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Alkyl/alkenyloxy phenyl/biphenylpyrimidines: dependence of the liquid crystal transition temperatures on the position of the nitrogen atoms and the position and configuration of carbon–carbon double bonds

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The influence on the transition temperatures of a carbon–carbon double bond in the terminal alkenyloxy (ether) chain of four series of three-ring phenyl/biphenyl-pyrimidines has been systematically investigated. The position and configuration of the double bond has been varied systematically in order to determine the optimal configuration and conformation of the terminal chains for smectic C formation. Four positions of the two nitrogen atoms were chosen. This produced four isomeric series of pyrimidines and differences in the mesomorphic behaviour were observed. The dependence of the transition temperatures on chain length was studied for the same four isomeric pyrimidine series. Comparisons between the new three-ring phenyl/biphenyl-pyrimidines and the corresponding two-ring phenylpyrimidines revealed almost identical tendencies. These results are consistent with a linearly-extended conformation of the chain. Several of the new ethers exhibit remarkably low viscosity values (i.e. short response times) and wide switching angles in an optically active base mixture used for evaluation and comparison purposes. Hence they can be used to widen the temperature range of mixtures designed for electro-optic display devices based on ferroelectric effects (FLCDs) without leading to longer response times.

1. Introduction

As part of a systematic study of the relationship between molecular structure and smectic mesophases and their transition temperatures (especially the smectic C phase [1–16] for electro-optic display devices based on ferroelectric effects FLCDs [17–21]), a carbon–carbon double bond has been introduced into a wide variety of liquid crystal materials [1–16]. At first a carbon–carbon double bond was introduced in a terminal position or in a *cis*-(*Z*) configuration in the middle of an alkoxy chain of a wide variety of phenyl benzoates [1] and phenylpyrimidines [2] with a second optically active branched chain. They sometimes incorporated an additional 1,4-disubstituted phenyl or *trans*-1,4-disubstituted cyclohexane ring linked to the aromatic core either by a direct bond or a two-unit linking group [1–7], and later four-unit linking groups [5, 8]. In all cases, this led to an often not insubstantial decrease in the transition temperatures of all the observed mesophases. However, the melting point (T_m) was often decreased more than the smectic C transition temperature (T_{S_C}) leading to a broadening of the smectic C temperature range (sometimes at or just above room temperature). The viscosity (γ) was generally high due to the ester group and/or chain branching at the chiral centre leading to relatively long response times (τ) [4, 5, 8].

The effect on the transition temperatures of a *trans*-(*E*) carbon–carbon double bond in the propenyloxy linking group in a central position of a variety of mesogens was investigated [5]. No significant difference in the smectic transition temperatures from those of the analogous propyloxy linked compounds was observed. These compounds, containing a four-unit linking group, exhibiting a higher γ than that of corresponding materials containing either a direct linkage or the corresponding two-unit linking group [5].

The first attempt to introduce a *trans*-double bond into a terminal chain (attached to the *trans*-1,4-disubstituted cyclohexane ring of a three-ring benzoate ester) led to a modest increase in T_{S_C} [6] and no discernible difference in γ (corrected for a slightly larger tilt angle) [7]. More significant changes were observed for alkenyloxy-substituted phenylpyrimidines/pyridines [8–12], where the position and nature (*E*/*Z*) of the double bond were varied systematically. The *trans*-(*E*) carbon–carbon double bond at an even number of carbon atoms from the

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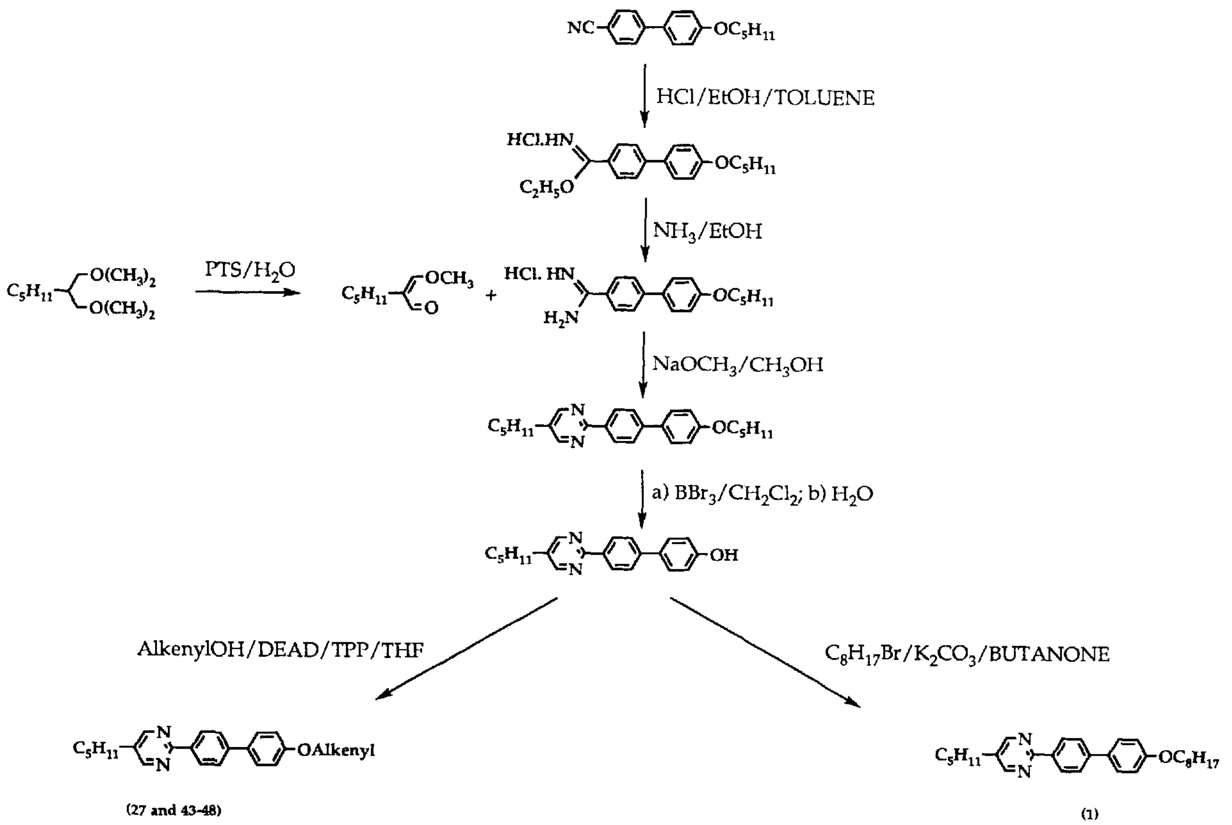
molecular core results generally in a higher T_{S_C}, lower smectic A transition temperatures (T_{S_A}), an increase in the tilt angle (θ) and spontaneous polarization (P_s), and in longer switching times (τ). A *cis*-double bond (*Z*) at an odd number of carbon atoms from the molecular core suppresses the nematic phase in favour of smectic phases, decreases θ and P_s and shortens τ. Other positional combinations strongly reduce the transition temperatures. These observations were related to a preferred configuration and conformation of the alkenyloxy chain [10]. However, the position and number of nitrogen atoms are also crucial in determining the type of phases observed and their temperature ranges.

As esters have often been found to exhibit lower γ and a higher T_{S_C} than ethers, phenylpyrimidinyl/pyridinyl esters were also studied [8]. The transition temperatures for each position of the double bond were lowered. An exception was found with the (*E*)-alken-2-enoates, which exhibited significant increases in the nematic transition temperature and, in admixture with smectic C materials, a high T_{S_C} and a low γ [13, 14].

Although significant differences between the trends observed for fully aromatic two-ring compounds and a three-ring model system incorporating one *trans*-1,4-disubstituted cyclohexane, one 1,4-disubstituted phenyl and one 2,5-disubstituted pyrimidine ring [15] were found, the latter also exhibited low γ and a relatively high T_{S_C}. For a number of related three-ring materials incorporating the *trans*-2,5-disubstituted dioxane ring and the biphenyl moiety, as well as a carbon–carbon double bond [16], T_m was either increased or stayed approximately the same, while the smectic C temperature range was often narrower due to the induction of an ordered smectic phase at a high temperature.

We now report the results of an investigation of the effect of a carbon–carbon double bond on the mesomorphic behaviour of ethers with a fully aromatic core (i.e. two benzene rings and one pyrimidine ring) in order to determine the effect of replacing the aliphatic, flexible cyclohexane or dioxane ring with the aromatic, rigid phenyl ring. This also offers the possibility of studying the effect of the position of the dipoles due to the nitrogen and oxygen atoms, as well as of the conformation of the terminal chains on the liquid crystal behaviour. This is of relevance to an understanding of the smectic C phase [22–27]. Although the thermal data for a wide variety of phenyl/biphenylpyrimidines are to be found in the literature [28–33], no systematic study of this kind has been undertaken to the authors' knowledge. The compounds are also important due to the wide variety of smectic



Scheme 1.

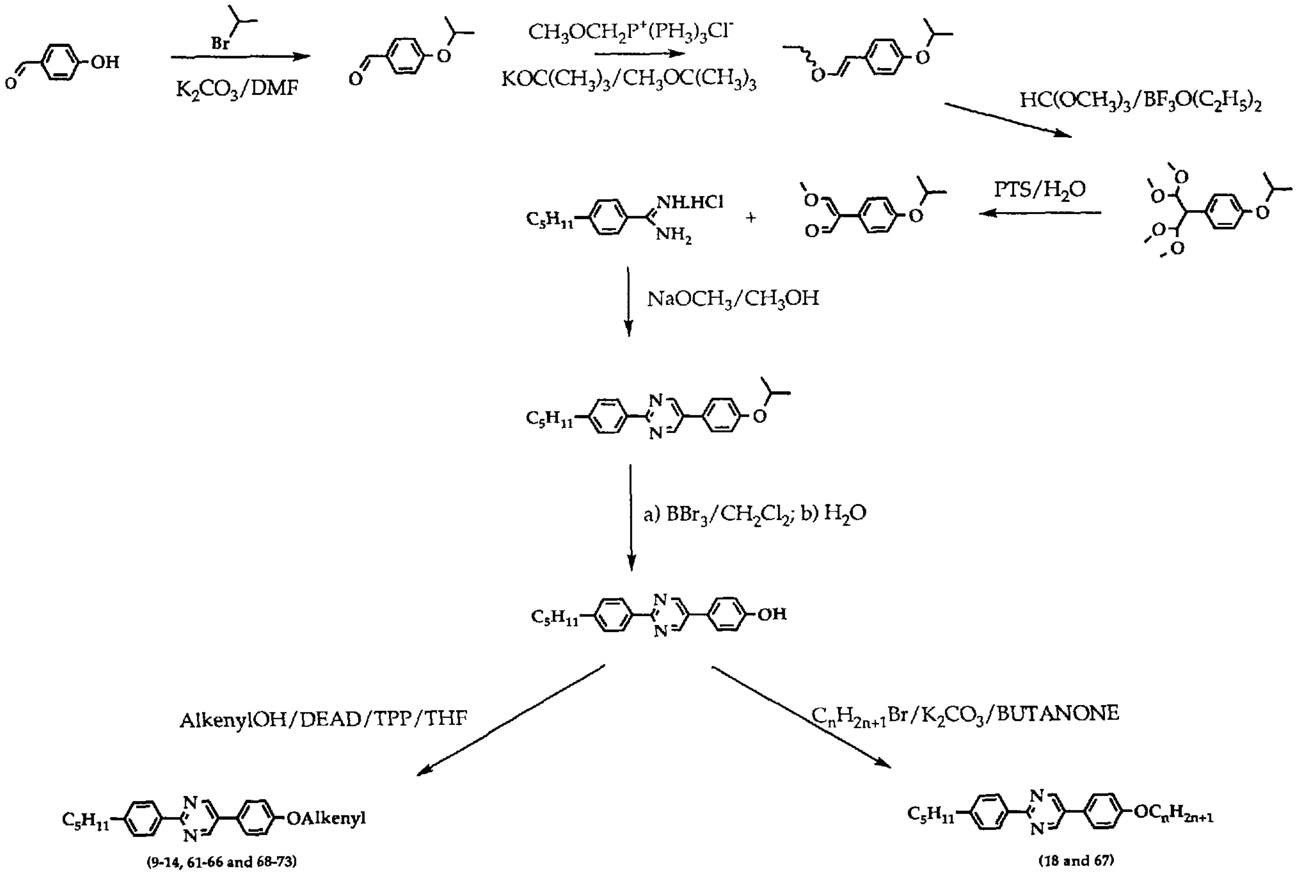
modifications they exhibit (for example, 2-(4-pentylphenyl)-5-(4-pentyloxyphenyl)pyrimidine is a standard for binary miscibility studies for smectic mesophase identification [28]).

