2-(4-Alkylphenyl)-5-(alkenyloxy)pyrimidines: Synthesis, liquid crystal transition temperatures and some physical properties

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2-(4-Alkylphenyl)-5-(alkenyloxy)pyrimidines: synthesis, liquid crystal transition temperatures and some physical properties

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We have recently reported the introduction of a carbon–carbon double bond into a wide variety of 5-*n*-alkyl-2-(4-*n*-alkoxyphenyl)pyrimidines to produce the corresponding alkenyloxy derivatives. The position and nature (E/Z) of the double bond were varied systematically and the effect on the liquid crystal transition temperatures studied. The position and nature (E/Z) of the double bond changed the conformation of the alkenyloxy chain substantially. This resulted in higher smectic C and nematic transition temperatures for compounds with a *trans*-double bond (**E**) at an even number of carbon atoms from the molecular core. Significantly lower transition temperatures (including the melting point) were observed for materials with a *cis*-double bond (Z) at an odd number of carbon atoms from the molecular core. We have now performed the same operation on the related 2-(4-*n*-alkylphenyl)-5-*n*-alkoxypyrimidines to produce the corresponding alkenyloxy derivatives. An interesting feature of the new results is the *high* melting points of the *trans*-substituted materials and the *low* melting points of the terminally substituted compounds. The smectic C transition temperatures of both series are high. No nematic phases could be observed. However, in admixture with other smectic C components, the new compounds lead to surprisingly fast switching times, high smectic C transition temperatures and low melting points/crystallization temperatures in experimental mixtures designed for electro-optic display devices based on ferroelectric effects.

1. Introduction

Many homologues of the 2-(4-*n*-alkylphenyl)-5-*n*-alkoxypyrimidines (**I**) [1] are known to possess relatively wide-range, enantiotropic smectic C phases at temperatures higher than those of the structurally related 5-*n*-alkyl-2-(4-*n*-alkoxyphenyl)pyrimidines (**II**) [2] (only the position of the nitrogen atoms is different).

<p align="center">Alkyl—⟨⟩—⟨N═N⟩—OAlkyl   (I)</p>

<p align="center">Alkyl—⟨N═N⟩—⟨⟩—OAlkyl   (II)</p>
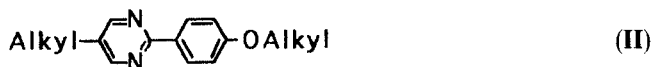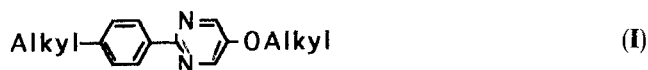
This could be of advantage in the development of commercial chiral smectic C mixtures with higher smectic C* transition temperatures for surface stabilized (SSFLCDs), short pitch bistable (SBFLCDs) and distorted helix (DHFLCDs) ferroelectric liquid crystal displays (FLCDs, i.e. electro-optic display devices based on

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ferroelectric effects [3–11]), where a wide operating temperature range is required. The introduction of a carbon–carbon double bond into the alkoxy chain of a wide variety of the 5-*n*-alkyl-2-(4-*n*-alkoxyphenyl)pyrimidines (**II**) resulted in a range of alkenyloxy substituted ethers (**III**) [12, 13] exhibiting improved physical properties for use in FLCDs.

$$\text{Alkyl} - \underset{N}{\overset{N}{\bigcirc}} - \bigcirc - \text{OAlkenyl} \qquad \textbf{(III)}$$

Many of these new alkenyl substituted ethers (**III**) possessed relatively wide-range, enantiotropic smectic C phases (beneath a nematic phase) at and above room temperature. Several of these new alkenyloxy ethers could be used to induce higher smectic C and nematic transition temperatures of chiral smectic C* mixtures for FLCDs, while reducing the smectic A temperature range. Fast response times in FLCDs could also be achieved [13].

Therefore, a carbon–carbon double bond has been introduced in the same systematic fashion into the 2-(4-*n*-alkylphenyl)-5-*n*-alkoxypyrimidines (**I**) [1] to produce the corresponding alkenyloxy derivatives (**IV**) in order to study the effect on the liquid crystal behaviour and some other physical properties of relevance to FLCDs.

$$\text{Alkyl} - \bigcirc - \underset{N}{\overset{N}{\bigcirc}} - \text{OAlkenyl} \qquad \textbf{(IV)}$$
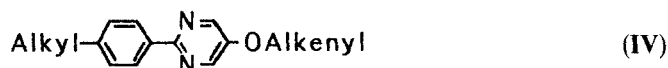
2. Synthesis

The alkenyloxy ethers to be investigated (**2–7, 9–14, 16–21** and **23–84**) could be synthesized as shown in the reaction scheme by alkylation of the 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-hydroxypyrimidines [1] with alkenyl alcohols and bromides incorporating a carbon–carbon double bond of a defined configuration (E/Z)
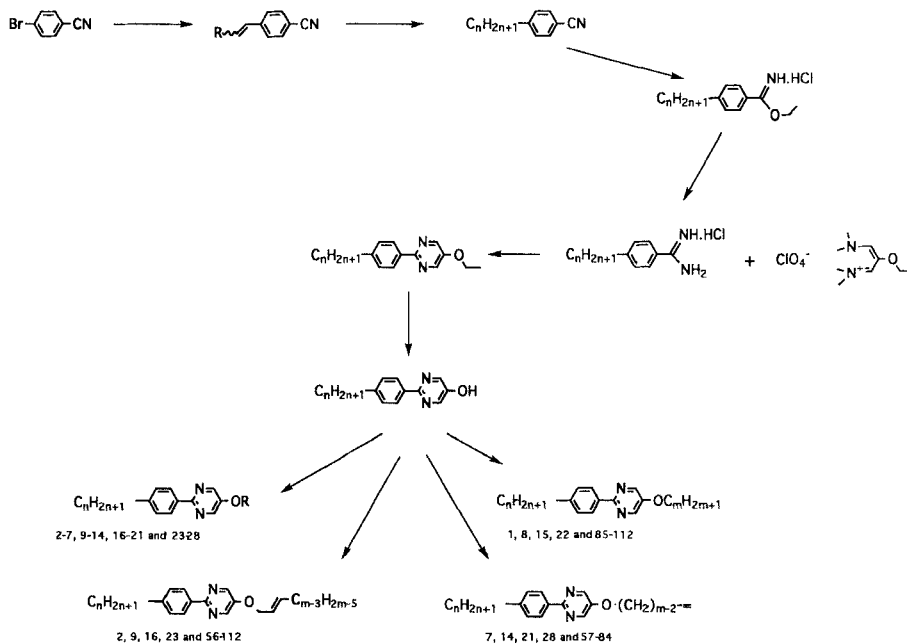
at various positions in the chain as previously described [13]. The 2-(4-hexyl-, heptyl, octyl-, and nonyl-phenyl)-5-hydroxypyrimidines were prepared by a Heck alkylation reaction [14] using commercially available bromobenzonitrile and 1-*n*-alkenes. The resulting alkenes were hydrogenated as usual over a palladium catalyst to 4-*n*-alkylbenzonitriles, which were converted into 4-*n*-alkylbenzamidines in two steps as previously described [15]. Reaction of these 4-*n*-alkylbenzamidines with 1,3-bis(dimethylamino)-2-ethoxytrimethinium perchlorate [16] yielded the two-ring 2-(4-*n*-alkylphenyl)-5-ethoxypyrimidines. Dealkylation using sodium hydroxide at high temperatures and alkylation of the resulting phenol [1] with the required alkenyl alcohols [12] and some commercially available bromides gave the desired 2-(4-*n*-alkylphenyl)-5-(alkenyloxy)pyrimidines (**2–7, 9–14, 16–21** and **23–84**) with a carbon–carbon double bond in the terminal alkenyloxy chain. The methods of synthesis and structural analysis of the new ethers are described in detail in the experimental section for a representative member (**2–7**) of each series. One homologue (**1**) of the known parent ethers [1] without an additional double bond in the alkoxy chain (synthesized as a reference compound) is also described. The configuration of the carbon–carbon double bond in the alkenyloxy chain of the new ethers (**2–7, 9–14, 16–21** and **23–84**) was confirmed by ^{1}H NMR spectroscopy (the *trans*-olefinic coupling constants $\approx$ 12–18 Hz are larger than those of the corresponding *cis*-olefinic coupling constants $\approx$ 7–11 Hz) and by infrared spectroscopy (the *trans*-absorption bands are narrow and exact $\approx$ 970–960 cm^{-1}, while the *cis*-absorption bands are observed at distinctly different wave lengths $\approx$ 730–675 cm^{-1}). Traces of undesired isomers formed during the preparation of the various alkenyl-1-ols required as reaction intermediates, or present in commercially available starting materials, could be removed by recyrstallization of the desired end product (see the experimental section). 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 [17].

