oxygen atom) was introduced into the middle of one of the (non-polarisable) alkyl chains of a model phenylpyrimidine. It has also been shown that the introduction of a carbon-carbon double bond into the alkoxy chain of such systems can increase the smectic C transition temperature and temperature range as well as other physical parameters of relevance to the performance of chiral smectic C mixtures in ferroelectric liquid crystal dispays (FLCDs).[10-15] Therefore, it was further decided to investigate the influence of an additional oxygen atom and a carbon-carbon double bond in 2-(4-n-alkylphenyl)-5-n-alkyloxy/alkenoxypyrimidines[15, 16] (ie., ethers with an oxygen atom attached to the pyrimidine ring) as a model system. These phenylpyrimidines with the alkoxy group attached to the pyrimidine ring have been found to exhibit advantageous combinations of transition temperatures and other physical properties in a standard chiral smectic C mixture. As the 4-(5-n-alkylpyrimidin-2-yl)phenyl alkanoates and alkenoates (ie., aromatic esters) have also been shown recently[14] to possess interesting properties for FLCDs, similar esters containing a carbon-carbon double bond and an oxygen atom in the terminal chain were also included in this investigation.

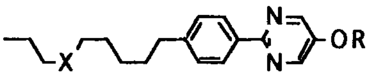
SYNTHESIS

The 5-(alkenyloxy)-2-(4-[5-propyloxypentyl]phenyl)pyrimidines (**9**-**26**) and the reference ether 5-(octyloxy)-2-(4-[5-propyloxypentyl]phenyl)pyrimidine (**8**)[17] were prepared starting from 4-bromobenzonitrile, which was converted in the usual way with hydrogen chloride to the corresponding benzimidoethylether hydrochloride and then with ethanolic ammonia to the corresponding benzamidine hydrochloride. Ring formation using 1,3-bis(dimethylamino)-2-ethoxytrimethium perchlorate[18] yielded 2-(4-bromophenyl)-5-ethoxypyrimidine. A Heck reaction[19] with pent-4-en-1-ol, hydrogenation of the resultant double bond and alkylation of the hydroxy group with bromopropane yielded 2-(4-[5-propyloxypentyl]phenyl)-5-ethoxypyrimidine. The ethoxy group attached to the pyrimidine ring could be selectively removed by heating with potassium hydroxide at 180°C. Alkylation of the resultant phenol in a Williamson ether synthesis with bromooctane (reference compound) or the appropriate alken-1-ols[11] in a Mitsunobu reaction[20] or esterification with octanoic acid (reference compound) and assorted alkenoic acids[14] incorporating a carbon-carbon double bond of a defined configuration (E/Z) at various positions in the chain using DCC as usual[21] yielded the desired ethers (8-26) and esters (34-48) respectively. The comparison esters (27-33) were prepared by esterifcation of 2-(4-nonylphenyl)-5-hydroxypyrimidine[15] with commercially available alkanoic acids using DCC as usual[21]. The methods of preparation and purity/structure determination are described in detail in the Experimental.

MESOMORPHIC PROPERTIES

The differences in the transition temperatures of two series (1-7 and 8-14) differing only in the presence of an oxygen atom in the chain (X = CH_2 or O, respectively) are illustrated by reference to table 1. Both series exhibit smectic C and smectic A phases. The major difference is that the melting point, smectic C transition temperature and clearing point of the diethers (8-14) containing an additional oxygen atom are all lower. However, the melting point (T_m) is decreased more than the smectic C transition temperatures (T_{SC}). Thus, the temperature range (25°C, on average) of the smectic C phase for the diethers (8-14) is larger than that (6°C, on average) for the mono-ethers (1-7). Another salient feature of the transition temperatures for the latter series is the higher (+11°C) smectic C transition temperature of the ether (9) with a *trans* carbon bond in the 2-position compared to that of the corresponding ether (5). However, in this case, the melting point is even higher still (+28°C) leading to a narrower smectic C phase at higher temperatures. The melting points of all the octenyloxy diethers (9-14) are higher than the reference octyloxy-substituted diether (8). Only the (Z)-oct-5-enyloxy and 7-octenyloxy ethers (10 and 12) exhibit melting points below room temperature. This is consistent with previous results for similar mono-ethers (ie., without an oxygen atom in the chain) and the same dependencies of the transition temperatures on the nature and position of the double bond are similar to those observed for the references ethers (1-7).[15]