2. Synthesis

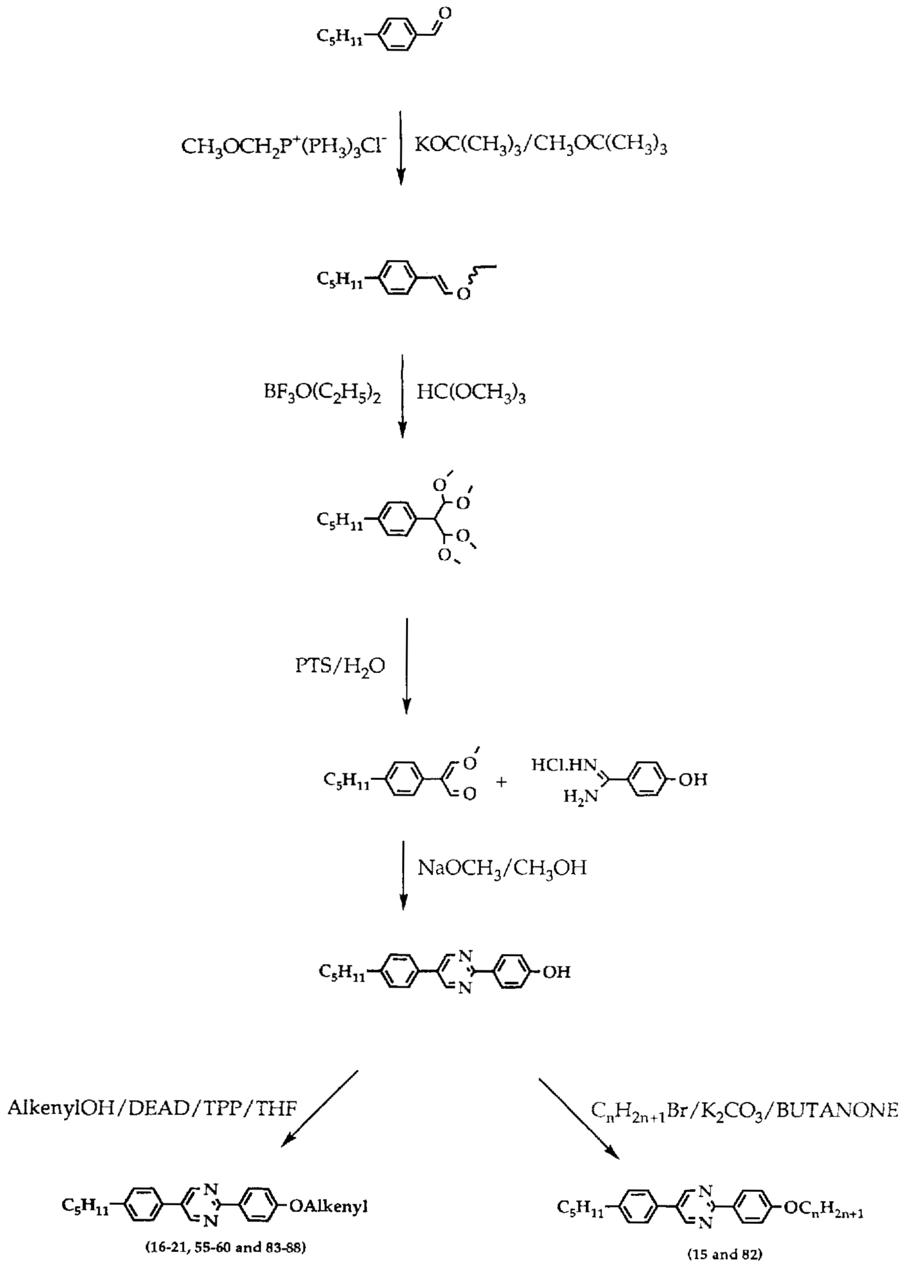
The 2-(4-octyloxybiphenyl-4′-yl)-5-pentylpyrimidine (**1**) and the 2-(4-alkenyloxybiphenyl-4′-yl)-5-pentylpyrimidines (**2**–**7** and **43**–**48**) were synthesized as depicted in reaction scheme 1. 4-Cyano-4′-pentyloxybiphenyl [34] was converted in the usual way [35–37] with ethanolic hydrogen chloride to the corresponding benzimidoethyl ether hydrochloride and then with ammonia to the corresponding benzimidamide hydrochloride. Condensation with (2-methoxymethylidene)heptanal prepared *in situ* from the corresponding tetramethyl acetal in the usual way [35–37] yielded 2-(4-pentyloxybiphenyl-4′-yl)-5-pentylpyrimidine. The pentyloxy group attached to the benzene ring was removed with boron tribromide [38]. Alkylation of the resultant phenol with bromo-octane in a Williamson ether synthesis yielded the reference compound (**1**). Alkylation in Mitsunobu reactions [39] with the appropriate alken-1-ols [9], incorporating a carbon–carbon double bond of a defined configuration (*E*/*Z*) at various positions in the chain, yielded the desired ethers (**2**–**7** and **43**–**48**).

The pathway shown in reaction scheme 2 was used to prepare the reference 2-(4-pentylphenyl)-5-(4-octyloxyphenyl)pyrimidine (**8**) and the 2-(4-pentylphenyl)-5-(4-alkenyloxyphenyl)pyrimidines (**9**–**14**, **49**–**54** and **67**–**73**). Commercially available 4-hydroxybenzaldehyde was alkylated with isopropyl bromide. A Wittig reaction with methoxymethyltriphenylphosphonium chloride [40] yielded the corresponding enol ether, which was converted with trimethyl orthoformate into a tetramethyl acetal. Condensation as usual with 4-pentylbenzimidamide hydrochloride [35, 37] yielded 2-(4-pentylphenyl)-5-(4-isopropyloxyphenyl)pyrimidine, which was dealkylated with boron tribromide and subsequently alkylated with bromo-octane and the same alkenols as above to yield the ethers (**8**) and (**9**–**14**, **49**–**54** and **67**–**73**).

The reference 2-(4-octyloxyphenyl)-5-(4-pentylphenyl)pyrimidine (**15**) and the 2-(4-alkenyloxyphenyl)-5-(4-pentylphenyl)pyrimidines (**16**–**21**, **55**–**60** and **83**–**88**) were prepared as shown in reaction scheme 3. Commer-



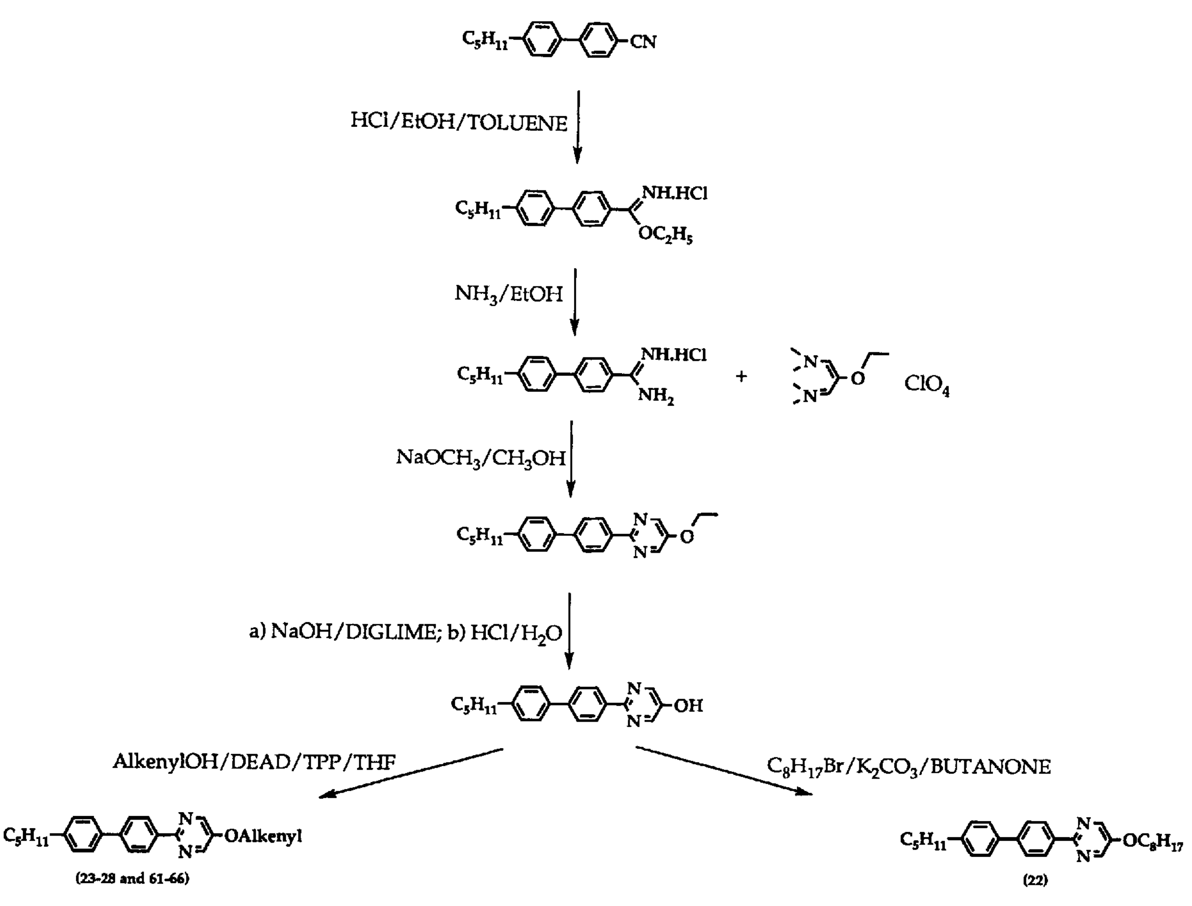
Scheme 2.



Scheme 3.

cially available 4-pentylbenzaldehyde was converted via a Wittig reaction with methoxymethyltriphenylphosphonium chloride [40] to the corresponding enol ether; then treatment with trimethyl orthoformate gave the corresponding tetramethyl acetal. Condensation as usual with 4-hydroxybenzimidamide hydrochloride [35, 37] yielded 4-[5-(4-pentylphenyl)pyrimidin-2-yl]phenol, which was alkylated as usual with bromo-octane and the same alkenols as above to yield the ethers (**15**) and (**16–21**, **55–60** and **83–88**).