3. Mesomorphic properties

The liquid crystal transition temperatures of the 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-octyloxypyrimidines (**1, 8, 15** and **22**) and those of the analogous 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-octenyloxypyrimidines (**2–7, 9–14, 16–21** and **23–28**) are collated in table 1. The position of the unsaturated carbon–carbon double bond is varied systematically from the beginning to the end of the terminal alkenyloxy chain in each series. The only difference between the octenyloxy ethers within each of the four separate homologous (**2–7, 9–14, 16–21** and **23–28**) series is the position and configuration of the double bond. The configuration at the olefinic double bond is alternately *trans* and *cis* (*E* and *Z*) [12]. The 7-octenyloxy 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. The width of the smectic C mesophase (i.e., the mesophase type of most direct interest for electro-optic effects based on ferroelectric effects) is recorded in the last column.

The ethers (**2, 9, 16** and **23**) with a *trans*-double bond in the 2-position exhibit significantly higher melting points (+24°C, on average) and smectic C transition temperatures (+11°C, on average) than the corresponding ethers (**1, 8, 15** and **22**) without a carbon–carbon double bond in the terminal alkoxy chain. The smectic A phase is marginally lower (−3°C, on average). Thus, the temperature ranges of both the smectic C and A phases are reduced (−13°C and −14°C, on average, respectively), although these transitions are still at high absolute temperatures.

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Table 1.   The liquid crystal transition temperatures for the 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-(octenyloxy)pyrimidines **1–28**.

$$C_nH_{2n+1}\!-\!\!\bigotimes\!\!-\!\!\underset{N}{\overset{N}{\diagdown}}\!\!\diagup\!\!-OR$$
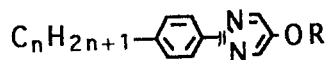
Ether	n	R	$C\text{–}S_C/S_A/I/^\circ C$	$S_C\text{–}S_A/^\circ C$	$S_A\text{–}I/^\circ C$	$\Delta T_{S_C}/^\circ C$
1	6		29	68	85	39
2	6		61	76	80	15
3	6		55	—	—	—
4	6		57	68	80	11
5	6		45	52	55	7
6	6		45	50	85	5
7	6		26	54	75	28
8	7		32	64	87	32
9	7		59	75	82	16
10	7		55	—	—	—
11	7		57	66	82	9
12	7		42	52	55	10
13	7		48	—	87	—
14	7		24	50	78	26
15	8		39	58	84	19
16	8		56	70	84	14
17	8		52	—	(43)	—
18	8		53	55	82	2
19	8		38	46	57	8
20	8		44	—	85	—
21	8		42	43	76	33
22	9		36	53	85	17
23	9		56	65	82	9
24	9		52	—	(44)	—
25	9		47	52	82	5
26	9		38	44	58	6
27	9		51	—	86	—
28	9		34	38	77	4

( ) Represents a monotropic transition temperature.

Only the melting point ($+20^\circ$C, on average) of the (E)-4 substituted ethers is higher than that of the reference ethers (**1, 8, 15** and **22**). The smectic C transition temperatures (-8°C, on average) and the clearing point (-3°C, on average) are both lower. Only one homologue (**6**) of the ethers (**6, 13, 20** and **27**) with a double bond in position 6 of the octenyloxy chain exhibits a smectic C phase. The other three homologues only possess a smectic A phase at almost the same temperatures (86°C, on average) as the reference ethers. Thus the introduction of a double bond in position 6 results in the conversion of a wide-range smectic C phase (27°C, on average) and smectic A phase (24°C, on

average) into a purely smectic A phase (39°C, on average). The smectic A phase range would be greater if the melting point were also not higher ($+13$°C, on average).
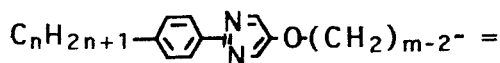
A totally different picture appears for the materials (**3, 5, 10, 12, 17, 19, 24** and **26**) with a *cis*-double bond in positions 3 and 5 compared to the standard compounds. A *cis*-double bond in positions 3 of the ethers (**3, 10, 17** and **24**) appears to be most disadvantageous for liquid crystal formation. Just one liquid crystal phase (smectic A) could be observed for only two homologues (**17** and **24**). On the other hand the ethers (**5, 12, 19** and **26**) with *cis*-double bond in position 5 all exhibit a smectic C and A phase at reasonably elevated temperatures (49°C and 56°C, on average, respectively). As the melting point is also relatively high (41°C, on average) the temperature range of the smectic C phase is modest (8°C, on average). The smectic C and A phases are observed

Table 2. The liquid crystal transition temperatures for the 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-[(*E*)-2-alkenyloxypyrimidines **2, 9, 16, 23** and **29–56**.

$$C_nH_{2n+1}\text{—}\langle\bigcirc\rangle\text{—}\!\!\overset{N}{\underset{N}{\diamondsuit}}\text{O}\diagup\!\!\diagup C_{m-3}H_{2m-5}$$

Ether	n	m	$C\text{–}S_3/S_C/S_A/$°C	$S_3\text{–}S_A/$°C	$S_C\text{–}S_A/I/$°C	$S_A\text{–}I/$°C
29	6	5	57	—	—	63
30	6	6	67	—	—	76
31	6	7	62	—	65	71
2	6	8	61	—	76	80
32	6	9	74	—	78	—
33	6	10	65	—	82	—
34	6	11	73	—	82	—
35	6	12	56	72	84	—
36	7	5	53	—	—	66
37	7	6	69	—	—	78
38	7	7	60	—	61	73
9	7	8	59	—	75	82
39	7	9	67	—	80	—
40	7	10	64	—	86	—
41	7	11	72	—	85	—
42	7	12	67	74	87	—
43	8	5	53	—	—	65
44	8	6	68	—	—	77
45	8	7	57	—	—	73
16	8	8	56	—	70	84
46	8	9	67	—	79	—
47	8	10	39	62	84	—
48	8	11	51	67	85	—
49	8	12	66	74	86	—
50	9	5	57	—	—	66
51	9	6	70	—	—	77
52	9	7	57	—	(48)	73
23	9	8	56	—	65	82
53	9	9	62	—	78	80
54	9	10	60	(56)	84	—
55	9	11	50	63	86	—
56	9	12	61	74	87	—

( ) Represents a monotropic transition temperature.