TABLE 1. Transition temperatures for the compounds below:

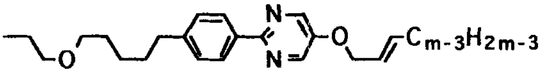


Ether		R	X	$C\text{-}S_C/S_A/I$ /°C	$S_C\text{-}S_A$ /°C	$S_A\text{-}I$ /°C
1			CH_2	36	53	85
2	(E)		CH_2	56	65	82
3	(Z)		CH_2	52	-	(44)
4	(E)		CH_2	47	52	82
5	(Z)		CH_2	38	44	58
6	(E)		CH_2	51	-	86
7			CH_2	34	38	77
8			O	8	47	69
9	(E)		O	36	58	63
10	(Z)		O	38	-	-
11	(E)		O	32	43	62
12	(Z)		O	10	33	37
13	(E)		O	21	-	70
14			O	15	35	60

( ) Represents a monotropic transition temperature

The transition temperatures for an homologous series of 5-[(E)-alk-2-enyloxy]-2-(4-[5-propyloxypentyl]phenyl)pyrimidines (9 and 15-20) are collated in table 2. The first two members of the series only possess a smectic A phase. For longer chains a smectic C phase is observed (64°C, on average). The smectic C transition temperatures increase almost linearly with increasing chain length. Ordered phases are observed and the smectic A phase disappears as the chain length increases. The melting point is relatively high (43°C, on average).

TABLE 2. Transition temperatures for the compounds below:



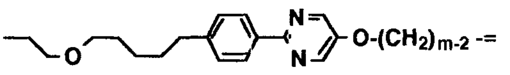
(E)

Ether	m	C-S_3/S_C/S_A /°C	S_3-S_C /°C	S_C-S_A/I /°C	S_A-I /°C	$\Delta T S_C$ /°C
15	6	47	-	-	56	-
16	7	20	-	-	41	-
9	8	36	-	58	63	22
17	9	51	-	60	-	9
18	10	44	-	65	-	21
19	11	50	(49)	68	-	18
20	12	53	59	71	-	12

( ) Represents a monotropic transition temperature

The corresponding data for the related series of 5-(alkenyloxy)-2-(4-[5-propyloxypentyl]phenyl)pyrimidines (14 and 21-26) with a double bond in a terminal position in the chain are collated in table 3. The same phases are observed as for the related (E)-alk-2-enyloxy-substituted ethers (9 and 15-20). However, the melting point is considerably lower (~41°C, on average) and the ordered phases are only observed for the longest chain length studied (n = 12). However, on moving the double bond from position 2 in the esters (9 and 15-20) to a terminal position in the esters (14 and 21-26) the melting point is reduced (-18°C, on average) more than the smectic C transition temperature (-7°C, on average, comparing only those homologues where a smectic C phase could be observed for both series). This results in a wider smectic C temperature range (43°C, on average). The smectic A transition temperature is high (62°C, on average). The smectic C transition temperature rises sharply as the number of carbon atoms in the alkenyloxy chain increases and replaces the smectic A phase for long chains. The normal pattern of alternation is observed.