The synthesis of 2-(4-pentylbiphenyl-4′-yl)-5-octyloxypyrimidine (**22**) and the 2-(4-pentylbiphenyl-4′-yl)-5-alkenyloxypyrimidines (**23–28** and **61–66**) is shown in reaction scheme 4. 4-Cyano-4′-pentylbiphenyl [34] is converted via the benzimidoethyl ether hydrochloride into the corresponding benzimidamide hydrochloride as described above. Condensation with 1,3-bis(dimethylamino)-2-ethoxytrimethium perchlorate [41] yielded the 2-(4-pentylbiphenyl-4′-yl)-5-ethoxypyrimidine, which was dealkylated [12, 16] with sodium hydroxide at 200°C to yield the corresponding phenol, alkylation of which, as above, gave the reference octyloxy-substituted ether (**22**)



Scheme 4.

and the desired alkenyloxy-substituted ethers (**23–28** and **61–66**).

3. Mesomorphic properties

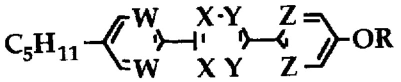
3.1. *Nitrogen atoms and double bonds*

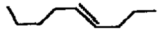
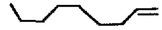
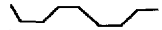
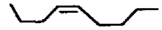
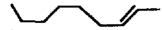
The effect of varying the position of the nitrogen atoms (*W*, *X*, *Y* and *Z*) and the position and configuration of the carbon–carbon double bond on the transition temperatures of four reference octyloxy-substituted three-ring phenyl/biphenylpyrimidines (**1**, **8**, **15** and **22**) and the corresponding octenyloxy-substituted ethers (**2–7**, **9–14**, **16–21** and **23–28**) is shown in table 1. The octenyloxy-substituted pyrimidines are constitutional isomers differing only in the position of the double bond and/or the two nitrogen atoms. In accordance with the results obtained for the corresponding two-ring phenylpyrimidines [10–12], the configuration at the olefinic double bond is alternately *trans* and *cis* (*E* and *Z*). 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. As the terminal chains are identical for all four series, observed differences in the average values for the transition temperatures must be due to the different positions of the nitrogen atoms (i.e. the pyrimidine rings).

The octenyloxy ethers (**3**, **5** and **7**) of the first isomer series (**2–7**) with either a *cis*- or a terminal double bond exhibit a lower (− 11°C, on average) T_C (N–I) than the reference octyloxy-substituted ether (**1**) without a double bond in the chain. T_C for the ethers (**2**, **4** and **6**) with a *trans*-double bond is higher (+ 2·5°C, on average). This is similar to the behaviour observed for the analogous two-ring ethers (i.e. 2-(4-octenyloxyphenyl)-5-alkylpyrimidines [9]). However, T_{S_C} is higher (+ 10°C, on average) for four ethers (**2–5**) (including the two *cis*-substituted ethers) than that of the reference ether (**1**), while two (**6** and **7**) give lower values. This behaviour is unusual. For all the two ring phenylpyrimidines studied, T_{S_C} was always considerably lower for the *cis*-substituted ethers. The fact that only two ethers (**3** and **4**) exhibit an (as yet unidentified) ordered crystal smectic phase is also unusual.

The first series of isomers with the pyrimidine ring in a central position (**9–14**) all exhibit a high T_{S_A} above a smectic C and an ordered phase, also at high temperatures. T_m is low due to the presence of the ordered phase. Thus, the displacement of the two nitrogen atoms from a

Table 1. The transition temperatures (in °C) for the ethers (**1**–**28**).



Ether	W	X	Y	Z		R	Cr–S	S_F–S_C	S_C–S_A/N	S_A–N/I	N–I
1	N	CH	CH	CH			91	—	114	—	183
2	N	CH	CH	CH	(E)		116	—	130	—	187
3	N	CH	CH	CH	(Z)		71	105	117	—	167
4	N	CH	CH	CH	(E)		70	117	125	—	186
5	N	CH	CH	CH	(Z)		100	—	122	—	172
6	N	CH	CH	CH	(E)		98	—	107	—	184
7	N	CH	CH	CH			85	—	109	—	178
8	CH	N	CH	CH			69	129	172	205	—
9	CH	N	CH	CH	(E)		58	136	173	211	—
10	CH	N	CH	CH	(Z)		65	127	169	185	—
11	CH	N	CH	CH	(E)		85	146	168	210	—
12	CH	N	CH	CH	(Z)		52	125	174	192	—
13	CH	N	CH	CH	(E)		55	129	143	205	—
14	CH	N	CH	CH			60	123	162	200	—
15	CH	CH	N	CH			80	—	85	195	—
16	CH	CH	N	CH	(E)		80	—	148	192	195
17	CH	CH	N	CH	(Z)		69	—	80	184	—
18	CH	CH	N	CH	(E)		77	—	81	196	—
19	CH	CH	N	CH	(Z)		64	—	82	187	—
20	CH	CH	N	CH	(E)		74	—	—	190	194
21	CH	CH	N	CH			72	—	—	190	—
22	CH	CH	CH	N			98	—	159	—	187
23	CH	CH	CH	N	(E)		99	—	161	—	185
24	CH	CH	CH	N	(Z)		87	—	137	—	166
25	CH	CH	CH	N	(E)		94	—	166	—	188
26	CH	CH	CH	N	(Z)		80	—	140	—	173
27	CH	CH	CH	N	(E)		105	—	165	—	188
28	CH	CH	CH	N			95	—	151	159	183

peripheral position in the ethers (**1**–**7**) to a central position in the ethers (**8**–**14**) results in an increase in the transition temperatures for the ordered, crystal and smectic C phases. The nematic phase is completely replaced by a smectic A phase, while T_m is lower. The dependence of T_{S_C} on the position and nature of the double bond is not the same for both series. Only two isomers (**9** and **12**) show a (marginally) higher T_{S_C}. The other ethers (**10**, **11**, **13**, and **14**) exhibit a low T_{S_C} (for example, the decrease (− 29°C) in T_{S_C} for the ether (**13**) with an (E-oct-2-enyloxy chain is much greater than that (− 7°C) observed for the corresponding ether (**6**) of the first series).

Displacing the two nitrogen atoms within the ring to produce the ethers (**15**–**21**) results in the disappearance of the ordered smectic phase and the smectic C phase or at least a significantly lower T_{S_C} for the reference ether (**15**) and for most of the alkenyloxy-substituted ethers. The difference between the T_{S_C} of these ethers and that of the (E)-oct-2-enyloxy-substituted ether (**16**) is very substantial. This behaviour is most unusual and not consistent with that exhibited by the other three series or any two-ring phenylpyrimidines [8–10].

Moving the two nitrogen atoms one ring further to produce the pyrimidines (**22**–**28**) restores T_{S_C} to high values. T_m is higher and the smectic A phase has been replaced by a nematic phase, while no ordered phase could be observed (at least above the recrystallization temperature). The ethers (**23**, **25** and **27**) with a *trans*-double bond exhibit a higher T_{S_C} (only + 5°C, on average) than the reference ether (**22**), while those with a *cis*-double bond or one in a terminal position exhibit lower values (− 16°C, on average).

Thus, for all four series studied (**1**–**7**, **2**–**8**, **9**–**15** and **22**–**28**) different trends in the dependence of the transition temperatures on the position and nature of the carbon–carbon double bond have been observed, although the octenyloxy chain is the same for each isomer series and the same manipulations have been made. This must be due to dipole–dipole interactions, as the configurations of the chains are identical for each series.

A terminal position of the pyrimidine ring favours the nematic phase, while a central position induces a smectic A phase. When the nitrogen atoms in the central pyrimidine ring point away from the alkoxy/alkenyloxy chain, then all smectic phases are favoured. When the nitrogen atoms in the central pyrimidine ring point towards the alkoxy/alkenyloxy chain, then the smectic C phase is destabilized.

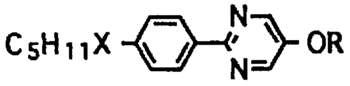
3.2. *Aliphatic/aromatic rings and double bonds*

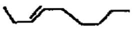
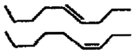
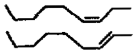
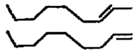
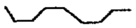
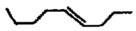
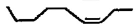
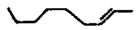
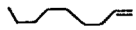
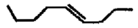
The effect of replacing four of the conformally flexible methylene units ($X = C_4H_8$) of the octyloxy/octenyloxy substituted two-ring phenylpyrimidines (**29–35**) [12] by the equally long, but more voluminous and relatively rigid *trans*-1,4-disubstituted cyclohexane ring ($X = C_6H_{10}$) to produce the three-ring ethers (**36–42**) [15] is shown in table 2. The salient feature of the results is the substantial increase in T_m and T_{S_C}. An ordered crystal smectic phase (as yet not identified) is observed for the octyloxy-substituted ether (**36**). Only two octenyloxy-substituted ethers (**41** and **42**) exhibit a smectic A phase, compared to all the isomers of the two-ring ethers), while two others (**36** and **37**) possess a nematic phase instead of the smectic A phase. One ether (**38**) with a *cis*-double bond is not mesomorphic (the corresponding two-ring ether (**31**) exhibits a smectic A phase).

If the aliphatic, conformationally relatively rigid *trans*-1,4-disubstituted cyclohexane ring ($X = C_6H_{10}$) in the ethers (**36–42**) is replaced by the much more rigid 1,4-disubstituted benzene ring ($X = C_6H_4$) of almost identical rotation volume to yield the fully-aromatic ethers (**22–28**), this leads generally to increases in all the transition temperatures. The temperature range of the smectic C phase is also broader. However, as already noted above, the ethers (**23**, **25** and **27**) with a *trans*-double bond possess a higher T_{S_C} (+ 5°C, on average) than that of the reference ether (**22**). The opposite is true (− 16°C, on average) for the *cis*-substituted ethers (**24** and **26**) and the terminally substituted ether (**28**). This does not correlate exactly with that observed for the two-ring phenylpyrimidines (**29–35**). The smectic A phase of the two-ring phenylpyrimidines (**29–35**) is replaced by a broad nematic phase (except for one isomer) for the corresponding three-ring biphenylpyrimidines (**22–28**).

Thus, although the relationship between chemical structure and smectic C phase transition temperatures is very complex for individual positions of the double bond, the rigidity and aromaticity of ring systems is seen,

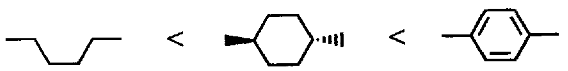
Table 2. The transition temperatures (in °C) for the two-ring ethers (**29–35**) and three-ring ethers (**36–42** and **22–28**).