Table 3. The liquid crystal transition temperatures for the 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-[alkenyloxy]pyrimidines **7**, **14**, **21**, **28** and **57–84**.

$$C_nH_{2n+1}-\!\!\!\left\langle\bigcirc\right\rangle\!\!-\!\!\left\langle\!\!\begin{array}{c}N\\N\end{array}\!\!\right\rangle\!\!-O\text{-}(CH_2)_{m-2}-\,=$$

Ether	n	m	$C\text{-}S_3/S_C/S_A/^\circ C$	$S_3\text{-}S_C/^\circ C$	$S_C\text{-}S_A/^\circ C$	$S_A\text{-}I/^\circ C$
57	6	5	39	—	—	69
58	6	6	35	—	—	64
59	6	7	34	—	—	79
7	6	8	26	—	54	75
60	6	9	20	—	65	81
61	6	10	33	35	73	80
62	6	11	29	(28)	76	82
63	6	12	33	35	76	81
64	7	5	48	—	—	72
65	7	6	37	—	—	67
66	7	7	35	—	—	81
14	7	8	24	—	50	78
67	7	9	16	23	62	84
68	7	10	32	33	72	82
69	7	11	28	29	77	85
70	7	12	38	40	79	84
71	8	5	43	—	—	69
72	8	6	33	—	—	64
73	8	7	37	—	—	80
21	8	8	42	—	43	76
74	8	9	20	—	60	83
75	8	10	36	—	72	81
76	8	11	38	—	78	84
77	8	12	43	—	80	82
78	9	5	50	—	—	70
79	9	6	33	—	—	65
80	9	7	38	—	—	81
28	9	8	34	—	38	77
81	9	9	30	—	53	84
82	9	10	35	—	71	82
83	9	11	38	—	78	85
84	9	12	43	—	82	83

( ) Represents a monotropic transition temperature.

at substantially lower temperatures ($-22^\circ C$ and $-29^\circ C$, on average, respectively) than those of the reference ethers (**1**, **8**, **15** and **22**).

Decreases in all the liquid crystal transition temperatures of the four compounds (**7**, **14**, **21** and **28**) with a terminal double bond are also observed. However, the smectic C transition temperature seems to be decreased more ($-14^\circ C$, on average) than either the melting point ($-2^\circ C$, on average) or the smectic A transition temperature ($-8^\circ C$, on average) relative to the saturated materials (**1**, **8**, **15** and **22**). However, the temperature range of the smectic C phase is still relatively large ($15^\circ C$, on average) and the melting point is low ($32^\circ C$, on average).

Initial investigations of the physical properties of the ethers under investigation indicated that the electro-optic response of the octenyloxy ethers (**2**, **9**, **16** and **23** and **7**,

14, 21 and **28**, respectively) incorporating a double bond in the (*E*)-2 and a terminal position was the most interesting for FLCDs (see physical properties). Thus a total of eight homologous series (**2** and **29–36, 9** and **37–44, 16** and **45–52, 23** and **53–60, 7** and **61–68, 14** and **69–76, 21** and **77–84, 28** and **85–92**) of these ethers (see tables 2 and 3) were chosen for further study. Four series contained the (*E*)-2-alkenyloxy chain (**2** and **29–36, 9** and **37–44, 16** and **45–52, 23** and **53–60**, respectively) as these seemed the most promising compounds of all due to their transition temperatures and relative ease of preparation (see table 2). They are characterized by a surprising similarity of trends and absolute values. A minor difference is the greater tendency of the ethers with longer alkyl chains to form ordered phases.
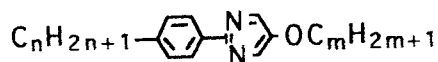
The plots of the smectic A–isotropic liquid crystal transition temperature (S_A–I) against chain length (*m*) of the 5-hexyl-2-(4-[(*E*)-2-alkenyloxyl]phenyl)pyrimidines (**2** and **29–36**) show a considerable degree of alternation at high temperatures (76°C, on average). The plots of the smectic C–nematic transition temperature (S_C–N) also show a degree of alternation, although to a lesser extent at comparable temperatures (78°C, on average). The plots begin at lower temperatures (65°C) for the shorter chain lengths (*m* = 7) and rise smoothly to reach the highest values (84°C) for the longest chain studied (*m* = 12). The plot of the melting point (C–S_A, C–S_C and C–S_3) is irregular and does not vary greatly with chain length, starting and ending at relatively high temperatures (57°C and 56°C, respectively) leading to a relatively high average value (65°C). Thus, the smectic C mesophase range is narrow (12°C, on average). An ordered smectic mesophase is observed for the longest chain studied (*m* = 12). The transition temperatures of the other three homologous series are very similar. An increased tendency to form an ordered phase for longer chain lengths is apparent.

The transition temperatures of the 5-hexyl-, heptyl-, octyl-, and nonyl-2-[4-(alkenyloxy)phenyl]pyrimidines (**7** and **61–68, 14** and **69–76, 21** and **77–84, 28** and **85–92**, respectively) with a terminal carbon–carbon double bond are collated in table 3. Broad range smectic A and C phases are observed. The melting point is often low. The most striking feature of the data for the four homologous series in the table is their similarity. The only major difference between them is the absence of the ordered smectic phase for the octyl and nonyl series (**21** and **77–84, 28** and **85–92**, respectively).

The most important differences between the transition temperatures for ethers (**2** and **29–36, 9** and **37–44, 16** and **45–52, 23** and **53–60**, respectively) with a *trans*-double bond in the 2-position (as shown in table 2) and the ethers (**7** and **61–68, 14** and **69–76, 21** and **77–84, 28** and **85–92**, respectively) with a double bond in a terminal position (as shown in table 3) are the lower melting points, the lower tendency to form ordered smectic phases and the presence of a broad smectic A phase for all the terminally substituted ethers. Thus, the range of the smectic C phase is often significantly broader for the terminally substituted ethers, as well as commencing at lower temperatures.

The situation with regard to the trends in the observed transition temperatures is complicated and average values have been quoted in order to be able to comment at all on such a large quantity of diverse data. There are a number of individual deviations from these general trends (evident from reference to tables 1–3). In order to make possible an independent interpretation of the transition temperatures collected in tables 1–3, for the new 5-hexyl-, heptyl-, octyl-, and nonyl-2-[4-(alkenyloxy)phenyl]pyrimidines (**2–7, 9–14, 16–21** and **23–84**), the transition temperatures [1] of the analogous alkoxy substituted parent compounds (**1, 8, 15, 22** and **85–112**, i.e. those without a carbon–carbon double bond in the terminal alkoxy chain) have also been collated in table 4.

Table 4.   The liquid crystal transition temperatures for the 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-(4-n-alkoxyphenyl)pyrimidines **1, 8, 15, 22** and **85–112**.

$$C_nH_{2n+1} - \langle \bigcirc \rangle - \langle \! \! \! \begin{array}{c} N \\ N \end{array} \! \! \! \rangle - OC_mH_{2m+1}$$

Ether	n	m	$C-S_3/S_C/S_A/°C$	$S_3-S_C/°C$	$S_C-S_A/I/°C$	$S_A-N/I/°C$	$N-I/°C$
85	6	5	48	—	—	62	—
86	6	6	49	—	—	77	—
87	6	7	33	—	51	77	—
1	6	8	29	—	68	85	—
88	6	9	48	—	77	84	—
89	6	10	38	(35)	82	87	—
90	6	11	39	42	84	86	—
91	6	12	35	47	86	87	—
92	7	5	46	—	—	64	66
93	7	6	51	—	—	78	—
94	7	7	32	—	45	78	—
8	7	8	32	—	64	87	—
95	7	9	34	—	76	85	—
96	7	10	32	33	83	88	—
97	7	11	39	45	87	89	—
98	7	12	46	54	88	89	—
99	8	5	47	—	—	61	—
100	8	6	46	—	—	76	—
101	8	7	47	—	(39)	78	—
15	8	8	39	—	58	84	—
102	8	9	41	—	76	85	—
103	8	10	42	—	84	88	—
104	8	11	54	—	87	—	—
105	8	12	57	58	89	—	—
106	9	5	49	—	—	62	63
107	9	6	48	—	—	77	—
108	9	7	40	—	—	78	—
22	9	8	36	—	53	85	—
109	9	9	39	—	74	85	—
110	9	10	37	(32)	83	87	—
111	9	11	45	46	87	—	—
112	9	12	47	59	89	—	—

( ) Represents a monotropic transition temperature.