TABLE 3. Transition temperatures for the compounds below:



Ether	m	C-S /°C	S_4-S_3 /°C	S_3-S_C /°C	S_C-S_A/I /°C	S_A-I /°C	ΔT_{S_C} /°C
21	6	18	-	-	-	55	-
22	7	10	-	-	-	59	-
14	8	15	-	-	35	60	20
23	9	-30	-	-	30	61	60
24	10	-3	-	-	57	64	60
25	11	0	-	-	55	65	55
26	12	19	36	59	70	-	21

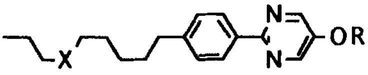
The thermal data for the two series of octenoyloxy esters (28-33 and 35-40) and the reference octanoyloxy esters (27 and 34) are recorded in table 4. Both the esters (28 and 35) incorporating a *trans* carbon-carbon double bond in the 2-position and one ester (33) with a terminal double bond exhibit mesomorphism (ie, a smectic A and a nematic phase). All the other esters possess high melting points (75°C and 61°C, on average, respectively). No monotropic liquid crystal phases could be observed despite substantial supercooling below the melting point. The high clearing point (T_{NI}) for the (E)-2-substituted esters is consistent with previous results for related esters series of phenylpyrimidines where the carboxy group is attached to the phenyl ring.[14] However, the phenyl esters containing a double bond in other positions were also liquid crystalline[14], suggesting that the combination of a carboxy group and the pyrimidine ring of the esters (**27-40**) is particularly disadvantageous for liquid crystal behaviour. This may be due to dipole-dipole interactions between the electron rich nitrogen atoms on the ring and the oxygen atoms in the ester group.

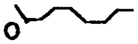
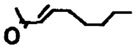
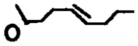
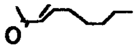
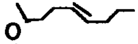
The transition temperatures of an homologous series of 5-[(E)-alk-2-enoyloxy]-2-(4-[5-propyloxypentyl]phenyl)pyrimidines (**35** and **41-48**) are given in table 5. The first two members of the series are not liquid crystalline. However, a nematic phase is exhibited by esters with intermediate and long chain lengths, while the esters with the longest chain lengths studied possess smectic C and smectic A phases. The absence of a nematic phase for the (E)-but-2-enoate (**41**) is most unusual. The melting point is consistently high (60°C, on average) resulting in a narrow smectic C temperature range and mostly monotropic transition temperatures.

EXPERIMENTAL

The configuration of the carbon-carbon double bond in the alkenyl and alkenoyloxy chain of the new ethers (**9-26**) and esters (**28-33** and **35-48**) was confirmed by ^{1}HNR 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 infra-red 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 could be removed by recrystallisation of the desired end product. The structural and isomeric purity was determined by differential thermal analysis and capillary gas chromatography as usual and , where necessary, on liquid crystal packed columns.

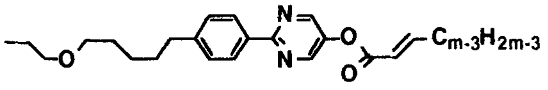
Table 4. Transition temperatures for the compounds below:



Ester		R	X	C-N/I /°C	S_A-I /°C	N-I /°C
27			CH_2	82	-	-
28	(E)		CH_2	78	-	84
29	(Z)		CH_2	57	-	-
30	(E)		CH_2	81	-	-
31	(Z)		CH_2	71	-	-
32	(E)		CH_2	80	-	-
33			CH_2	70	(66)	-
34			O	70	-	-
35	(E)		O	68	-	(64)
36	(Z)		O	46	-	-
37	(E)		O	68	-	-
38	(Z)		O	51	-	-
39	(E)		O	67	-	-
40			O	54	-	-

( ) Represents a monotropic transition temperature

TABLE 5. Transition temperatures for the compounds below:



(E)

Ester	m	C-S_C/N/I /°C	S_C-S_A/N/I /°C	S_A-N /°C	N-I /°C	ΔTS_C /°C
41	4	71	-	-	-	-
42	5	44	-	-	-	-
43	6	61	-	-	(57)	-
44	7	51	-	-	-	-
35	8	68	-	-	(64)	-
45	9	64	-	-	(60)	-
46	10	63	(61)	-	69	-
47	11	53	62	64	68	9
48	12	63	73	-	-	10