Ether	*X*		*R*	Cr–S/I	S_F–S_C	S_C–S_A/N/I	S_A–N/I	N–I	Reference
29	$-C_4H_8-$			36	—	53	85	—	[9]
30	$-C_4H_8-$	(*E*)		56	—	65	82	—	[9]
31	$-C_4H_8-$	(*Z*)		52	—	—	(44)	—	[9]
32	$-C_4H_8-$	(*E*)		47	—	52	82	—	[9]
33	$-C_4H_8-$	(*Z*)		38	—	44	58	—	[9]
34	$-C_4H_8-$	(*E*)		51	—	—	86	—	[9]
35	$-C_4H_8-$			34	—	38	77	—	[9]
36	$-C_6H_{10}-$			65	83	119	—	181	[15]
37	$-C_6H_{10}-$	(*E*)		97	—	115	—	176	[15]
38	$-C_6H_{10}-$	(*Z*)		93	—	—	—	—	[15]
39	$-C_6H_{10}-$	(*E*)		87	—	93	—	—	[15]
40	$-C_6H_{10}-$	(*Z*)		86	—	95	—	—	[15]
41	$-C_6H_{10}-$	(*E*)		81	—	111	130	—	[15]
42	$-C_6H_{10}-$			67	—	96	121	—	[15]
22	$-C_6H_4-$			98	—	159	—	187	
23	$-C_6H_4-$	(*E*)		99	—	161	—	185	
24	$-C_6H_4-$	(*Z*)		87	—	137	—	166	
25	$-C_6H_4-$	(*E*)		94	—	166	—	188	
26	$-C_6H_4-$	(*Z*)		80	—	140	—	173	
27	$-C_6H_4-$	(*E*)		105	—	165	—	188	
28	$-C_6H_4-$			95	—	151	159	183	

Parentheses denote a monotropic transition temperature.

in general, to increase the tendency for smectic C formation:



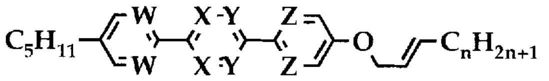
3.3. (*E*)-*Alk-2-enyloxy-substituted pyrimidines*

The effect on the transition temperatures of varying the position of the nitrogen atoms of four short homologous series ($n = 3$–9) of (*E*)-alk-2-enyloxy-substituted pyrimidines (**2** and **43–48**; **9** and **49–54**; **26** and **55–60**; **23** and **61–66**), which are otherwise identical, is shown in table 3. These series eliminate differences in the transition temperatures due to the terminal chains and allow a valid comparison to be made. All four series exhibit a similar dependence of transition temperature on the length of the (*E*)-alk-2-enyloxy chain (i.e., T_m and T_C[S$_A$–I or *N*–I]) decrease and T_{S_C} increases with increasing number (*n*) of methylene units (CH$_2$) in the terminal chain).

The displacement of the nitrogen atoms from the first phenyl ring to the phenyl ring in the middle of the molecule to produce the ethers (**9** and **49–54**) results in an increase in all the liquid crystal transition temperatures. T_{S_C} and T_C are both higher (+55°C and +38°C, on average, respectively), although the nature of the highest temperature mesophases is not the same (smectic A and nematic). Although T_m is lower (−36°C, on average) an ordered smectic phase (not as yet identified) is observed at a high temperature (139°C, on average). Thus, the temperature range of the smectic C phase is only increased marginally (+4°C, on average), despite the much higher T_{S_C}.

The displacement of the two nitrogen atoms within the central ring to yield the ethers (**16** and **55–60**) results in a lower T_m (−9°C, on average) and lower smectic C and smectic A temperatures (−26°C and −16°C, on average,

Table 3. Transition temperatures (in °C) for the ethers (**2**, **43–48**; **9**, **49–54**; **16**, **55–60** and **23**, **61–66**).



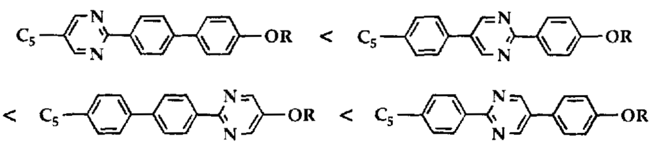
(E)

Ether	*W*	*X*	*Y*	*Z*	*n*	Cr–S$_F$/S$_C$/N	S$_F$–S$_C$	S$_C$–S$_A$/N	S$_A$–S$_C$/N	N–I
43	N	CH	CH	CH	3	124	—	—	—	196
44	N	CH	CH	CH	4	119	—	128	—	188
2	N	CH	CH	CH	5	116	—	130	—	187
45	N	CH	CH	CH	6	104	—	133	—	180
46	N	CH	CH	CH	7	103	—	134	—	178
47	N	CH	CH	CH	8	93	—	134	—	172
48	N	CH	CH	CH	9	89	—	134	—	169
49	CH	N	CH	CH	3	107	—	147	219	—
50	CH	N	CH	CH	4	100	—	171	215	—
9	CH	N	CH	CH	5	58	136	173	211	—
51	CH	N	CH	CH	6	48	140	180	206	—
52	CH	N	CH	CH	7	63	142	179	204	—
53	CH	N	CH	CH	8	58	139	178	201	—
54	CH	N	CH	CH	9	62	139	176	198	—
55	CH	CH	N	CH	3	94	—	152	197	203
56	CH	CH	N	CH	4	94	—	144	194	196
16	CH	CH	N	CH	5	80	—	148	192	195
57	CH	CH	N	CH	6	80	—	144	192	—
58	CH	CH	N	CH	7	77	—	145	190	—
59	CH	CH	N	CH	8	72	—	140	187	—
60	CH	CH	N	CH	9	74	—	137	185	—
61	CH	CH	CH	N	3	131	—	144	—	195
62	CH	CH	CH	N	4	100	—	151	—	187
23	CH	CH	CH	N	5	99	—	161	—	185
63	CH	CH	CH	N	6	100	—	164	—	179
64	CH	CH	CH	N	7	106	—	168	—	177
65	CH	CH	CH	N	8	109	—	169	—	173
66	CH	CH	CH	N	9	108	—	170	—	172

respectively). A narrow nematic phase is observed for three homologues.

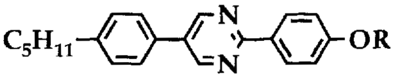
A further transfer of the two nitrogen atoms into the terminal ring bearing the alkoxy chain to produce the ethers (**23** and **61–66**) results in an increase in T_m and T_{S_C} ($+46°C$ and $+15°C$, on average, respectively). The clearing point is lower ($-9°C$, on average). An ordered smectic phase or a smectic A phase could not be observed. Thus, the thermal range of the smectic C phase is relatively large (53°C, on average) and comparable with that (64°C, on average) of the first ether series (**16** and **55–60**) with the nitrogen atoms in a central position, and about double that (24°C and 29°C, on average, respectively) for the other ether series (**2** and **43–48**; **9** and **49–54**).

All four series of (*E*)-alk-2-enyloxy-substituted pyrimidines (**2** and **43–48**; **9** and **49–54**); **16** and **55–60**; **23** and **61–66**) exhibit high smectic C transition temperatures (134°C, 172°C, 146°C, 161°C, on average, respectively). This is in contrast to the low T_{S_C} observed for the pyrimidines (**15–21**) either without a double bond or with the double bond in a different position (see table 1). The order of increasing T_{S_C} is as follows:



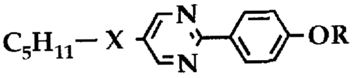
This indicates that the dipoles due to the two nitrogen

Table 4. Transition temperatures (in °C) for the ethers (**49** and **67–73**).



Ether	*R*	Cr–CrS$_5$/CrG/S$_C$	CrS$_5$–CrG	CrG–S$_F$	S$_F$–S$_C$	S$_C$–S$_A$	S$_A$–I
67	Hexyl	57	65	99	117	154	211
49	(*E*)-Hex-2-enyl	107	—	—	—	147	219
68	(*Z*)-Hex-2-enyl	96	—	—	—	116	128
69	(*E*)-Hex-3-enyl	85	—	—	—	144	170
70	(*Z*)-Hex-3-enyl	74	—	118	130	165	197
71	(*E*)-Hex-4-enyl	64	78	80	98	126	217
72	(*Z*)-Hex-4-enyl	85	—	96	114	153	182
73	Hex-5-enyl	61	—	94	116	153	206

Table 5. The transition temperatures (in °C) for the hexyl- and hexenyl-substituted two-ring ethers (**74–81**) and three-ring ethers (**55** and **82–88**).



Ether	*X*	*R*	Cr–S$_C$/S$_A$	S$_C$–S$_A$	S$_A$–N/I	N–I	Reference
74	$-C_4H_8-$	Hexyl	33	48	71	72	[10]
75	$-C_4H_8-$	(*E*)-Hex-2-enyl	49	63	70	72	[9, 10]
76	$-C_4H_8-$	(*Z*)-Hex-2-enyl	32	—	(17)	—	[10]
77	$-C_4H_8-$	(*E*)-Hex-3-enyl	26	—	42	—	[10]
78	$-C_4H_8-$	(*Z*)-Hex-3-enyl	58	(41)	(56)	—	[9, 10]
79	$-C_4H_8-$	(*E*)-Hex-4-enyl	48	(35)	70	72	[10]
80	$-C_4H_8-$	(*Z*)-Hex-4-enyl	22	—	46	—	[10]
81	$-C_4H_8-$	5-Hexenyl	48	—	62	—	[9, 10]
82	$-C_6H_4-$	Hexyl	82	110	198	201	
55	$-C_6H_4-$	(*E*)-Hex-2-enyl	94	152	197	203	
83	$-C_6H_4-$	(*Z*)-Hex-2-enyl	76	—	156	—	
84	$-C_6H_4-$	(*E*)-Hex-3-enyl	83	(63)	176	—	
85	$-C_6H_4-$	(*Z*)-Hex-3-enyl	84	112	190	191	
86	$-C_6H_4-$	(*E*)-Hex-4-enyl	92	—	195	204	
87	$-C_6H_4-$	(*Z*)-Hex-4-enyl	65	68	180	—	
88	$-C_6H_4-$	Hex-5-enyl	73	99	193	194	

Parentheses denote a monotropic transition temperature.

atoms and the oxygen atom should be opposed (i.e. $\Delta\varepsilon \approx 0$) for high T_{S_C} values. This is in crude agreement with theories of the smectic C phase, which postulate that the C phase is favoured by the presence of opposed terminal outboard dipoles [22–27]. This is consistent with the order of increasing T_{S_C} for the corresponding two-ring systems:

3.4. *Conformation of the terminal chains*

The totally smectic nature (S_F S_C and S_A) and high transition temperatures of the ethers (**8–14**) and (**49–54**) with a pyrimidine ring in a central position rendered this series ideal for an investigation of the dependence of the nature and transition temperatures of the smectic phases on the conformation (as determined by the configuration) of the terminal chain, see table 4. The configuration at each position of the double bond in the hexenyloxy chain of the ethers (**67–73**) is (*E*) and (*Z*). There is a clear correlation between T_c (S_A–I) and an odd–even effect for both the *cis*- and *trans*-double bonds. This is consistent with a linearly extended conformation of the chain. This model is also almost applicable to the smectic C (except for the ethers (**71** and **72**) with the double bond in position 4) and to a lesser extent the other smectic phases observed.

This is shown more completely in table 5 and figures 1 and 2, where a comparison between the transition temperatures of similar two-ring phenylpyrimidines (**74–81**) [10] and three-ring phenylpyrimidines (**55** and **82–88**) with a terminal hexyloxy or hexenyloxy chain is possible. T_c (S_A–I or N–I) or both series conform to the odd–even, linearly extended model (i.e. the chain is not fully extended in an all *trans*-conformation, but is alternately *cis* and *trans* in order to form a linearly

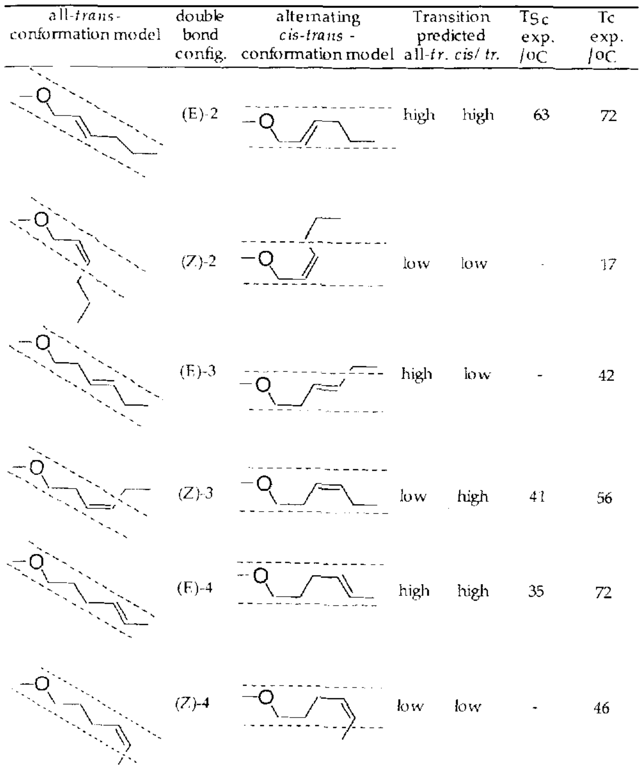


Figure 1. Two possible notations that model the conformations of the hexenyloxy chain of the two-ring ethers (**75–80**): on the left the all-*trans*-conformation leads, for every position of the double bond, to the straightest chain and the highest smectic C transition temperature T_{S_C} (S_C–S_A) and clearing point T_c (S_A–I or N–I). The alternating *cis–trans*-notation also predicts higher values for T_{S_C} and T_c for the (*Z*)-hex-3-enyloxy-substituted ether (**78**) than for the (*E*)-hex-3-enyloxy-substituted ether (**77**) as is observed experimentally (see also table 5).