4. Physical properties

In order to investigate the suitability of the 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-(octenyloxy)pyrimidines (**2–7, 9–14, 16–21** and **23–28**) as non-optically active components of chiral smectic C mixtures for electro-optic display device applications based on ferroelectric effects a fixed amount (15 wt %) 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 Experimental section). The liquid crystal transition temperatures ($C-S_C^*$, $S_X-S_C^*$, $S_C^*-S_A$, 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 Vpp/μ square wave, time to maximum current, at
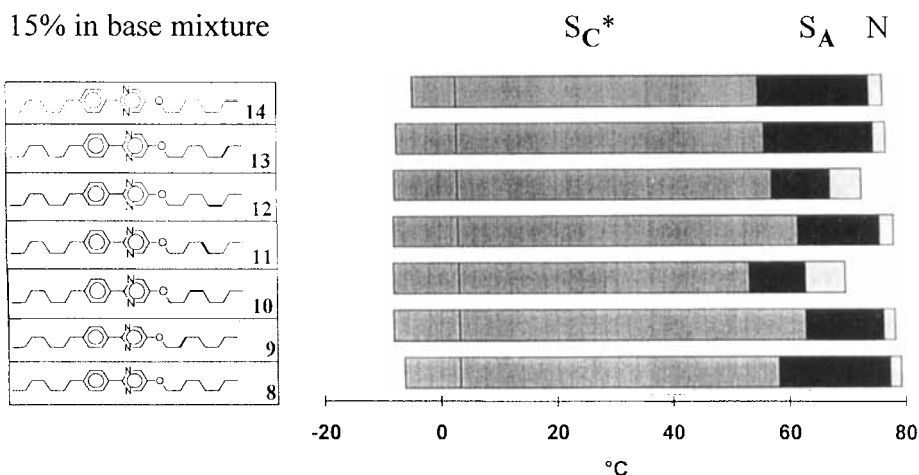
Plot of the transition temperatures against the position and configuration of the carbon–carbon double bond in the octenyloxy chain of the 2-(4-heptylphenyl)-5-(octenyloxy)pyrimidines (**9–14**) and the reference 2-(4-heptylphenyl)-5-octyloxypyrimidine (**8**).

$25°C$; P_s: 10 Hz, 10 Vpp/μ, triangle). The transition temperatures shown schematically in the figure show that the addition of the octenyloxy-substituted ethers (**9–14**) to the base mixture results in a higher chiral smectic C–smectic A transition temperature ($+4°C$, on average) for two ethers (**9** and **11**) and in a lower melting/crystallization temperature (≈ 1–$6°C$) for five ethers (**9–13**) than those observed for the corresponding mixture containing the octyloxy-substituted reference ether (**8**). For certain ethers this leads to an increase in the temperature range of the chiral smectic C mesophase ($+4.2°C$, on average). The addition of the octenyloxy-substituted ethers (**9–14**) to the base mixture also results in a decrease in the temperature range of the smectic A mesophase ($-5°C$, on average). The spontaneous polarization ($P_s \approx 13$–16 nC cm^{-2}) of all seven mixtures follows the changes in the smectic C–smectic A transition temperature. Since they are measured at $25°C$, this reflects the well-known temperature dependence of the spontaneous polarization as a function of the temperature difference between the measuring temperature and the smectic C–smectic A transition temperature. A strong dependency of the switching times ($\tau \approx 75$–105 μs) on the position of the double bond cannot be explained using the same arguments. This must be due to differences in the viscosity of the individual isomers. No direct correlations between structure and switching times could be identified. The values for the physical properties obtained for the new ethers demonstrated a strong dependency on the matrix (i.e. base chiral smectic C* mixture) in which they were measured. Selected homologues of the new alkenyloxy ethers (**IV**) have been used in optimized base mixtures to produce commercial wide-range chiral smectic C* mixtures with short response times for FLCDs [18].

5. Discussion

There are major differences between the observed changes in the transition temperatures on introducing a carbon carbon double bond into the 2-(4-*n*-alkylphenyl)-5-*n*-alkoxypyrimidines (**I**) with an octyloxy chain (i.e., **1, 8, 15** and **22**) [1] to produce the analogous 2-(4-*n*-alkylphenyl)-5-*n*-alkenyloxypyrimidines (**IV**) with an

octenyloxy chain (i.e., **2–7, 9–14, 16–21** and **23–28**) and performing the same procedure on octyloxy homologues of the structurally related 5-*n*-alkyl-2-(4-alkyloxyphenyl)pyrimidines **(II)** [2] (differing only in the position of the nitrogen atoms) to produce the corresponding octenyloxy homologue of the 5-*n*-alkyl-2-[4-alkenyloxy)phenyl]pyrimidines **(III)** [12].

In general the 5-*n*-alkyl-2-[4-(octenyloxy)phenyl]pyrimidines [12] incorporating a *trans*-double bond in positions 2, 4 and 6 in the terminal octenyloxy chain exhibit similar melting points, smectic C transition temperatures, smectic A transition temperatures and nematic–isotropic transition temperatures to those of their analogues [2] containing no double bond in the alkoxy chain. However, average values fail to reveal a significant rise in the smectic C–smectic A transition temperature for some (*E*)-2-octenyloxy substituted ethers accompanied by a decrease in the smectic A transition temperature resulting in only a narrow smectic A mesophase range above the smectic C mesophase. Additionally, a narrow-range nematic mesophase is observed for the (*E*)-octenyloxy substituted ether and not for the reference ether. Thus, some (*E*)-2-substituted ethers [12] exhibit the ideal order and range of mesophases for mixtures designed for electro-optic effects based on ferroelectric effects [13]. In contrast, only the (4-alkylphenyl)-5-[(*E*)-2-octenyloxy]-2-pyrimidines (**2, 9, 16** and **23**; with a *trans*-double bond in the 2-position) reported here show higher smectic C transition temperatures (see table 1). The new ethers (**4, 6, 11, 13, 18, 20, 25** and **27**) with a *trans*-double bond in the 4 and 6 positions exhibit liquid crystal transition temperatures below those of the corresponding reference ethers [1] (see table 1).

The situation is somewhat different for the 5-*n*-alkyl-2-[4-(octenyloxy)phenyl]pyrimidines [12] with a *cis*-double bond in positions 3 and 5 compared to the standard compounds [2]. The melting point, smectic C, smectic A and nematic transition temperatures are all lower than those of the analogous materials with saturated alkoxy chains. However, this often results in enantiotropic, relatively wide-range (<20°C) smectic C mesophases at and above room temperature. This is not the case for the novel ethers (**3, 5, 10, 12, 17, 19, 24** and **26**) with a *cis*-double bond in positions 3 and 5, where more substantial decreases in the transition temperatures are observed. Thus, the *cis*-3-substituted ethers (**3, 10, 17** and **24**) are not mesomorphic and the *cis*-5-substituted ethers (**5, 12, 19** and **26**) only possess a smectic A phase at low temperatures (see table 1).

A double bond in a terminal position in both series induces similar decreases in the liquid crystal properties. Comparisons are difficult because the three homologues of the 5-*n*-alkyl-2-[4-(octenyloxy)phenyl]pyrimidines [12] do not always exhibit the same phases. However, the smectic C transition temperature seems to be decreased more (−17°C, on average) than either the melting point (−7°C, on average), the smectic A transition temperature (−8°C, on average) or the nematic–isotropic transition temperature (−10°C, on average) relative to the saturated materials **(II)**. This behaviour is also observed for the terminally substituted 2-(4-hexyl-, heptyl-, octyl-, and nonyl-phenyl)-5-octenyloxypyrimidines (**7, 14, 21** and **28**), where the smectic C phase transition temperature and temperature range are both substantially reduced.

The salient difference between the mesomorphic behaviour of the new 2-(4-*n*-alkylphenyl)-5-alkenyloxypyrimidines **(IV)** reported here and the corresponding 5-*n*-alkyl-2-[4-(alkenyloxy)phenyl]pyrimidines **(III)** [11] is the total absence of a nematic phase for any members of the former (see table 1). The absolute values of all the other transition temperatures are also higher. This may be due to the higher degree of polarization of the pyrimidine ring attributable to a greater degree of conjugation between the two nitrogen atoms and the oxygen atom on the same ring for the new

alkenyloxy substituted ethers (**IV**). This could result in increased intermolecular attractions between the chains and the cores.