( ) Represents a monotropic transition temperature

The transition temperatures of the ethers and esters (8-26 and 27-48, respectively) prepared recorded in tables 1-5 were determined by optical microscopy using a Leitz Otholux II POL BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All the monotropic liquid crystal phases could be observed directly using a microscope. When necessary the Mettler stage could be cooled (-50°C) by allowing N_2 gas , cooled by liquid N_2, to pass through the stage at a controlled rate.The transition temperatures were also determined using a Mettler DTA TA 2000.

The purity of the compounds was determined by thin layer chromatography (TLC) gas chromatography (GC) and differential thermal analysis (DTA). A Perkin Elmer 8310 capillary gas chromatograph and GP-100 graphics printer were used. 4 cm x 8 cm precoated TLC plates, SiO_2 SIL G/UV_{254}, layer thickness 0.25 mm (Machery-Nagel, Düren, Germany) were utilised.

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 270 MHz (Bruker HX-270). Tetramethylsilane was used as the internal standard. Mass spectra were recorded on a 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 ester (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 given in table 6 of the chiral mixtures containing the new esters was carried out as previously described.[12]

5.1. *Bromobenzimidoethylether Hydrochloride*

A solution of 4-bromobenzonitrile (50 g, 0.275 mol) in ethanol (70 cm^3) and toluene (200 cm^3) was saturated with hydrogen chloride at 0°C and then stirred at room temperature for 2 days. The reaction mixture was evaporated down under reduced pressure, shaken with ether (500 cm^3), filtered, washed with portions of ether and finally dried under vacuum to give the hydrochloride (yield 68 g, 94 per cent), mp. 250°C (decomposition). IR (KBr) *vmax*: 2931, 1707, 1631, 1597, 1496, 1457, 1069, 807 cm^{-1}. MS *m/z*: 226 (M^+), 199, 201 ($C_7H_6BrNO^+$), 155, 157 ($C_6H_4Br^+$).

5.2. *4-Bromobenzamidine Hydrochloride*

A saturated ethanolic ammonia solution (4000 cm^3) was added to a solution of bromobenzimidoethylether hydrochloride (68 g, 257 mmol) and ethanol (350 cm^3). the reaction mixture was stirred at room temperature for 2 days and then evaporated. The solid residue was shaken with ether (500 cm^3), filtered, washed with portions of ether and finally dried under vacuum to give the benzamidine (yield 59 g, 97 per cent); mp. 265°C. IR (KBr) *vmax*:

3229, 3183, 3137, 3070, 1670, 1594, 1594, 1479, 1072, 843 cm^{-1}. MS *m/z*: 198, 200 (M$^+$), 182, 184 ($C_7H_5BrN^+$), 155, 157, ($C_6H_4Br^+$).

5.3. *2-(4-Bromophenyl)-5-ethoxypyrimidine*

1,3 -bis(Dimethylamino)-2-ethoxytrimethinium perchlorate[18], (5.4 g, 20 mmol) and 4-bromobenzamidine hydrochloride (4.7 g, 20 mmol) were added to a solution of 5.4 M sodium methoxide (45 mmol) in methanol (40 cm^3) at room temperature under an atmosphere of nitrogen. The reaction mixture was heated under gentle reflux overnight, poured onto water (500 cm^3), cooled to 0°C, acidified with 25% hydrochloric acid (pH 3≈4) and then stirred for 30 min at this temperature. The precipitate was filtered off, washed with portions of a cold water/methanol mixture (1:1 v/v), sucked dry and then crystallised from ethanol to yield 2-(4-bromophenyl)-5-ethoxypyrimidine (yield 5.2 g, 94 per cent); mp. 134°C. IR (KBr) *vmax*: 2983, 2891, 1591, 1441, 1279, 1039, 781, 642 cm^{-1}. MS *m/z*: 278, 280 (M$^+$) 250, 252 ($C_{10}H_7N_2OBr^+$).