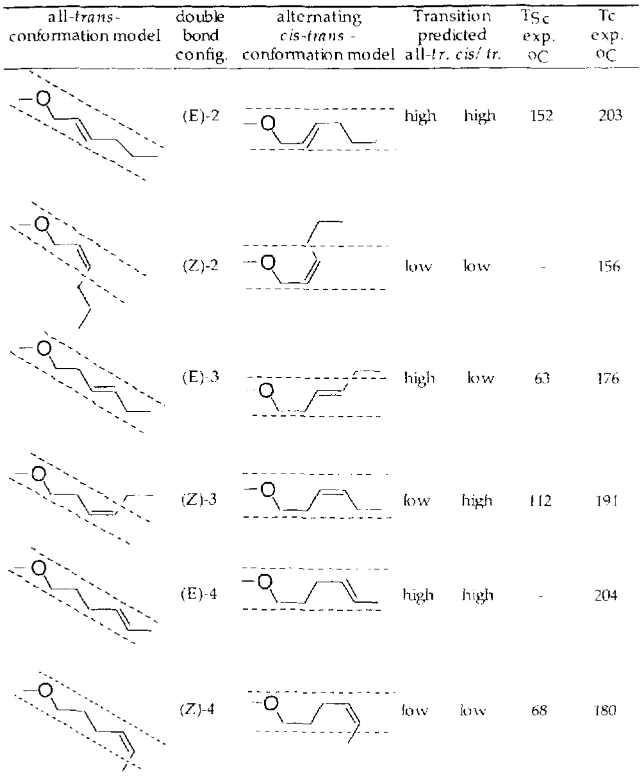
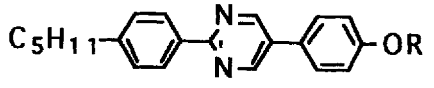


Figure 2. Two possible notations that model the conformations of the hexenyloxy chain of the three-ring ethers (**55** and **83–87**): on the left the all-*trans*-conformation leads, for every position of the double bond, to the straightest chain and the highest smectic C transition temperature T_{S_C} (S_C–S_A) and clearing point T_C (S_A–I or N–I). The alternating *cis–trans*-notation also predicts higher values for T_{S_C} and T_c for the (*Z*)-hex-3-enyloxy-substituted ether (**85**) than for the (*E*)-hex-3-enyloxy-substituted ether (**84**) as is observed experimentally (see also table 5).

Table 6. The liquid crystal transition temperatures (in °C), spontaneous polarizations and response times for a series of mixtures consisting of 15 wt % of the ethers (**49**, **67–73**).



Ether	*R*	S_C^*–S_A	S_A–N*/I	N*–I	P_s/nC cm^{-2}	τ/µs
67	Hexyl	63·9	83·2	—	14·5	96
49	(*E*)-Hex-2-enyl	67·9	84·5	—	16·0	122
68	(*Z*)-Hex-2-enyl	63·1	72·8	79·5	18·4	121
69	(*E*)-Hex-3-enyl	65·2	78·8	84·1	18·5	117
70	(*Z*)-Hex-3-enyl	69·4	82·0	86·4	17·9	110
71	(*E*)-Hex-4-enyl	65·0	81·1	85·3	17·6	119
72	(*Z*)-Hex-4-enyl	61·1	82·9	—	15·0	98
73	Hex-5-enyl	63·0	83·2	—	15·8	99

extended chain in the axis of the molecule), see figures 1 and 2. This is consistent with the concept that liquid crystal formation is favoured by a linear rod-like shape. According to this model there should be no large differences in the transition temperatures of hexyloxy- and (*E*-hex-2-enyloxy-substituted compounds (**74** and **75**; **55** and **83**) and this is indeed observed to be the case. The alternating *cis–trans* notation also predicts higher values for T_c for the (*Z*)-hex-3-enyloxy-substituted ethers (**78** and **85**) than for the (*E*)-hex-3-enyloxy-substituted ethers (**77** and **84**) as is observed experimentally (see also table 5). However, this linearly-extended conformation also appears strongly to promote S_C formation. This dependency decreases as the double bond is moved further away from the core of the molecule, perhaps due to induced dipole–dipole interactions and non-linear conformations. The orders of increasing T_c and T_{S_C} for both the two- and three-ring pyrimidines are almost identical, i.e. for T_c: (*Z*)-2 < (*E*)-3 < (*Z*)-4 < (*Z*-3 < (*E*)-4 ≈ (*E*)-2 and for T_{S_C} (*Z*)-2 ≈ (*E*)-3 ≈ (*Z*)-4 < (*E*)-4 ≈ (*Z*)-3 < (*E*)-2. This is a surprisingly consistent picture and is not always apparent for other series (see tables 1–4).

4. Physical properties in mixtures

In order to investigate the suitability of the ethers (**1–88**) as non-optically active components of S_C^* mixtures for electro-optic display device applications based on ferroelectric effects (SSFLCDs, DHFLCDs and SBFLCDs) a fixed amount (15 wt %) was dissolved in a standard S_C^* mixture (SCO 1014; S_C^*–S_A = 60·6°C, S_A–N* = 67·7°C and N*–I = 74·6°C; see the Experimental section). The transition temperatures (S_C^*–S_A, S_C^*–N*, S_A–N*, S_A–I and N*–I), P_s and 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).

The effect of the position and configuration of the double bond in the ethers (**49** and **67–73**) on the transition temperatures, P_s and τ is shown in table 6. The same dependence of the transition temperatures of the mixtures on position and configuration of the double bond as in the pure ethers is observed, see table 4. τ for the ethers with a *trans*-double bond is higher than that of the reference ether or the ethers with a *cis*-double bond. P_s and τ are higher for all the alkenyloxy-substituted ethers than that of the reference ether (**67**). This is either due to the higher $T_{S_C^*}$, or greater θ or a combination of both factors. The high $T_{S_C^*}$ P_s, and short τ of the *cis*-substituted ether (**70**) is remarkable. These values are consistent with a linearly-extended conformation of the terminal chains for optimal S_C behaviour.

The plots of the transition temperatures, P_s and τ of the ethers (**1–28**) versus the position of the double bond (*n*, see figure 3) shown in the figures 4–6 reveal odd–even effects. The salient feature of the results shown pictorially in figures 4–6 is the disadvantageous combination of high values for τ, low P_s values and low transition temperatures for the ethers (**1–7**; W = N; $X = Y = Z$ = H) with the pyrimidine ring furthest from the octyl/octenyloxy chain. In contrast, the ethers (**15–21**; Y = N; $W = X = Z$ = H) with the pyrimidine ring in the middle of the molecule exhibit the most advantageous combination of these parameters for several positions of the double bond. For most ethers a low value for P_s can be correlated to a low tilt angle by the relationship [42] $P_s = P_0 \sin\theta$ and/or a lower $T_{S_C^*}$ value.

5. Experiment

5.1. *Analysis*

The configuration of the carbon–carbon double bond in the alkenyloxy chain of the new ethers (**2–7**, **9–14**, **16–21**, **23–28**, **43–66**, **68–73** and **83–88**) 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

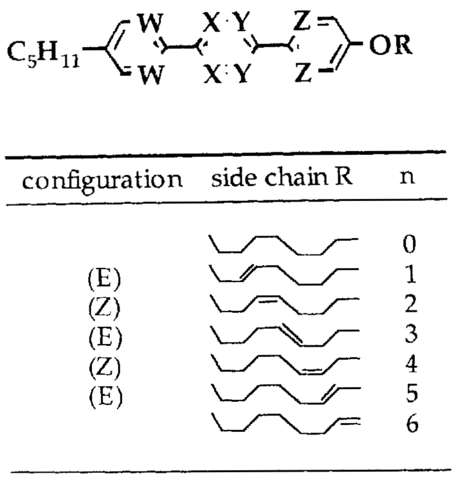


Figure 3. The four series of ethers (**1–28**; symbols used in figures 4–6: □, *W*, ○, *X*, △, *Y*, ◇, *Z*) each incorporate the side chain *R* (octyl and octenyloxy with the given alternating [*E*/*Z*] configuration). The number *n* indicates the position of the double bond (for octyl: *n* = 0).

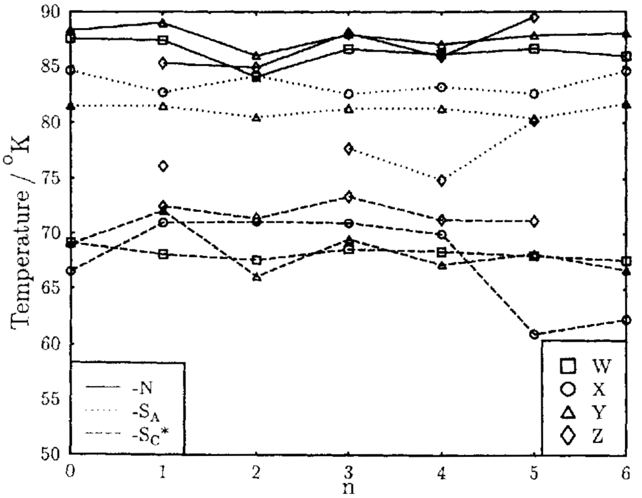


Figure 4. Plot of the smectic A–isotropic/chiral nematic–isotropic (S_A–I and N*–I; solid lines), smectic A–chiral nematic/isotropic (S_A–N* and S_A–I; dotted lines) and the chiral smectic C–smectic A/chiral nematic (S_C^*–S_A; and S_C^*–N*; broken lines) transition temperatures of the mixtures containing 15 wt % of the ethers (**1–28**; □, *W*; ○, *X*, △, *Y*, ◇, *Z*) and 85 wt % of the chiral smectic C mixture SCO 1014 versus the position (*n*) of the carbon–carbon double bond in the octenyloxy chain as defined in figure 3 for each series.

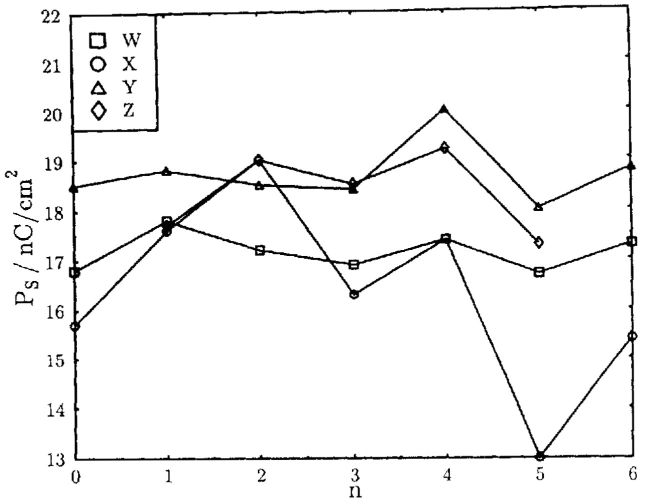


Figure 5. Plot of the spontaneous polarization (P_s) of the mixtures containing 15 wt % of the ethers (**1–28**; □, *W*; ○, *X*, △, *Y*, ◇, *Z*) and 85 wt % of the chiral smectic C mixture SCO 1014 versus the position (*n*) of the carbon–carbon double bond in the octenyloxy chain as defined in figure 3 for each series.