Comparisons between individual, homologous series of the 2-(4-*n*-alkylphenyl)-5-alkenyloxypyrimidines (**IV**) shown in tables 2 and 3 and the corresponding 5-*n*-alkyl-2-[4-(alkenyloxy)phenyl]pyrimidines (**III**) [11] reveal distinctly different results for each series and are of very little value. They demonstrate once again the strong dependence on chain length of the type and transition temperatures of liquid crystal mesophases and the difficulty involved in extrapolating from known systems.

6. Experimental

The liquid crystal transition temperatures of the compounds prepared recorded in tables 1–4 were determined by optical microscopy using a Leitz Otholux II POL BK microscope in conjunction with a Mettler FP82 heating stage and FP80 control unit. All the monotropic liquid crystal phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. 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 liquid crystal 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 gas capillary chromatograph equipped with a 25 m OV 61 column and GP-100 graphics printer was used. TLC plates (4 cm × 8 cm) coated with SiO_2 SIL/G/UV_{254} (Machery-nagel, Düren, Germany) were utilized. The purity of the final liquid crystalline products (**1–84**) was >99·7 per cent by GC and DTA. Column chromatography was carried out using silica gel 60 (330–400 mesh ASTM). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were carried out under nitrogen unless water was present as solvent or reagent. All temperatures were measured externally unless otherwise stated. The ^1H NMR spectra were recorded at 60 MHz (Varian T-60), 80 MHz (Bruker WP-80) or 270 MHz (Bruker HX-270). 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-octyloxybenzoate (16 wt %), 2-(4-hexyloxyphenyl)-5-nonylpyrimidine (24 wt %), 2-4-nonyloxyphenyl)-5-nonylpyrimidine (24 wt %), 2-(4-nonyloxyphenyl)-5-heptylpyrimidine (12 wt %), 2-(4-hexyloxyphenyl)-5-octylpyrimidine (12 wt %) and 2-(4-decyloxyphenyl)-5-octylpyrimidine (12 wt %). The determination of the physical properties of the chiral mixtures containing the new ethers was carried out as previously described [12].

6.1. *4-(E/Z)-Nonenylbenzonitrile*

A mixture of 4-bromobenzonitrile (50 g, 0·275 mol), 1-nonene (69·5 g, 0·550 mol), sodium bicarbonate (69·3 g, 0·825 mol), triphenylphosphine (1·8 g, 0·007 mol), palladium (II) acetate (0·7 g) and *N*-methylpyrrolidone (160 ml) was heated overnight under gentle reflux. The reaction solution was poured onto water (500 ml) and shaken with ethyl acetate (2 × 50 ml). The combined organic layers were washed with water (2 × 50 ml), dried (MgSO$_4$), filtered and evaporated down to yield 4-(*E/Z*)-nonenylbenzonitrile (62·6 g, 99 per cent) as an oil. IR (KBr) v_{max}: 2958, 2927, 2854, 2226, 1650, 1605, 1504, 1461, 968, 850 cm^{-1}. MS *m/z*: 227 (M$^+$), 143 ($C_{10}H_9N^+$), 129, ($C_9H_7N^+$).

4-(E/Z)-Hexenylbenzonitrile (82 per cent), (MS *m/z*: 185 (M$^+$)), *4-(E/Z)-heptenylbenzonitrile* (85 per cent), (MS *m/z*: 199 (M$^+$)), and *4-(E/Z)-octenylbenzonitrile* (97 per cent), (IR (KBr) ν_{max}: 2958, 2928, 2855, 2226, 1650, 1605, 1504, 1461, 968, 858 cm^{-1}. MS *m/z*: 213 (M$^+$), 143 (C$_{10}$H$_9$N$^+$), 129, (C$_9$H$_7$N$^+$)) were prepared using the same procedure.

6.2. *4-Nonylbenzonitrile*

A mixture of 4-(*E/Z*)-nonenylbenzonitrile (62·6 g, 0·275 mol), 10 per cent palladium on active charcoal (2 g) and tetrahydrofuran (700 ml) was hydrogenated until the absorption of hydrogen was completed. The inorganic material was removed by filtration and the filtrate evaporated down under reduced pressure. The residue was purified by distillation under reduced pressure to yield 4-nonylbenzonitrile (48·6 g, 77 per cent); b.p. 135–140°C/1·6 mbar. IR (KBr) ν_{max}: 2958, 2920, 2853, 2227, 1607, 1504, 1459, 843, 821 cm^{-1}. MS *m/z*: 229 (M$^+$), 130, (C$_9$H$_8$N$^+$). NMR (CDCl$_3$): 0·85–0·90 (3 H, overlapping peaks), 1·21–1·30 (12 H overlapping peaks), 1·58–1·61 (2 H, t), 2·62–2·68 (2 H, t), 7·25–7·28 (2 H, d), 7·54–7·57 (2 H, d).

4-Hexylbenzonitrile (72 per cent), (MS *m/z*: 187 (M$^+$)), *4-heptylbenzonitrile* (65 per cent), (MS *m/z*: 201 (M$^+$)), and *4-octylbenzonitrile* (52 per cent) (b.p. 120–125°C/1·6 mbar), IR (KBr) ν_{max}: 2959, 2923, 2854, 2227, 1608, 1504, 1462, 844, 828 cm^{-1}) (MS *m/z*: 215 (M$^+$), 130, (C$_9$H$_8$N$^+$), 117, (C$_8$H$_7$N$^+$)), (NMR (CDCl$_3$): 0·85–0·88 (3 H overlapping peaks), 1·22–1·26 (12H, overlapping peaks), 1·61 (2H, t), 2·62–2·68 (2 H), t), 7·16–7·29 (2 H, d), 7·54–7·58 (2 H, d)) were prepared using the same procedure.

6.3. *4-Nonylphenyl-imidoethyl ether*

A saturated solution of hydrogen chloride in ethanol (70 ml) was added to a solution of 4-nonylbenzonitrile (48·6 g, 0·212 mol) and toluene (200 ml) at room temperature. The reaction mixture was stirred at this temperature for 48 h then taken up in diethyl ether, stirred at room temperature for 30 min, then at 0°C for 1 h. The precipitate was filtered off, washed with portions of cold diethyl ether and then dried under vacuum to yield 4-nonylphenyl-imidoethyl ether (51 g, 77 per cent). IR (KBr) ν_{max}: 2955, 2921, 2850, 1646, 1612, 1518, 1463, 862, 850 cm^{-1}. MS *m/z*: 275 (M$^+$), 247, (C$_{16}$H$_{25}$NO$^+$). 231, (C$_{16}$H$_{25}$N$^+$). NMR (CDCl$_3$): 0·88 (3 H, overlapping peaks), 1·26 (12 H, overlapping peaks), 1·58–1·63 (2 H, t), 2·68 (2 H, t), 4·91–4·94 (2 H, q), 7·26–7·38 (2 H, d), 8·29–8·23 (2 H, d).

4-Hexylphenyl-imidoethyl ether (55 per cent), (MS *m/z*: 233 (M$^+$)), *4-heptylphenyl-imidoethyl ether* (65 per cent), (MS *m/z*: 247 (M$^+$)), and *4-octylphenyl-imidoethyl ether* (50 per cent), (IR (KBr) ν_{max}: 3005, 2954, 2918, 2851, 2755, 1596, 1520, 1488, 868, 828 cm^{-1}), (MS *m/z*: 261 (M$^+$), (NMR (CDCl$_3$): 0·85 (3 H, overlapping peaks), 1·24 (12 H, overlapping peaks), 1·58 (2 H, t), 2·50–2·57 (2 H, t), 7·21–7·24 (2 H, d), 7·36–7·39 (2 H, d), 9·21 (3 H, s)) were prepared using the same procedure.

