

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

2-[4-Alkenyloxy)phenyl]-5-alkylpyrimidines The relationship between position and nature (*E/Z*) of the double bond and transition temperatures

S. M. Kelly^a

^a Dept. RLCR, F. Hoffmann-La Roche Inc., Basel, Switzerland

To cite this Article Kelly, S. M.(1993) '2-[4-Alkenyloxy)phenyl]-5-alkylpyrimidines The relationship between position and nature (*E/Z*) of the double bond and transition temperatures', *Liquid Crystals*, 14: 3, 675 – 698

To link to this Article: DOI: 10.1080/02678299308027747

URL: <http://dx.doi.org/10.1080/02678299308027747>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

2-[4-Alkenyloxy)phenyl]-5-alkylpyrimidines

The relationship between position and nature (*E/Z*) of the double bond and transition temperatures

by S. M. KELLY

F. Hoffmann-La Roche Inc., Dept. RLCR,
4002 Basel, Switzerland

The 5-*n*-alkyl-2-[4-(*n*-alkoxy)phenyl]pyrimidines are essential components of most commercial chiral smectic C mixtures for electrooptic display devices based on ferroelectric effects. This is due to their generally relatively low melting points, enantiotropic, relatively wide range smectic C mesophases, low viscosity and ease of preparation. An unsaturated carbon-carbon double bond has now been introduced into the terminal alkoxy chain of the 5-*n*-alkyl-2-[4-(alkoxy)phenyl]pyrimidines to produce the corresponding alkenyloxy substituted derivatives. The position and nature (*E/Z*) of the double bond has been varied systematically and the effect on the liquid crystal transition temperatures studied. A number of homologous series of the most interesting alkenyloxy substituted materials has been prepared and evaluated. The position and nature (*E/Z*) of the double bond changes the conformation of the alkenyloxy chain substantially. This can result in significantly higher smectic C 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) are observed for materials with a *cis* double bond (*Z*) at an odd number of carbon atoms from the molecular core. Comparisons with the corresponding alkoxy substituted materials (i.e. without a double bond) are made.

1. Introduction

Most substances exhibiting pronounced smectic polymorphism recorded in the literature consist of a central aromatic core made up of two or more aromatic rings (one of which is often heterocyclic) and two terminal alkyl/alkoxy chains (sometimes branched or substituted with heteroatoms) [1, 2]. The majority of new smectogens synthesized in the past decade have been designed for use in mixtures for electrooptic display devices [3] originally based on laser addressed dynamic scattering (smectic A mesogens: S_A), then ferroelectric effects [4–12] (requiring the chiral smectic C mesophase: S_C^*) and more recently antiferroelectric effects [13, 14] (using chiral antisemctic C mesophases: S_{CA}^*). The object of most synthetic work was concerned with modifying the core structure (for example with lateral substituents) [15–23] and the central linking units (for example the introduction of ethyl [18–21] or four unit linking groups [22]). Optical activity [23–36] was also introduced into the terminal alkyl/alkoxy chain (for example via chain branching or the introduction of heteroatoms). Some attempts [37–41] have been undertaken to modify the alkyl/alkoxy chains more substantially, for example via the replacement of a methylene unit ($-CH_2-$) of the chain by an oxygen atom [37], fluorocarbon units [38], an epoxy group [39–41], or silicon [40], or via replacement of oxygen by sulphur [41].

The results of our first attempts [19, 21, 42–44] to influence the smectogenic properties of compounds designed for use in electrooptic display device applications

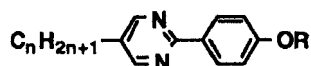
based on ferroelectric effects [4–14] by modifying the alkyl/alkoxy chains via the introduction of an unsaturated carbon–carbon double bond ($-\text{CH}=\text{CH}_2$) revealed a general lowering of all the liquid crystal transition temperatures (often by about 20°C). However, the melting point was sometimes decreased by a larger amount than the smectic C mesophase transition temperature, leading in some cases to a widening of the smectic C mesophase range. In contrast to these results a small number of compounds incorporating a carbon–carbon double bond in the central four unit linking group [44] or in short chains attached to a 1,4-disubstituted cyclohexane ring [21] were seen to lead to marginal increases in the smectic C transition temperatures. These results indicated that the optimal position and possibly the configuration of the unsaturated carbon–carbon double bond had not been found. This encouraged us to conduct a thorough and systematic study of the dependence of the liquid crystal transition temperatures of a standard system on the position of the carbon–carbon double bond in one terminal alkoxy chain, while keeping all the other parameters constant.

The model system chosen was the 5-*n*-alkyl-2-[4-(*n*-alkoxy)phenyl]pyrimidines [45]. These are essential components of most commercial chiral smectic C mixtures for electrooptic display devices based on ferroelectric effects. This is due to the smectic morphology (enantiotropic smectic C, smectic A and nematic mesophases combined with the absence of highly ordered mesophases), generally low melting points, low viscosity and general ease of preparation (the two aromatic rings are not laterally substituted and are directly bonded to each other).

In order to investigate the suitability of these new alkenyloxy substituted materials as non-optically active components of chiral smectic C mixtures for electrooptic display devices based on ferroelectric effects (SSFLCDs, DHFLCDs and SBFLCDs) a parallel study of their physical properties in admixture with each other and in a standard chiral S_C^* mixture was also carried out [46]. The liquid crystal transition temperatures of the new 5-*n*-alkyl-2-[4-(*n*-alkenyloxy)phenyl]pyrimidines (2–7, 9–14 and 16–96) with an unsaturated carbon–carbon double bond in the terminal alkenyloxy chain are recorded in tables 1–4 and those of the corresponding ethers [45] without an additional double bond are given for three homologues (1, 8 and 15) in table 1 and for the complete three homologous series (1, 8, 15 and 97–119) in table 5 (where available).