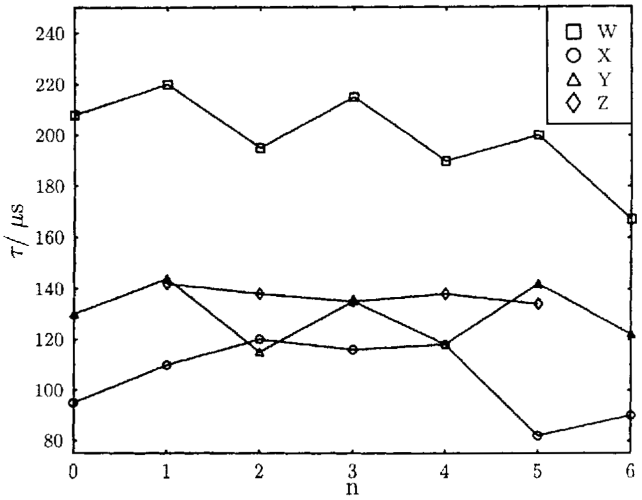


Figure 6. Plot of the switching times (τ) of the mixtures containing 15 wt % of the ethers (**1–28**; □, *W*; ○, *X*, △, *Y*, ◇, *Z*) and 85 wt % of the chiral smectic C mixture SCO 1014 versus the position (*n*) of the carbon–carbon double bond in the octenyloxy chain as defined in figure 3 for each series.

(the *trans*-absorption bands are observed at distinctly different wavelengths ≈ 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 thermal analysis (DTA) and capillary gas chromatography (GC) as usual and, where necessary, on liquid crystal packed columns [43].

The transition temperatures of the ethers prepared, recorded in tables 1–5, 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 liquid crystal 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 (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-fluorohexanoyloxycyclohexyl] phenyl 2,3-difluoro-4-octyloxybenozate ester (16 wt %), 2-(4-hexyloxyphenyl)-5-nonylpyrimidine (24 wt %), 2-(4-nonyloxyphenyl)-5-nonylpyrimidine (24 wt %), 20(4-nonyloxyphenyl)-5-heptylpyrimidine (12 wt %), 2-(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 esters was carried out as previously described [4, 7, 8, 10].

5.2. *Synthesis*

5.2.1. *4-(4-Pentyloxyphenyl)benzimidoethyl ether hydrochloride*

A solution of 4-cyano-4-pentyloxybiphenyl [34] (45 g, 170 mmol) in ethanol (56 cm^3) and toluene (200 cm^3) was saturated with hydrogen chloride at 0°C, and stirred at room temperature for 2 d. 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 yield the desired hydrochloride (yield 60 g, 98 per cent); IR (KBr) ν_{max}: 2935, 2871, 1695, 1630, 1602, 1502, 1446, 1253, 1073, 821 cm^{-1}. MS *m/z*: 311 ($C_{20}H_{25}NO_2^+$), 283 ($C_{18}H_{21}NO_2^+$), 267 ($C_{18}H_{21}NO^+$). ^{1}H NMR ($CDCl_3$): 0·92–0·97 (3 H, t), 1·42 (4 H, overlapping peaks), 1·61–1·67 (3 H, t), 1·82 (2 H, q), 4·02 (2 H, overlapping peaks), 4·95–4·98 (2 H, q). 6·98–7·02 (2 H, d), 7·56–7·59 (2 H, d), 7·73–7·76 (2 H, d), 8·44–8·48 (2 H, d), 11·90 (1 H, s), 12·50 (1 H, s).

5.2.2. *4-(4-Pentyloxyphenyl)benzimidamide hydrochloride*

A saturated ethanolic ammonia solution (350 cm^3) was added to a solution of 4-(4-pentyloxyphenyl)benzimidoethyl ether hydrochloride (60 g, 166 mmol) and ethanol (300 cm^3). The reaction mixture was stirred at room temperature for 2 d 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 benzimidamide (yield 52 g, 98 per cent); IR (KBr) ν_{max}: 3245, 3085, 2958, 1671, 1605, 1482, 1252, 824 cm^{-1}. MS *m/z*: 282 ($C_{18}H_{22}N_2O^+$), 265 ($C_{18}H_{19}NO^+$), 212 ($C_{13}H_{12}N_2O^+$).

5.2.3. *2-(4-Pentyloxybiphenyl-4′-yl)-5-pentylpyrimidine*

A 5·4 M solution of sodium methoxide in methanol (31 cm^3) was added dropwise to a mixture of (2-methoxymethylidene)heptanal [35, 36] (222 mmol), 4-(4-pentyloxyphenyl)benzimidamide hydrochloride (35·4 g, 111 mmol) and methanol (170 cm^3) at room temperature and then stirred overnight. Concentrated hydrochloric acid was added (pH 3–4) and the inorganic material filtered off. The filtrate was concentrated under reduced pressure, dichloromethane was added and the resultant solution washed with water (2 × 250 cm^3) and then dried ($MgSO_4$). Column chromatography (flash) on silica gel using a 2 : 1 mixture of cyclohexane/ethyl acetate as eluent and recrystallization from ethanol yielded the desired ether (yield 40 g, 93 per cent). IR (KBr) ν_{max}: 2933, 2866, 1606, 1500, 1430, 1249, 1072, 830 cm^{-1}. MS *m/z*: 388 (M$^+$), 318 ($C_{21}H_{22}N_2O^+$), 261, ($C_{17}H_{13}N_2O^+$). ^{1}H NMR ($CDCl_3$): 0·91–0·97 (6 H, t), 1·36–1·46 (8 H, overlapping peaks), 1·61–1·67 (2 H, overlapping peaks), 1·79–1·82 (2 H, q), 2·60–2·66 (2 H, t), 4·00–4·04 (2 H, t) 7·00–7·02 (2 H, d), 7·59–7·59 (4 H, overlapping peaks), 8·43–8·47 (2 H, d), 8·63 (2 H, s).

5.2.5. *4-Isopropyloxybenzaldehyde*

A mixture of isopropyl bromide [Fluka] (46 g, 375 mmol), 4-hydroxybenzaldehyde [Fluka] (30·5 g, 250 mmol), potassium carbonate (104 g, 750 mmol) and *N*,*N*-dimethylformamide (300 cm^3) was stirred for 48 h at room temperature, filtered, added to water and shaken with ether (3 × 100 cm^3), dried ($MgSO_4$), filtered and evaporated down to yield the desired ether (yield 41 g, 99 per cent); IR (KBr) ν_{max}: 2980, 2734, 1687, 1600, 1506, 1258, 1159, 833 cm^{-1}. MS *m/z*: 164 (M$^+$).

5.2.6. *2-(4-Isopropyloxyphenyl)-1-methoxyethene*

A solution of 4-isopropyloxybenzaldehyde (41·0 g, 250 mmol) and *t*-butyl methyl ether (100 cm^3) was added dropwise to a mixture of methoxymethyltriphenylphosphonium chloride (140 g, 407 mmol), potassium *t*-butylate (45 g, 400 mmol) and *t*-butyl methyl ether (400 cm^3) at 0°C. The reaction mixture was stirred at room temperature for a further 48 h and then added to water (1000 cm^3) and shaken with ether (3 × 100 cm^3). The combined organic layers were washed with water (2 × 200 cm^3), dried ($MgSO_4$), filtered and evaporated down. Hexane (100 cm^3) was added and the solution cooled to 0°C. The precipitated triphenylphosphonium oxide was filtered off and the filtrate evaporated down again. Purification of the residue by column chromatography (flash) on silica gel using a 9 : 1 cyclohexane/ethyl acetate mixture as eluent yielded the desired ethene (yield 48 g, 99 per cent); IR (KBr) ν_{max}: 2977, 2934, 1650, 1607, 1508, 1242, 955, 837, 745, 698 cm^{-1}. MS *m/z*: 192 (M^+), 150 ($C_9H_{10}O_2^+$).

5.2.7. *2-(4-Isopropyloxyphenyl)malonic anhydride-tetramethylacetal*

2-(4-Isopropyloxyphenyl)-1-methoxyethene (48 g, 250 mmol) was added dropwise to a freshly prepared solution of trimethyl orthoformate (273 cm^3, 2·5 mmol) and boron trifluoride diethyl ether (9·8 cm^3, 78 mmol) cooled using an ice bath. The reaction solution was stirred for a further 2 h, neutralized using triethylamine (5·5 cm^3, 41 mmol), added to water and then shaken with ether (3 × 100 cm^3). The combined organic layers were washed with concentrated sodium carbonate solution (2 × 100 cm^3) and with water (2 × 500 cm^3), dried ($MgSO_4$), filtered and evaporated down under reduced pressure. Purification of the residue by column chromatography (flash) on silica gel using a 1 : 1 dichloromethane/ethyl acetate mixture as eluent and then distillation (b.p., 135–137°C/1 Torr) yielded the desired tetramethyl acetal (44 g, 59 per cent); IR (KBr) ν_{max}: 2978, 2932, 1612, 1510, 1243, 1120, 836, 776 cm^{-1}. MS *m/z*: 192 ($C_{12}H_{16}O_2^+$), 150 ($C_9H_{10}O_2^+$). ^{1}H NMR ($CDCl_3$): 1·30–1·32 (6 H, d) 3·09–3·14 (1 H, t), 3·30 (6 H, s), 3·41 (6 H, s), 3·45–4·54 (1 H, overlapping peaks), 4·63–4·65 (2 H, d), 6·78–6·81 (2 H, d), 7·17–7·26 (2 H, d).

5.2.8. *(4-Isopropyloxyphenyl)-(2-methoxymethylidene) ethanal*

A mixture of 2-(4-isopropyloxyphenyl)malonic anhydride-tetramethyl acetal (22·5 g, 75 mmol), 4-toluene sulphonic acid-mono hydrate (0·65 g) and water (2 cm^3) was heated at 80°C for 7 h. Sodium bicarbonate was added to the cooled solution. The resultant mixture was stirred for about 5 min, filtered to remove inorganic material and then the residue was washed with small amounts of methanol. The filtered methanolic solution was used in the next reaction without further purification and assuming a quantitative yield.

5.2.9. *5-(4-Isopropyloxyphenyl)-2-(4-pentylphenyl) pyrimidine*

A 5·4 molar solution of sodium methoxide in methanol (20 cm^3) was added dropwise to a mixture of (4-isopropyloxyphenyl)-2-methoxymethylidene)ethanal (75 mmol), 4-pentylbenzimidoethyl ether hydrochloride [35, 36] (16·1 g, 71 mmol) and methanol (80 cm^3) at room temperature, stirred overnight and then worked up and purified as described above to yield the desired ether (yield 18·5 g, 72 per cent). IR (KBr) ν_{max}: 2928, 2867, 1607, 1510, 1435, 1246, 835, 793 cm^{-1}. MS *m/z*: 360 (M^+), 318 ($C_{21}H_{22}N_2O^+$), 261 ($C_{17}H_{13}N_2O^+$).