6.4. *4-Nonylbenzamidine hydrochloride*

A saturated solution of ammonia in ethanol (300 ml) was added dropwise at 0°C to a solution of 4-nonylphenyl-imidoethyl ether (51 g, 0·162 mol) and ethanol (250 ml). The reaction mixture was stirred overnight at room temperature, evaporated down, then taken up in diethyl ether, stirred at room temperature for 30 min, then at 0°C for 1 h. The precipitate was filtered off, washed with portions of cold diethyl ether and then dried under vacuum to yield 4-nonylbenzamidine hydrochloride (45 g, 97 per cent);

m.p., 118–120°C. IR (KBr) v_{max}: 3424, 3275, 3218, 3112, 2956, 2916, 2746, 1651, 1612, 1581, 1542, 1498, 1461, 849 cm^{-1}. MS m/z: 246 (M$^+$), 230, (C$_{16}$H$_{24}$N$^+$). NMR (CDCl$_3$: 0·88 (3 H, overlapping peaks), 1·25 (12 H, overlapping peaks), 1·58 (2 H, t), 2·56 (2 H, t), 7·23–7·26 (2 H, d), 7·81–7·84 (2 H, d), 9·21 (3 H, s).

4-Hexylbenzamidine hydrochloride (93 per cent), (m.p., 165–167°C), (IR (KBr) v_{max}: 3425, 3275, 3218, 3114, 2956, 2916, 2746, 1651, 1614, 1581, 1542, 1498, 1461, 849 cm^{-1}), (MS m/z: 200 (M$^+$)), (NMR (CDCl$_3$): 0·87 (3 H, overlapping peaks), 1·22–1·24 (12 H, overlapping peaks), 1·60 (2 H, t), 2·51–2·70 (2 H, t), 7·42–7·46 (2 H, d), 7·75–7·78 (2 H, d), 9·21 (4 H, s)), *4-heptylbenzamidine hydrochloride* (96 per cent), (m.p., 117–118°C), (IR (KBr) v_{max}: 3422, 3275, 3220, 3112, 2956, 2916, 2746, 1650, 1612, 1581, 1542, 1498, 1461, 849 cm^{-1}), (MS m/z: 214 (M$^+$)), (NMR (CDCl$_3$): 0·85 (3 H, overlapping peaks), 1·24 (12 H, overlapping peaks), 1·58 (2 H, t), 2·54–2·70 (2 H, t), 7·44–7·46 (2 H, d), 7·75–7·78 (2 H, d), 9·21 (4 H, s)), and *4-octylbenzamidine hydrochloride* (98 per cent), (m.p., 110–114°C), (IR (KBr) v_{max}: 3278, 3112, 3053, 2956, 2917, 2850, 1651, 1611, 1580, 1542, 1496, 1464, 852 cm^{-1}), (MS m/z: 233 (M + H$^+$)), (NMR (CDCl$_3$): 0·88 (3 H, overlapping peaks), 1·25 (12 H, overlapping peaks), 1·58 (2 H, t), 2·55 (2 H, t), 7·23–7·26 (2 H, d), 7·81–7·84 (2 H, d), 9·18 (3 H, s)) were prepared using the same procedure.

6.5. *2-(4-Nonylphenyl)-5-ethoxypyrimidine*

1,3-bis(dimethylamino)-2-ethoxytrimethinium perchlorate [15] (20·3 g, 0·075 mol) and 4-nonylbenzamidine hydrochloride (21·2 g, 0·075 mol) were added to a solution of 31·5 mol sodium methoxide (0·169 mol) in methanol (180 ml) at room temperature under an atmosphere of nitrogen. The reaction mixture was heated under gentle reflux overnight, poured onto water (500 ml), cooled to 0°C, acidified with 25 per cent 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 crystallized from ethanol to yield 2-(4-nonylphenyl)-5-ethoxypyrimidine (19·5 g, 80 per cent); $T_{CI} = 81$–82°C; $T_{NI} = (64)$°C. IR (KBr) v_{max}: 2955, 2851, 1577, 1546, 1447, 1290, 784 cm^{-1}. MS m/z: 326 (M$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$). NMR (CDCl$_3$): 0·85–0·87 (3 H, overlapping peaks), 1·28–1·31 (12 H, overlapping peaks), 1·45 (2 H, t), 1·64 (2 H, t), 2·62–2·68 (2 H, t), 4·14–4·21 (2 H, q), 7·26–7·29 (2 H), d), 8·22–8·25 (2 H, d), 8·44 (2 H, s).

2-(4-Hexylphenyl)-5-ethoxypyrimidine (87 per cent), ($T_{CI} = 76$°C; $T_{NI} = (61)$°C), (IR (KBr) v_{max}: 2955, 2923, 2851, 1609, 1577, 1546, 1447, 1288, 1043, 783 cm^{-1}), (MS m/z: 284 (M$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$)), (NMR (CDCl$_3$): 0·85–0·87 (3 H, overlapping peaks), 1·27–1·33 (8 H, overlapping peaks), 1·45–1·50 (2 H, t), 1·64 (2 H, t), 2·62–2·69 (2 H, t), 4·13–4·21 (2 H, q), 7·26–7·29 (2 H, d), 8·22–8·26 (2 H, d), 8·44 (2 H, s)). *2-(4-heptylphenyl)-5-ethoxypyrimidine* (95 per cent), ($T_{CI} = 80$·81°C; $T_{NI} = (68)$°C), (IR (KBr) v_{max}: 2955, 2923, 2851, 1609, 1577, 1546, 1447, 1288, 1043, 783 cm^{-1}), (MS m/z: 298 (M$^+$), 213, (C$_{13}$H$_{13}$N$_2$O$^+$)) 185, (C$_{11}$H$_9$N$_2$O$^+$)), (NMR (CDCl$_3$): 0·85–0·87 (3 H, overlapping peaks), 1·27–1·33 (8 H, overlapping peaks), 1·45–1·50 (2 H, t) 1·64 (2 H, t), 2·62–2·69 (2 H, t), 4·13–4·21 (2 H, q), 7·26–72·9 (2 H, d), 8·22–8·26 (2 H, d), 8·44 (2 H, s)), and *2-(4-octylphenyl)-5-ethoxypyrimidine* (59 per cent, ($T_{CI} = 79$–80°C; $T_{NI} = (60)$°C), (IR (KBr) v_{max}: 2973, 2953, 2921, 2851, 1577, 1546, 1448, 1289, 780 cm^{-1}), (MS m/z: 312 (M$^+$), 227, (C$_{14}$H$_{15}$N$_2$O$^+$), 213, (C$_{13}$H$_{13}$N$_2$O$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$)), (NMR (CDCl$_3$): 0·88 (3 H, overlapping peaks), 1·26 (10 H, overlapping peaks), 1·45–1·50 (2 H, t), 1·64 (2 H, t), 2·62–2·69 (2 H, t), 4·13–4·21 (2 H, q), 7·26–7·29 (2 H, d), 822–8·26 (2 H, d), 8·44 (2 H, s)) were prepared using the same procedure.

6.6. *2-(4-Nonylphenyl)-5-hydroxypyrimidine*

A solution of 2-(4-nonylphenyl)-5-ethoxypyrimidine (18·8 g, 0·058 mol), sodium hydroxide (23 g, 0·576 mol) and diethylene glycol was heated at 200°C for 13 h. The reaction solution was poured onto water (500 ml), acidified with 25 per cent hydrochloric acid and shaken with ethyl acetate (2 × 50 ml). The combined organic layers were washed with dilute sodium bicarbonate solution (2 × 50 ml), dried (MgSO$_4$), filtered and evaporated down. Recrystallization from ethyl acetate yielded 2-(4-nonylphenyl)-5-hydroxypyrimidine (11·7 g, 95 per cent); m.p., 140°C. IR (KBr) ν_{max}: 2925, 2853, 2717, 2668, 2577, 1606, 1544, 1432, 1286, 848 cm^{-1}. MS m/z: 298 (M$^+$), 199, (C$_{12}$H$_{11}$N$_2$O$^+$) 185, (C$_{11}$H$_9$N$_2$O$^+$). NMR (CDCl$_3$): 0·83–0·89 (3 H, overlapping peaks), 1·24 (12 H, overlapping peaks), 1·60 (2 H, t), 2·59–2·65 (2 H, t), 7·24–7·27 (2 H, d), 8·07–8·10 (2 H, d), 8·32 (2 H, s).