5.4. *5-Ethoxy-2-(4-[(E/Z)-5-hydroxypent-1-enyl]phenyl)pyrimidine*

A mixture of 2-(4-bromophenyl)-5-ethoxypyrimidine (10 g, 36 mmol), pent-4-en-1-ol (6.2 g, 72 mmol), triphenylphosphine (0.3 g), palladium acetate (0.11 g), sodium carbonate (9 g) and N-methylpyrolidone (20 cm^3) was heated at 115°C for 3 h. The reaction mixture was added to water (200 cm^3). The organic layer was separated off and the aqueous layer extracted into ethyl acetate (3 x 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 x 100 cm^3), dried ($MgSO_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 2:1 hexane/ethylacetate mixture as eluent and recrystallisation from tert. butyl methyl ether to yield the desired alcohol (yield 5.1 g, 50 per cent); mp. 60°C. IR (KBr) *vmax*: 3358, 2974, 2931, 1605, 1573, 1543, 1446, 1289, 1289, 1114, 1040, 857 cm^{-1}. MS *m/z*: 284 (M$^+$), 253 ($C_{16}H_{17}N_2O$), 240 ($C_{15}H_{16}N_2O$) 175.

5.5. *2-(4-[5-Hydroxypentyl]phenyl)-5-ethoxypyrimidine*

A mixture of 5-ethoxy-2-(4-[(E/Z)-5-hydroxypent-1-enyl]phenyl)pyrimidine (8.1 g, 28.5 mmol), tetrahydrofuran (350 cm^3) and 10 per cent palladium on active charcoal (0.5 g) were hydrogenated until no more hydrogen was taken up. The catalyst was filtered off and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using a 1:1 hexane/ethyl acetate mixture as eluent and recrystallisation from acetone at -25°C to yield the desired alcohol (yield 8.1 g, 96 per cent); IR (KBr) *vmax*: 3350, 2975, 2933, 1610, 1577, 1544, 1437, 1277, 1040, 850, 786 cm^{-1}. MS *m/z*: 286 (M^+), 227 ($C_{14}H_{15}N_2O^+$).

5.6. *5-Ethoxy-2-(4-[5-propyloxypentyl]phenyl)pyrimidine*

A solution of 5-ethoxy-2-(4-[5-hydroxypentyl]phenyl)pyrimidine (8.1 g, 28 mmol) in tetrahydrofuran (300 cm^3) was added dropwise to a suspension (50 w/w per cent in mineral oil) sodium hydride (2.1 g, 42 mmol) in tetrahydrofuran (50 cm^3) at room temperature. After stirring for 4 h, propyl bromide (5.2 g, 42 mmol) was added dropwise and the reaction mixture stirred overnight. Methanol (10 cm^3) and then water (50 cm^3) were added and the resultant mixture extracted into diethyl ether (3 x 50 cm^3). The combined organic layers were washed with brine (2 x 100 cm^3), dried ($MgSO_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 2:1 hexane/ethyl acetate mixture as eluent and recrystallisation from ethanol to yield the desired ether (yield 4.55 g, 48 per cent); C-I, 52°C; N-I, (39°C); IR (KBr) *vmax*: 2934, 2858, 1611, 1578, 1540, 1437, 1282, 1113, 851, 786 cm^{-1}. MS *m/z*: 328 (M^+), 285 ($C_{17}H_{21}N_2O_2^+$); 213 ($C_{13}H_{13}N_2O^+$). ^{1}H NMR ($CDCl_3$). 0.88-0.94 (3H, t), 1.45-1.64 (11H, overlapping peaks), 2.64-2.70 (2H, t), 3.33-3.43 (4H, overlapping peaks), 4.13-4.22 (2H, q), 7.26-7.29 (2H, d), 8.23-8.26 (2H, d), 8.44 (2H, s).