5.2.10. *4-(2-[4-Pentylphenyl]pyrimidin-5-yl)phenol*

A one molar solution of boron tribromide (34 cm^3, 33 mmol) was added dropwise to a solution 5-(4-isopropyloxyphenyl)-2-(4-pentylphenyl)pyrimidine (10 g, 28 mmol) in dichloromethane (100 cm^3) at 0°C. The reaction mixture was stirred overnight and then worked up and purified as above to give the phenol (yield 8·7 g, 98 per cent). IR (KBr) ν_{max}: 3418, 3190, 2926, 1611, 1517, 1275, 832 cm^{-1}. MS *m/z*: 318 (M^+), 261 ($C_{17}H_{13}N_2O^+$), 195 ($C_{13}H_9NO$). ^{1}H NMR ($CDCl_3$): 0·90 (3 H, t) 1·34 (4 H, overlapping peaks), 1·70 (2 H, overlapping peaks), 2·69 (2 H, t), 5·90 (1 H, s), 6·99–7·02 (2 H, d), 7·26–7·35 (2 H, d), 7·48–7·52 (2 H, d), 8·37–8·41 (2 H, d), 8·98 (2 H, s).

5.2.11. *4-Hydroxybenzimidoethyl ether hydrochloride*

A solution of 4-hydroxybenzonitrile [Fluka] (51 g, 43 mmol) in ethanol (140 cm^{-3}) and toluene (200 cm^3) was saturated with hydrogen chloride at 0°C, and stirred at room temperature for 24 h. 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 yield the desired hydrochloride (yield 85 g, 98 per cent). IR (KBr) ν_{max}: 3046, 2744, 1679, 1630, 1611, 1559, 1448, 1232, 1007, 845 cm^{-1}. MS *m/z*: 165 (M^+), 164 ($C_9H_{10}NO_2^+$), 120 ($C_7H_6NO^+$), 93 ($C_6J_7N^+$). ^{1}H NMR ($CDCl_3$): 1·43–1·49 (3 H, t), 4·54–4·62 (2 H, q), 6·99–7·03 (2 H, d), 8·02–8·06 (2 H, d), 10·95 (1 H, s), 11·18 (1 H, s), 11·75 (1 H, s).

5.2.12. *4-Hydroxybenzimidamide hydrochloride*

A saturated ethanolic ammonia solution (700 cm^3) was added to a solution of 4-hydroxybenzimidoethyl ether hydrochloride (85 g, 419 mmol) and ethanol (400 cm^3). The reaction mixture was stirred at room temperature for 24 h 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 77 g, 98 per cent). IR (KBr) ν_{max}: 3218, 3135, 2820, 1668, 1609, 1448, 1231, 1183, 849 cm^{-1}. MS *m/z*: 136 (M^+), 120 ($C_7H_6NO^+$), 93 ($C_6H_7N^+$).

5.2.13. *(2-Methoxymethylidene)-(4-pentylphenyl) ethanal*

A mixture of 2-(4-pentylphenyl)malonic anhydride-tetramethyl acetal [35, 36] (30 g, 97 mmol), 4-toluene sulphonic acid-mono hydrate (0·9 g) and water (3 cm^3) was heated at 80°C for 8 h. Sodium bicarbonate was added to the cooled solution. The resultant mixture was stirred for about 5 min, filtered to remove inorganic material and then the residue was washed with small amounts of methanol. The filtered methanolic solution was used in the next reaction without further purification and assuming a quantitative yield.

5.2.14. *4-(5-[4-Pentylphenyl]pyrimidin-2-yl)phenol*

A 5·4 molar solution of sodium methoxide in methanol (35 cm^3) was added dropwise to a mixture of (2-methoxymethylidene)-4-pentylphenyl)ethanal (97 mmol), 4-hydroxybenzimidamide hydrochloride (15·8 g, 91 mmol) and methanol (90 cm^3) at room temperature, stirred overnight and then worked up and purified as described above to yield the desired ether (yield 17 g, 55 per cent). IR (KBr) ν_{max}: 3430, 2926, 2853, 1612, 1584, 1435, 1235, 833, 791 cm^{-1}. MS *m/z*: 318 (M$^+$), 261, ($C_{17}H_{13}N_2O^+$). ^{1}H NMR ($CDCl_3$): 0·91 (3 H, t), 1·35 (4 H, overlapping peaks), 1·61 (2 H, overlapping peaks), 2·67 (2 H, t), 5·67 (1 H, s), 6·92–6·96) (2 H, d), 7·26–7·35 (2 H, d), 7·51–7·55 (2h, d), 8·36–8·40 (2 H, d), 8·96 (2 H, s).

5.2.15. *4-(4-Pentylphenyl)benzimidoethyl ether hydrochloride*

A solution of 4-cyano-4′-pentylbiphenyl [34] (70 g, 280 mmol) in ethanol (100 cm^3) and toluene (270 cm^3) was saturated with hydrogen chloride at 0°C, stirred at room temperature for 2 d and then worked up and purified as described above to give the hydrochloride (yield 89 g, 96 per cent). IR (KBr) ν_{max}: 2927, 2856, 1700, 1633, 1606, 1502, 1445, 1073, 814 cm^{-1}. MS *m/z*: 295 (M$^+$), 267 ($C_{18}H_{21}NO^+$), 210 ($C_{14}H_{12}NO^+$). ^{1}H NMR ($CDCl_3$): 0·84–0·90 (3 H, t), 1·29–1·31 (4 H, overlapping peaks), 1·41–1·61 (5 H, overlapping peaks), 2·60–2·66 (2 H, 1), 4·62–4·71 (2 H, q), 7·28–7·36 (2 H, d), 7·62–7·74 (2 H, d), 7·92–7·96 (2 H, d), 8·21–8·24 (2 H, d), 12·00 (2 H, s).

5.2.16. *4-(4-Pentylphenyl)benzimidamide hydrochloride*

A saturated ethanolic ammonia solution (535 cm^3) was added to a solution of 4-(4-pentylphenyl)benzimidoethyl ether hydrochloride (89 g, 267 mmol) and ethanol (470 cm^3). The reaction mixture was stirred at room temperature for 2 d and then worked up and purified as described above to give the benzamidine (yield 79 g, 98 per cent). IR (KBr) ν_{max}: 3080, 2956, 2924, 2854, 1682, 1657, 1611, 1471, 841 cm^{-1}. MS *m/z*: 266 ($C_{18}H_{22}H_2^+$), 209 ($C_{14}H_{13}N_2^+$). ^{1}H NMR ($CDCl_3$): 0·84–0·90 (3 H, t), 1·30 (4 H, overlapping peaks), 1·60 (2 H, overlapping peaks), 2·51–2·63 (2 H, t), 7·32–7·36 (2 H, d), 7·68–7·71 (2 H, d), 7·92 (4 H, d), 9·50 (4 H, overlapping peaks).

5.2.17. *5-Ethoxy-2-(4-pentylbiphenyl-4′-yl)pyrimidine*

1,3-bis(Dimethylamino)-2-ethoxytrimethinium perchlorate [41], (7·4 g, 28 mmol) and 4-(4-pentylphenyl) benzimidamide hydrochloride (10·4 g, 34 mmol) were added to a solution of 5·4 molar sodium methoxide (69 mmol) in methanol (13 cm^3, 68 mmol) at room temperature. The reaction mixture was heated under gentle reflux overnight, poured onto water (500 cm^3), 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 purified by column chromatography (flash) on silica gel using a 1 : 1 mixture of cyclohexane/ethyl acetate as eluent followed by crystallization from ethanol to yield the desired ether (yield 8·1 g, 68 per cent). IR (KBr) ν_{max}: 2928, 2863, 1561, 1495, 1276, 1039, 789 cm^{-1}. MS *m/z*: 346 (M$^+$) 289 ($C_{19}H_{17}N_2O^+$). ^{1}H NMR ($CDCl_3$): 0·91 (3 H, overlapping peaks), 1·35–1·38 (4 H, overlapping peaks), 1·46–1·52 (3 H, t), 1·57 (2 H, overlapping peaks), 2·63 (2 H, t), 4·11–4·21 (2 H, q), 7·26–7·29 (2h, d) 7·58–7·62 (2 H, d), 7·68–7·71 (2 H, d), 8·38–8·41 (2 H, d), 8·47 (2 H, s).

5.2.18. *5-Hydroxy-2-(4-pentylbiphenyl-4′-yl)pyrimidine*

A solution of 5-ethoxy-2-(4-pentylbiphenyl-4′-yl)pyrimidine (8·0 g, 23 mmol), sodium hydroxide (9·3 g, 231 mmol) and diethylene glycol (150 cm^3) was heated at 200°C for 6 h. The cooled reaction solution was poured into water (500 cm^3), acidified with 25 per cent hydrochloric acid and shaken with ethyl acetate (4 × 150 cm^3). The combined organic layers were washed with dilute sodium bicarbonate solution (2 × 150 cm^3), dried ($MgSO_4$), filtered and evaporated down. The residue was purified by recrystallization from ethyl acetate to yield the desired phenol (yield 7·0 g, 95 per cent); IR (KBr) ν_{max}: 3027, 2927, 2856, 1609, 1566, 1432, 1281, 787 cm^{-1}. MS *m/z*: 318 (M$^+$), 261, ($C_{17}H_{13}N_2O^+$). ^{1}H NMR ($CDCl_3$): 0·91 (3 H, t), 1·34 (4 H, overlapping peaks), 1·67 (2 H, overlapping peaks), 2·65 (2 H, overlapping peaks), 6·0 (1 H, s) 7·25–7·28 (2 H, t), 7·56–7·59 (2 H, d), 7·68–7·71 (2 H, d), 8·34–8·37 (2 H, d), 8·46 (2 H, s).

5.2.19. *5-(4-Hexyloxyphenyl)-2-(4-pentylphenyl) pyrimidine* (**67**)

A mixture of 1-bromohexane [Fluka] (0·2 g, 0·6 mmol), 4-(2-[4-pentylphenyl]pyrimidin-5-yl)phenol (0·2 g, 0·6 mmol), potassium carbonate (0·4 g, 2·5 mmol) and 2-butanone (20 cm^3) was heated under gentle reflux overnight, filtered and then evaporated down. The residue was purified by column chromatography on silica gel using an 8:2 cyclohexane/ethyl acetate mixture as eluent and recrystallization from ethanol to yield the desired ether (yield 0·17 g, 68 per cent); IR (KBr) ν_{max}: 2928, 2867, 1608, 1515, 1437, 1247, 1184, 832, 792 cm^{-1}. MS *m/z*: 402 (M^+), 261, ($C_{17}H_{13}N_2O^+$). ^{1}H NMR ($CDCl_3$): 0·90–0·92 (6 H, overlapping peaks), 1·34 (14 H, overlapping peaks), 2·68 (2 H, t), 4·00–4·05 (2 H, t), 7·02–7·06 (2 H, d), 7·26–7·34 (2 H, d), 7·53–7·57 (2 H, d), 8·35–8·39 (2 H, d), 8·96 (2 H, s). The transition temperatures of the ether (**67**) and similar ethers (**1**, **8**, **15**, **22** and **82**), synthesized using this general method, are collated in tables 1, 4 and 5.