2-(4-Hexylphenyl)-5-hydroxypyrimidine (92 per cent), (m.p., 140–142°C), (IR (KBr) ν_{max}: 2926, 2853, 2717, 2668, 2577, 1608, 1544, 1432, 1286, 849 cm^{-1}), (MS m/z: 256 (M$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$)), NMR (CDCl$_3$): 0·84–0·89 (3 H, overlapping peaks), 1·24 (8 H, overlapping peaks), 1·62 (2 H, t), 2·59–2·65 (2 H, t), 7·24–7·27 (2 H, d), 8·07–8·10 (2 H, d), 8·32 (2 H, s)). *2-(4-Heptylphenyl)-5-hydroxypyrimidine* (82 per cent), (m.p., 147°C), (IR(KBr) ν_{max}: 3042, 3018, 2956, 2928, 2853, 2717, 2684, 2578, 1610, 1554, 1432, 1288, 849 cm^{-1}), (MS m/z: 270 (M$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$)), (NMR (CDCl$_3$): 0·84–0·86 (3 H, overlapping peaks), 1·26–1·28 (8 H, overlapping peaks), 1·62 (2 H, t), 2·59–2·66 (2 H, t), 7·24–7·28 (2 H, d), 8·09–8·13 (2 H, d), 8·36 (2 H, s)), and *2-(4-octylphenyl)-5-hydroxypyrimidine* (87 per cent), (m.p., 149°C), (IR (KBr) ν_{max}: 2925, 2853, 2716, 2680, 2575, 1609, 1553, 1432, 1287, 849 cm^{-1}), (MS m/z: 284 (M$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$)), (NMR (CDCl$_3$): 0·84–0·89 (3 H, overlapping peaks), 1·25 (10 H, overlapping peaks), 1·61 (2 H, t), 2·59–2·65 (2 H, t), 7·24–7·27 (2 H, d), 8·08–8·11 (2 H, d), 8·34 (2 H, s)) were prepared using the same procedure.

6.7. *2-(4-Hexylphenyl)-5-octyloxypyrimidine* (1)

A mixture of 1-bromooctane [Fluka] (0·46 g, 0·0034 mol), 2-(4-hexylphenyl)-5-hydroxypyrimidine (0·5 g, 0·002 mol), potassium carbonate (1·02 g, 0·0078 mol) and N,N-dimethylformamide (50 ml) was stirred at room temperature overnight, then filtered to remove inorganic material. The filtrate was diluted with water (1000 ml) and then shaken with diethyl ether (3 × 100 ml). The combined organic extracts were washed with water (2 × 500 ml), 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 recrystallization from ethanol to yield the pure ether (0·64 g, 89 per cent), $T_{C S_C} = 29°C$; $T_{S_C S_A} = 68°C$; $T_{S_A I} = 85°C$. IR (KBr) ν_{max}: 2924, 2854, 1577, 1546, 1439, 1282, 1015, 845, 786 cm^{-1}, MS m/z: 368 (M$^+$), 256 (C$_{16}$H$_{20}$N$_2$O$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$), NMR (CDCl$_3$): 0·88–0·89 (6 H, overlapping peaks), 1·31 (16 H, overlapping peaks), 1·64 (2 H, overlapping peaks), 1·83 (2 H, overlapping peaks), 2·62–2·68 (2 H, t), 4·06–4·11 (2 H, t), 7·26–7·29 (2 H, d), 8·22–8·26 (2 H, d), 8·44 (2 H, s). The liquid crystal transition temperatures of this ether (1) and similar ethers (8, 15, 22 and 85–112) prepared using this general method are collated in tables 1 and 4.

6.8. *2-(4-Hexylphenyl)-5-[(E)-2-octenyloxy]pyrimidine* (2)

A solution of diethyl azodicarboxalylate (0·44 g, 0·0025 mol) and tetrahydrofuran (10 ml) was added dropwise at 0°C and under an atmosphere of nitrogen to a solution of (E)-2-octen-1-ol [Johnson Matthey] (0·35 g, 0·0019 mol), 2-(4-hexylphenyl)-5-hydroxypyrimidine (0·5 g, 0·0018 mol), triphenylphosphine (0·66 g, 0·0025 mol) and

tetrahydrofuran (25 ml). The reaction solution was stirred at room temperature overnight. Several drops of aqueous hydrogen peroxide solution (30 per cent) were added and the reaction solution stirred for a further 20 min, washed twice with saturated sodium hydropyrite solution (20 ml), dried ($MgSO_4$) filtered and then evaporated down. The solid residue was taken up in warm hexane (25 ml), 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 recrystallization from ethanol yielded the pure ether (0·36 g, 50 per cent); $T_{CS_C} = 61°C$; $T_{S_CS_A} = 76°C$; $T_{S_AI} = 80°C$. IR (KBr) v_{max}: 2956, 2925, 1575, 1543, 1439, 1277, 999, 973, 847, 783 cm^{-1}. MS m/z: 366 (M$^+$), 256 ($C_{16}H_{20}N_2O^+$), 185, ($C_{11}H_9N_2O^+$). NMR (CDCl$_3$): 0·85–0·87 (6 H, overlapping peaks), 1·27–1·31 (14 H, overlapping peaks), 1·64 (2 H, t), 2·08–2·11 (2 H, q), 2·62–2·68 (2 H, t), 4·59–4·61 (2 H, d), 5·71–5·87 (2 H, overlapping peaks), 7·25–7·29 (2 H, d), 8·22–8·25 (2 H, d), 8·45 (2 H, s). The liquid crystal transition temperatures of this ether (**2**) and similar ethers (**9, 16, 23** and **29–56**) prepared using this general method are recorded in the tables 1 and 2.

6.9. *2-(4-Hexylphenyl)-5-[(Z)-3-octenyloxy]pyrimidine* (**3**)

A solution of diethyl azodicarboxalylate (0·44 g, 0·0025 mol) and tetrahydrofuran (10 ml) was added to a solution of (Z)-3-octen-1-ol [K and K Laboratories] (0·32 g, 0·0025 mol), 2-(4-hexylphenyl)-5-hydroxypyrimidine (0·5 g, 0·0019 mol), triphenylphosphine (0·66 g, 0·0019 mol) and tetrahydrofuran (25 ml) at 0°C under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature overnight and then worked up and purified as described above to yield the pure ether (0·34 g, 50 per cent); $T_{Cl} = 55°C$. IR (KBr) v_{max}: 2958, 2924, 1608, 1576, 1548, 1447, 1287, 856, 785 cm^{-1}. MS m/z: 366 (M$^+$), 256 ($C_{16}H_{20}N_2O^+$), 185, ($C_{11}H_9N_2O^+$). NMR (CDCl$_3$): 0·88–0·94 (6 H, overlapping peaks), 1·32–1·36 (10 H, overlapping peaks), 1·64 (2 H, t), 2·08 (2 H, d), 2·57–2·68 (2 H, overlapping peaks), 4·06–4·11 (2 H, t), 5·47–5·56 (2 H, overlapping peaks), 7·26–7·29 (2 H, d), 8·22–8·25 (2 H, d), 8·44 (2 H, s). The liquid crystal transition temperatures of this ether (**3**) and similar ethers (**10, 17** and **24**) prepared using this general method are collated in table 1.