5.7. *5-Hydroxy-2-(4-[5-propyloxypentyl]phenyl)pyrimidine*

A solution of 5-ethoxy-2-(4-[5-propyloxypentyl]phenyl)pyrimidine (2.1 g, 6.4 mmol), sodium hydroxide (2.6 g, 6.4 mmol) and diethylene glycol (100 cm^3) was heated at 200°C for 6 h. The reaction solution was poured onto water (500 cm^3), acidified with 25% hydrochloric acid and extracted with ethyl acetate (2 x 50 cm^3). The combined organic layers were washed with dilute sodium bicarbonate solution (2 x 50 cm^3), dried (MgSO4), filtered and evaporated down. The residue was purified by column chromatography on silica gel using a 2:1 hexane/ethyl acetate mixture as eluent and recrystallisation from ethanol to yield the desired phenol (yield 1.7 g, 90 per cent); IR (KBr) *vmax*: 2935, 2855, 2794, 2715, 2574, 1611, 1553, 1431, 1278, 1115, 847, 784 cm^{-1}. MS *m/z*: 300 (M$^+$), 257 ($C_{15}H_{17}N_2O_2$), 240 ($C_{15}H_{16}N_2O$), 199 ($C_{12}H_{11}N_2O$). ^{1}H NMR (CDCl$_3$). 0.87-0.93 (3H, overlapping peaks), 1.24-1.28 (2H, d), 1.30-1.64 (8H, overlapping peaks), 2.65 (2H, t), 3.36-3.43 (4H, overlapping peaks), 7.23-7.26 (2H, d), 8.12-8.16 (2H, d), 8.33-8.37 (2H, s).

5. 8. *5-Octyloxy-2-(4-[5-propyloxypentyl]phenyl)pyrimidine* (8)

A mixture of 1-bromooctane [Fluka] (0.19 g, 1.0 mmol), 5-hydroxy-2-(4-[5-propyloxypentyl]phenyl)pyrimidine (0.25 g, 0.8 mol), potassium carbonate (0.46 g, 3.3 mmol) and 2-butanone (25 cm^3) was heated under gentle reflux overnight. The reaction mixture was poured onto water (100 cm^3) and then extracted into diethyl ether (3 x 30 cm^3). The combined organic extracts were washed with water (2 x 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down. The residue was purified by column chromatography on silica gel using a 9:1 hexane/ethyl acetate mixture as eluent and recrystallisation from ethanol to yield the pure ether (yield 12 g, 35 per cent); IR (KBr) *vmax*:: 2929, 2854, 1577, 1544, 1438, 1279, 1119, 851, 786 cm^{-1}. MS *m/z*: 412 (M$^+$), 369 ($C_{23}H_{33}N_2O_2^+$). ^{1}H NMR (CDCl$_3$). 0.87-0.94 (6H, overlapping peaks), 1.29-1.66 (20H, overlapping peaks), 2.64-2.70 (2H, t), 3.33-3.42 (4H, t), 4.02 (2H, overlapping peaks), 4.05-4.11 (2H, t), 7.26-7.29 (2H, d), 8.22-8.26 (2H, d), 8.43 (2H, s). The transition temperatures of this ether (8) are given in table 1.