5.2.20. *5-(4-[(E)-Hex-2-enyloxy]phenyl)-2-(4-pentylphenyl)pyrimidine* (**49**)

A solution of diethyl azodicarboxylate (0·13 g, 0·8 mmol) and tetrahydrofuran (10 cm^3) was added dropwise at 0°C to a solution of (*E*)-hex-2-en-1-ol [Johnson Matthey] (0·08 g, 0·8 mmol), 4-(2-[4-pentylphenyl] pyrimidin-5-yl)phenol (0·25 g, 0·8 mmol), triphenylphosphine (0·20 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. 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 ether (yield 0·08 g, 25 per cent); IR (KBr) ν_{max}: 2928, 2869, 1608, 1517, 1436, 1247, 1187, 969, 831, 792 cm^{-1}. MS *m/z*: 400 (M^+), 318 ($C_{21}H_{22}N_2O^+$), 261 ($C_{17}H_{13}N_2O^+$), 195 ($C_{13}H_9NO$). ^{1}H NMR ($CDCl_3$): 0·90–0·96 (6 H, overlapping peaks), 1·36–1·39 (6 H, overlapping peaks), 1·58–1·67 (2 H, overlapping peaks), 2·08–2·10 (2 H, q), 2·65–2·71 (2 H, t), 4·53–4·56 (2 H, overlapping peaks), 5·76–5·85 (2 H, overlapping peaks), 7·03–7·07 (2 H, d) 7·26–7·37 (2 H, d), 7·53–7·57 (2 H, d), 8·35–8·39 (2 H, d), 8·96 (2 H, s). The transition temperatures of this ether (**49**) and similar ethers (**3–7**, **9–14**, **16–21** and **36–53**), prepared using this general method, are recorded in tables 1–5.

5.2.21. *5-(4-[(Z)-Hex-2-enyloxylphenyl)-2-(4-pentylphenyl)pyrimidine* (**68**)

A solution of diethyl azodicarboxylate (0·11 g, 0·6 mmol) and tetrahydrofuran (10 cm^3) was added dropwise at 0°C to a solution of (*Z*)-hex-2-en-1-ol [Aldrich] (0·07 g, 0·6 mmol), 4-(2-[4-pentylphenyl]pyrimidin-5-yl)phenol (0·20 g, 0·6 mmol) and tetrahydrofuran (25 cm^3), stirred at room temperature overnight and then worked up and purified as described above to yield the desired ether (yield 0·12 g, 48 per cent). IR (KBr) ν_{max}: 2927, 2870, 1608, 1516, 1438, 1247, 1039, 832, 796 cm^{-1}. MS *m/z*: 400 (M^+), 318 ($C_{21}H_{22}N_2O^+$), 261, ($C_{17}H_{13}N_2O^+$). ^{1}H NMR ($CDCl_3$): 0·90–0·98 (6 H, overlapping peaks), 1·34–1·67 (8 H, overlapping peaks), 2·13–2·16 (2 H, q), 2·65–2·71 (2 H, t), 4·64–4·66 (2 H, t), 5·70–5·74 (2 H, overlapping peaks), 7·04–7·08 (2 H, d) 7·26–7·34 (2 H, d), 7·54–7·57 (2 H, d), 8·35–8·39 (2 H, d), 8·96 (2 H, s). The transition temperatures of this ether (**68**) and the similar ether (**83**), prepared using this general method, are recorded in tables 4 and 5.

5.2.22. *5-(4-[(E)-Hex-3-enyloxy]phenyl)-2-(4-pentylphenyl)pyrimidine* (**69**)

A solution of diethyl azodicarboxylate (0·11 g, 0·6 mmol) and tetrahydrofuran (10 cm^3) was added dropwise at 0°C to a solution of (*E*)-hex-3-en-1-ol [Fluka] (0·07 g, 0·6 mmol), 4-(2-[4-pentylphenyl]pyrimidin-5-yl)phenol (0·20 g, 0·6 mmol), triphenylphosphine (0·17 g, 0·6 mmol) and tetrahydrofuran (25 cm^3), stirred at room temperature overnight and then worked up and purified as described above to yield the desired ether (yield 0·12 g, 48 per cent); IR (KBr) ν_{max}: 2928, 2869, 1609, 1438, 1248, 1184, 965, 832, 792 cm^{-1}. MS *m/z*: 400 (M^+), 318 ($C_{21}H_{22}N_2O^+$), 261, ($C_{17}H_{13}N_2O^+$), 195 ($C_{13}H_9NO$). ^{1}H NMR ($CDCl_3$): 0·89–1·03 (6 H, overlapping peaks), 1·34 (4 H, overlapping peaks), 157 (2 H, overlapping peaks), 2·09 (2 H, q), 2·53 (2 H, q) 2·68 (2 H, t), 4·01–4·06 (2 H, t), 5·66 (2 H, overlapping peaks, 7·02–7·06 (2 H, d) 7·26–7·34 (2 H, d), 7·53–7·57 (2 H, d), 8·35–8·39 (2 H, d), 8·96 (2 H, s). The transition temperatures of this ether (**69**) and the similar ether (**84**), prepared using this general method, are recorded in tables 4 and 5.

5.2.23. *5-(4-[(Z)-Hex-3-enyloxy]phenyl)-2-(4-pentylphenyl)pyrimidine* (**70**)

A solution of diethyl azodicarboxylate (0·11 g, 0·6 mmol) and tetrahydrofuran (10 cm^3) was added dropwise at 0°C to a solution of (*Z*)-hex-3-en-1-ol [Aldrich] (0·07 g, 0·6 mmol), 4-(2-[4-pentylphenyl]pyrimidin-5-yl)phenol (0·20 g, 0·6 mmol), triphenylphosphine (0·17 g, 0·6 mmol) and tetrahydrofuran (25 cm^3), stirred at room temperature overnight and then worked up and purified as described above to yield the desired ether (yield 0·13 g, 52 per cent). IR (KBr) ν_{max}: 2926, 2869, 1608, 1515, 1438, 1246, 1184, 833, 793 cm^{-1}. MS *m/z*: 400 (M^+), 318 ($C_{21}H_{22}N_2O^+$), 261 ($C_{17}H_{13}N_2O^+$), 195 ($C_{13}H_9NO$). ^{1}H NMR ($CDCl_3$): 0·89–1·04 (6 H, overlapping peaks), 1·34 (4 H, overlapping peaks), 1·56 (2 H, overlapping peaks), 2·12 (2 H, q), 2·68 (4 H, t), 4·00–4·05 (2 H, t), 5·50 (2 H, overlapping peaks, 7·02–7·06 (2 H, d) 7·26–7·33 (2 H, d) 7·53–7·57 (2 H, d), 8·35–8·39 (2 H, d), 8·96 (2 H, s). The transition temperatures of this ether (**70**) and the similar ethers (**3**, **10**, **17**, **24** and **85**), prepared using this general method, are recorded in tables 1, 4 and 5.

5.2.24. *5-(4-[(E)-Hex-4-enyloxy]phenyl)-2-(4-pentylphenyl)pyrimidine* (**71**)

A solution of diethyl azodicarboxylate (0·11 g, 0·6 mmol) and tetrahydrofuran (10 cm^3) was added dropwise at 0°C to a solution of (*E*)-hex-4-en-1-ol [Aldrich] (0·07 g, 0·6 mmol), 4-(2-[4-pentylphenyl]pyrimidin-5-yl)phenol (0·20 g, 0·6 mmol), triphenylphosphine (0·17 g, 0·6 mmol) and tetrahydrofuran (25 cm^3), stirred at room temperature overnight and then worked up and purified as described above to yield the desired ether (yield 0·13 g, 52 per cent). IR (KBr) ν_{max}: 2928, 2856, 1608, 1517, 1437, 1249, 1185, 865, 793 cm^{-1}. MS *m/z* 400 (M^+), 318 ($C_{21}H_{22}N_2O^+$), 261 ($C_{17}H_{13}N_2O^+$), 195 ($C_{13}H_9NO$). ^{1}H NMR ($CDCl_3$): 0·90 (3 H, t), 1·34–1·37 (4 H, overlapping peaks), 1·57–1·68 (5H, overlapping peaks), 1·88 (2 H, overlapping peaks), 2·20, (2 H, overlapping peaks), 2·65–2·68 (2H, t), 3·99–4·04) (2 H, t), 5·47 (2 H, overlapping peaks), 7·02–7·06 (2 H, d) 7·26–7·33 (2 H, d), 7·53–7·57 (2 H, d), 8·35–8·39 (2 H, d), 8·96 (2 H, s). The transition temperatures of this ether (**71**) and the similar ethers (**4**, **13**, **18**, **25** and **86**), prepared using this general method, are recorded in tables 1, 4 and 5.

5.2.25. *5-(4-[(Z)-Hex-4-enyloxy]phenyl)-2-(4-pentylphenyl)pyrimidine* (**72**)

A solution of diethyl azodicarboxylate (0·11 g, 0·6 mmol) and tetrahydrofuran (10 cm^3) was added dropwise at 0°C to a solution of (*Z*)-hex-4-en-1-ol [Johnson Matthey] (0·07 g, 0·6 mmol), 4-(2-[4-pentylphenyl] pyrimidin-5-yl)phenol (0·20 g, 0·6 mmol), triphenylphosphine (0·17 g, 0·6 mmol) and tetrahydrofuran (25 cm^3), stirred at room temperature overnight and then worked up and purified as described above to yield the desired ether (yield 0·10 g, 40 per cent). IR (KBr) ν_{max}: 2928, 2860, 1609, 1518, 1436, 1251, 1186, 830, 792 cm^{-1}. MS *m/z*: 400 (M^+), 318 ($C_{21}H_{22}N_2O^+$), 261, ($C_{17}H_{13}N_2O^+$), 195 ($C_{13}H_9NO$). ^{1}H NMR ($CDCl_3$): 0·90–0·93 (3 H, t), 1·34–1·37 (4 H, overlapping peaks), 1·61–1·64 (5 H, overlapping peaks), 1·86–1·92 (2 H, overlapping peaks), 2·26–2·28 (2 H, q), 2·65–2·71 (2 H, t), 3·99–4·04) (2 H, t), 5·45–5·50 (2 H, overlapping peaks), 7·02–7·06 (2 H, d) 7·26–7·33 (2 H, d), 7·53–7·57 (2 H, d), 8·35–8·39 (2 H, d), 8·96 (2 H, s). The transition temperatures of this ether (**72**) and the similar ether (**87**), prepared using this general method, are recorded in tables 4 and 5.

5.2.26. *5-(4-[Hex-5-enyloxy]phenyl)-2-(4-pentylphenyl) pyrimidine* (**73**)

A mixture of 6-bromo-1-hexene [Fluka] (0·16 g, 0·9 mmol), 4-(2-[4-pentylphenyl]pyrimidin-5-yl)phenol (0·2 g, 0·6 mmol), potassium carbonate (0·35 g, 2·5 mmol) and 2-butanone (20 cm^3) was heated under gentle reflux overnight, filtered and then worked up and purified as described above to yield the desired ether (yield 0·13 g, 52 per cent). IR (KBr) ν_{max}: 2926, 2865, 1608, 1516, 1437, 1248, 1050, 910, 831, 793 cm^{-1}. MS *m/z*: 400 (M^+), 318 ($C_{21}H_{22}N_2O^+$), 261, ($C_{17}H_{13}N_2O^+$), 195 ($C_{13}H_9NO$). ^{1}H NMR ($CDCl_3$): 0·90 (3 H, t), 1·34–1·37 (4 H, overlapping peaks), 1·59–1·63 (4 H, overlapping peaks), 1·85 (2 H, overlapping peaks), 2·14–2·16 (2 H, q), 2·65–2·71 (2 H, t), 4·00–4·06 (2 H, t), 4·97–5·09 (2 H, overlapping peaks), 5·75–5·95 (2 H, overlapping peaks), 7·02–7·06 (2 H, d) 7·26–7·33 (2 H, d), 7·53–7·57 (2 H, d), 8·35–8·39 (2 H, d), 8·96 (2 H, s). The transition temperatures of this ether (**73**) and similar ethers (**7**, **14**, **21**, **28** and **88**) synthesized using this general method of preparation are collated in tables 1, 4 and 5.

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