6.10 *2-(4-Hexylphenyl)-5-[(E)-4-octenyloxy]pyrimidine* (**4**)

A solution of diethyl azodicarboxalylate (0·44 g, 0·0025 mol) and tetrahydrofuran (10 ml) was added to a solution of (E)-4-octen-1-ol [11] (0·32 g, 0·0025 mol), 2-(4-hexylphenyl)-5-hydroxypyrimidine (0·5 g, 0·0019 mol), triphenylphosphine (0·66 g, 0·0019 mol) and tetrahydrofuran (25 ml) at 0°C under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature overnight and then worked up and purified as described above to yield the pure ether (0·40 g, 56 per cent); $T_{CS} = 57°C$; $T_{S_CS_A} = 68°C$; $T_{S_AI} = 80°C$. IR (KBr) v_{max}: 2958, 2926, 1609, 1576, 1546, 1444, 1285, 1182, 966, 852 cm^{-1}. MS m/z: 366 (M$^+$), 256 ($C_{16}H_{20}N_2O^+$), 185, ($C_{11}H_9N_2O^+$). NMR (CDCl$_3$): 0·85–0·91 (6 H, overlapping peaks), 1·31–1·41 (8 H, overlapping peaks), 1·64 (2 H, t), 1·86–1·99 (4 H), 2·19 (2 H, t), 2·63–2·68 (2 H, t), 4·06–4·11 (2 H, t), 5·41–5·48 (2 H, overlapping peaks), 7·25–7·29 (2 H, d), 8·22–8·25 (2 H, d), 8·43 (2 H, s). The liquid crystal transition temperatures of this ether (**4**) and similar ethers (**11, 18** and **25**) prepared using this general method are given in table 1.

6.11. *2-(4-Hexylphenyl-5-[(Z)-5-octenyloxy]pyrimidine* (**5**)

A solution of diethyl azodicarboxalylate (0·44 g, 0·0025 mol) and tetrahydrofuran (10 ml) was added to a solution of (Z)-5-octen-1-ol [K and K Laboratories] (0·32 g,

0·0025 mol), 2-(4-hexylphenyl)-5-hydroxypyrimidine (0·5 g, 0·0019 mol), triphenyl-phosphine (0·66 g, 0·0019 mol) and tetrahydrofuran (25 ml) at 0°C under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature overnight and then worked up and purified as described above to yield the pure ether (0·40 g, 59 per cent); $T_{CS_C} = 45°C$; $T_{S_CS_A} = 52°C$; $T_{S_AI} = 55°C$. IR (KBr) ν_{max}: 2959, 2928, 1609, 1576, 1547, 1445, 1285, 851, 783 cm^{-1}. MS m/z: 366 (M$^+$), 256 (C$_{16}$H$_{20}$N$_2$O$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$). NMR (CDCl$_3$): 0·88–1·00 (6 H, overlapping peaks), 1·31 (6 H, overlapping peaks), 1·55–1·581 (4 H, overlapping peaks), 1·85 (2 H overlapping peaks), 2·05–2·14 (4 H, overlapping peaks), 2·62–2·68 (2 H, t), 4·06–4·12 (2 H, t), 5·36–5·40 (2 H), 7·26–7·29 (2 H, d), 8·22–8·25 (2 H, d), 8·43 (2 H, s). The liquid crystal transition temperatures of this ether (5) and similar ethers (12, 19 and 26) prepared using this general method are given in table 1.

6.12. 2-(4-Hexylphenyl)-5-[(E)-6-octenyloxy]pyrimidine (6)

A solution of diethyl azodicarboxalylate (0·44 g, 0·0025 mol) and tetrahydrofuran (10 ml) was added to a solution of (E)-6-octen-1-ol [12] (0·32 g, 0·0025 mol), 2-(4-hexylphenyl)-5-hydroxypyrimidine (0·5 g, 0·0019 mol), triphenylphosphine (0·66 g, 0·0019 mol) and tetrahydrofuran (25 ml) at 0°C under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature overnight and then worked up and purified as described above to yield the pure ether (0·42 g, 60 per cent); $T_{CS_C} = 45°C$; $T_{S_CS_A} = 50°C$; $T_{S_AI} = 85°C$. IR (KBr) ν_{max}: 2928, 2854, 1610, 1577, 1544, 1439, 1286, 966, 847, 783 cm^{-1}. MS m/z: 366 (M$^+$), 256 (C$_{16}$H$_{20}$N$_2$O$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$). NMR (CDCl$_3$): 0·88 (3 H, overlapping peaks), 1·31 (10 H, overlapping peaks), 1·64–1·66 (5 H, overlapping peaks), 1·83 (2 H overlapping peaks), 2·01 (2 H, overlapping peaks), 2·62–2·68 (2 H, t), 4·05–4·10 (2 H, t), 5·41–5·43 (2 H, overlapping peaks), 6·95–7·00 (2 H, d), 8·32–8·36 (2 H, d), 8·57 (2 H, s). The liquid crystal transition temperatures of this ether (6) and similar ethers (13, 20 and 27) prepared using this general method are recorded in table 1.

6·13. 2-(4-Hexylphenyl)-5-[7-octenyloxy]pyrimidine (7)

A mixture of 7-bromo-1-octene [Aldrich] (0·35 g, 0·0019 mol), 2-(4-hexylphenyl)-5-hydroxypyrimidine (0·5 g, 0·0019 mol), potassium carbonate (1·02 g, 0·0074 mol) and 2-butanone (25 ml) was heated under gentle reflux overnight, filtered to remove inorganic material and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent and recrystallization from ethanol to yield the pure ether (0·48 g, 68 per cent); $T_{CS_C} = 26°C$; $T_{S_CS_A} = 54°C$; $T_{S_AI} = 75°C$. IR (KBr) ν_{max}: 2927, 2851, 1641, 1607, 1584, 1543, 1428, 1253, 917, 851, 790 cm^{-1}. MS m/z: 366 (M$^+$), 256 (C$_{16}$H$_{20}$N$_2$O$^+$), 185, (C$_{11}$H$_9$N$_2$O$^+$). NMR (CDCl$_3$): 0·88 (3 H, overlapping peaks), 1·28–1·42 (15 H, overlapping peaks), 1·42–1·81 (2 H, t), 1·84–2·06 (2 H, q), 2·56–2·62 (2 H, t), 4·00–4·05 (2 H, t), 4·93–5·04 (2 H, d), 5·81–5·83 (1 H, overlapping peaks), 6·95–7·00 (2 H, d), 8·33–8·36 (2 H, d), 8·57 (2 H, s). The liquid crystal transition temperatures of this ether (7) and similar ethers (14, 21, 28 and 57–84) prepared using this general method are collated in tables 1 and 3.

7. Conclusions

Four homologous series of 2-(4-n-alkylphenyl)-5-(octenyloxy)pyrimidines (IV) have been prepared. The position and configuration (E/Z) of the double bond has been varied systematically and the effect on the liquid crystal transition temperatures studied. Higher smectic C and lower smectic A transition temperatures for compounds

with an (*E*)-2-substituted alkenyloxy chain were observed. The melting point is also higher. In contrast the melting point and other liquid crystal transition temperatures of the terminally substituted compounds are lower. However, the melting point is decreased more than the smectic C transition temperature. This results in relatively wide-range smectic C phases for both series. Surprisingly, no nematic phases could be observed for either series. However, in admixture with other smectic C components the new compounds lead to surprisingly fast switching times, high smectic C transition temperatures and low melting points/crystallization temperatures in mixtures designed for electro-optic display devices based on ferroelectric effects. Significantly lower transition temperatures (including the melting point) were observed for materials with a *cis*-double bond (*Z*) at an odd number of carbon atoms from the molecular core. A *trans*-double bond in position 4 and 6 leads to no change in the smectic C transition temperature for short chains. However, this transition temperature decreases dramatically with increasing chain length, while the melting point remains high. Thus, the smectic C phase range is narrow or non existent. Based on these results eight homologous series of the 2-(4-*n*-alkylphenyl)-5-(alkenyloxy)pyrimidines with a double bond in the (*E*)-2 and terminal position were synthesized and evaluated. Many of these new alkenyloxy ethers can be used to produce wide-range chiral smectic C mixtures with short response times for electro-optic display devices based on ferroelectric effects (FLCDs).

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