5.9. *5-[(E)-Oct-2-enyloxy]-2-(4-[5-propyloxypentyl]phenyl)pyrimidine* (9)

A solution of diethyl azodicarboxylate (0.15 g, 0.8 mmol) and tetrahydrofuran (10 cm^3) was added dropwise at 0°C to a solution of (E)-oct-2-en-1-ol [Johnson Mathey] (0.11 g, 0.8 mmol), 5-hydroxy-2-(4-[5-propyloxypentyl]phenyl)pyrimidine (0.25g, 0.8 mmol), triphenylphosphine (0.22 g, 0.8 mmol) and tetrahydrofuran (25 cm^3), then stirred at room temperature overnight. The reaction mixture was evaporated down and the solid residue taken up in warm hexane (25 cm^3), filtered to remove precipitate (PPh_3O) and evaporated down once more. Purification of the residue by column chromatography on silica gel using a 9:1 hexane/ethyl acetate mixture as eluent and then recrystallisation from ethanol yielded the pure ether (yield 0.37g, 53 per cent); IR (KBr) *νmax*: 2927, 2853, 1674, 1608, 1576, 1543, 1439, 1279, 1122, 974, 848, 785 cm^{-1}. MS *m/z*: 412 (M^+), 300 ($C_{18}H_{24}N_2O_2^+$), 257 ($C_{15}H_{17}N_2O_2^+$), 240 ($C_{15}H_{16}N_2O^+$). ^1H NMR ($CDCl_3$). 0.86-0.94 (6H, overlapping peaks), 1.26-1.68 (14H, overlapping peaks), 2.09-2.12 (2H, q), 2.64-2.70 (2H, t), 3.33-3.42 (4H, overlapping peaks), 4.60-4.62 (2H, d), 5.71 (1H, overlapping peaks), 5.88 (1H, overlapping peaks), 7.26-7.29 (2H, d), 8.22-8.26 (2H, d), 8.46 (2H, s). The transition temperatures of this ether (9) and similar ethers (10-26) prepared using this general method are recorded in the tables 1-3.

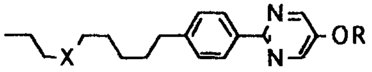
5.10 *4-(5-Heptyl-pyrimidin-2-yl)phenyl Octanoate* (27)

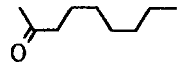
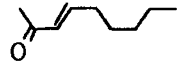
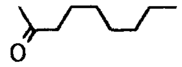
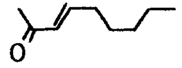
A solution of N,N-dicyclohexylcarbodiimide (0.16 g, 0.8 mmol) in dichloromethane (10 cm^3) was added slowly to a solution of 4-(5-heptyl-pyrimidin-2-yl)phenol (0.20 g, 0.7 mmol), octanoic acid (0.10 g, 0.7 mmol), 4-(dimethylamino)pyridine (0.04 g) and dichloromethane (25 cm^3) at 0°C. The reaction mixture was worked up and purified as described above to give the pure ester (yield 0.24 g, 84 per cent); IR (KBr) *νmax*: 2923, 2852, 1763, 1609, 1581, 1555, 1433, 1236, 1136, 948, 845, 780 cm^{-1}. MS *m/z*: 424 (M^+), 298 ($C_{19}H_{26}N_2O$), 185 ($C_{11}H_9N_2O$). The transition temperatures of this ester (27) and similar esters (28-48) prepared using this general method are collated in the tables 4 and 5.

PHYSICAL PROPERTIES IN MIXTURES

In order to investigate the suitability of the ethers (8-26) and esters (27-48) as non-optically active components of chiral smectic C mixtures for electrooptic display device applications based on ferroelectric effects a fixed amount (15 wt%) of the ethers (1, 2, 8 and 9) and the esters (27, 28, 34 and 35) was dissolved in a standard chiral smectic C mixture (SCO 1014; C/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 the

TABLE 6. Transition temperatures, spontaneous polarisation and switching times of the mixtures consisting of 15 wt% of the ethers (1, 2, 8 and 9) or esters (27, 28, 34 and 35) and 85 wt% SCO 1014:



Ether/ Ester		R	X	I-N* /°C	N*-S$_A$ /°C	S$_A$-S$_C$* /°C	P$_s$ /nCcm^{-2}	τ /μs
1			CH$_2$	74.1	71.9	55.0	14.0	95
2	(E)		CH$_2$	73.1	70.6	58.5	15.8	112
8			O	72.0	68.0	52.0	13.5	100
9	(E)		O	69.4	67.1	55.2	15.2	100
27			CH$_2$	72.2	66.5	59.8	16.7	108
28	(E)		CH$_2$	75.0	64.8	56.8	15.5	140
34			O	69.3	63.6	57.2	16.0	108
35	(E)		O	70.0	59.2	51.6	15.0	125

Experimental part). The transition temperatures (S_C*-S_A, S_A-N* and N*-I) the spontaneous polarisation (P_S) and the observed switching time (τ) of the resulting mixtures were determined under standard conditions (τ: 10 $V_{pp}/\mu m$ square wave, time to maximum current, at 25°C; Ps : 10 Hz, 10 $V_{pp}/\mu m$, triangle), see table 6.

The values for the spontaneous polarisation (P_S) and T_{Sc^*} of the mixtures containing the octenoyloxy-substituted ethers (**2** and **9**) are higher than those of the corresponding mixtures incorporating the analogous octyloxy-substituted ethers (**1** and **8**), although the other transition temperatures are lower. The presence of an additional oxygen atom in the chain of the diethers (**8** and **9**) results in lower values for the transition temperatures and P_S of the mixtures incorporating them. If high spontaneous polarisation (indicative of a larger Sc* tilt angle [12]) combined with a short switching time is a measure of merit, the ether (**9**) is the best compound of this series.

The transition temperatures and P_S of the mixtures containing the esters (**28**, **34** and **35**) with either an additional oxygen atom and/or a carbon-carbon double bond in the chains compared with the ester (**27**) are all lower that those values of the mixture incorporating the ester (**27**). However, only the clearing point (N-I*) is increased by the presence of the double bond in the esters. The switching time τ is also increased which must be due to a higher viscosity as P_S (and thus the switching angle) is lower.

The introduction of a carboxy (ester) group into the octyloxy-substituted ethers (**1** and **8**) to produce the octanoyloxy-substituted esters (**27** and **34**) results in a decrease the transition temperatures, a large increase P_S and a small increase in τ. This indicates a larger switching angle or a lower viscosity as τ is not increased to the same extent. The opposite is true of the octenoyloxy-substituted esters (**28** and **35**), where P_S is almost unchanged and τ is significantly higher indicating a higher viscosity. This is contsistent with the situation observed for the analogous esters with the carboxy group attached to the phenyl ring, where the viscosity for the esters has normally been found to be lower than that of the corresponding ethers.

These results confirm the recent results indicating that isolated (ie., non-conjugated) dipole moments (in this case in the middle of one of the terminal chains) lead to a destablisation of the smectic C phase. This implies that standard theories of the smectic C phase are only valid when the terminal outboard dipole moments are conjugated with aromatic rings in the core of the molecule.

CONCLUSIONS

The presence of an isolated, non-conjugated oxygen atom in the chain of the ethers and esters leads to a decrease in T_{SC}. However, the melting point is sometimes decreased to a greater extent leading to a widening of the smectic C temperature range. A *trans* double bond in the 2-position [(E)-2-] leads to the highest T_{SC} values and lowest smectic A transition temperatures. A double bond in a terminal position of the alkenyloxy chain results in the widest smectic C mesophase ranges. The (E)-alk-2-enyloxy-substituted ethers with an additional oxygen atom in the second chain exhibit an advantageous combination of high spontaneous polarisation and relatively short switching times (low viscosity). The (E)-alk-2-enoyloxy (ester) group suppresses liquid crystal tendencies in the pure substances, but increases T_{NI} in mixtures. The viscosity of the (E)-alk-2-enoyloxy-substituted esters is higher than that of the (E)-alk-2-enyl-substituted ethers, while the viscosity of the corresponding esters without a double bond is lower than that of the analogous ethers.

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