2. Synthesis

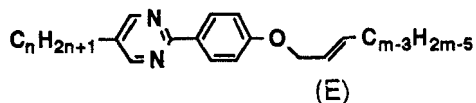
The methods of synthesis of the new 5-*n*-alkyl-2-[4-*n*-alkenyloxy)phenyl]pyrimidines (2–7, 9–14 and 16–96) with an unsaturated carbon–carbon double bond in the terminal alkenyloxy chain are shown in reaction schemes 1–4. The methods of preparation are described in general below and then in detail in the Experimental for a representative member (1–7) of each series. One homologue (1) of the parent compounds (without an additional unsaturated carbon–carbon double bond in the alkoxy chain) is included as a reference compound. The configuration of the unsaturated carbon–carbon double bond in the alkenyloxy chain of the new ethers (2–7, 9–14 and 16–96) was confirmed by ^1H 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 IR spectroscopy (the *trans* absorption bands are narrow and exact ≈ 970 – 960 cm^{-1} , while the *cis* absorption bands are observed at distinctly different wavelengths ≈ 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

Table 1. The liquid crystal transition temperatures for the 5-heptyl-, octyl-, and nonyl-2-[4-*n*-(octenyloxy)phenyl]pyrimidines 1–21.

<i>n</i>	<i>R</i>	$T_{CS_{cSA/N}}/^{\circ}C$	$T_{ScSA/N}/^{\circ}C$	$T_{SA/N/I}/^{\circ}C$	$T_{NI}/^{\circ}C$	$\Delta T_{Sc}/^{\circ}C$
1	7	51	(45)	—	72	—
2	7	38	(35)	—	68	—
3	7	28	—	43	44	—
4	7	39	45	—	65	+6
5	7	2	24	47	53	+22
6	7	53	—	—	72	—
7	7	36	(33)	48	62	—
8	8	34	56	64	70	+22
9	8	24	56	—	68	+32
10	8	25	38	45	—	+13
11	8	32	56	59	63	+24
12	8	10	38	53	—	+28
13	8	40	52	57	67	+12
14	8	22	34	56	60	+12
15	9	33	61	75	—	+28
16	9	42	70	72	73	+28
17	9	24	43	54	—	+19
18	9	42	64	73	—	+22
19	9	24	45	61	—	+21
20	9	39	53	71	72	+14
21	9	37	—	67	—	—

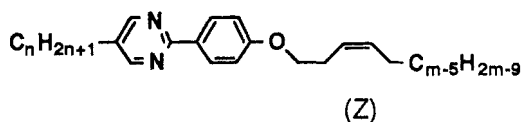
() Represents a monotropic transition temperature.

Table 2. The liquid crystal transition temperatures for the 5-heptyl-, octyl-, and nonyl-2-[4-*n*-((*E*)-2-alkenyloxy)phenyl]pyrimidines **2**, **9**, **16**, **22–45**.



<i>n</i>	<i>m</i>	$T_{CS_C/S_A/N/I}/^{\circ}C$	$T_{S_C S_A/N}/^{\circ}C$	$T_{S_A N/I}/^{\circ}C$	$T_{NI}/^{\circ}C$	
22	7	4	52	—	—	72
23	7	5	31	(30)	—	62
24	7	6	52	—	—	68
25	7	7	22	33	—	63
2	7	8	38	(35)	—	68
26	7	9	40	41	—	66
27	7	10	49	(42)	—	68
28	7	11	43	47	—	66
29	7	12	55	(49)	—	68
30	8	4	48	(45)	—	68
31	8	5	53	(49)	55	61
32	8	6	43	51	—	66
33	8	7	30	55	—	64
9	8	8	24	56	—	68
34	8	9	29	58	—	66
35	8	10	31	59	—	68
36	8	11	40	60	—	66
37	8	12	44	62	—	68
38	9	4	59	—	65	75
39	9	5	56	(42)	68	—
40	9	6	49	63	70	72
41	9	7	46	66	70	—
16	9	8	42	70	72	73
42	9	9	20	70	71	72
43	9	10	37	72	73	74
44	9	11	36	72	73	—
45	9	12	42	74	—	—

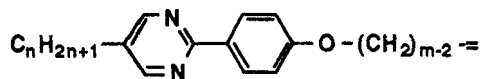
() Represents a monotropic transition temperature.

Table 3. The liquid crystal transition temperatures for the 5-heptyl-, octyl-, and nonyl-2-[4-*n*-((*Z*)-3-alkenyloxy)phenyl]pyrimidines **3**, **10**, **17**, **46**–**69**.

<i>n</i>	<i>m</i>	$T_{CS_C/S_A/N}/^{\circ}C$	$T_{SCS_A}/^{\circ}C$	$T_{S_A/N/I}/^{\circ}C$	$T_{NI}/^{\circ}C$	
46	7	4	38	—	41	49
47	7	5	45	—	(41)	47
48	7	6	43	—	45	48
49	7	7	20	—	44	—
3	7	8	28	—	43	44
50	7	9	25	—	40	—
51	7	10	33	—	39	—
52	7	11	40	—	(37)	—
53	7	12	31	—	35	38
54	8	4	34	—	46	—
55	8	5	34	—	45	—
56	8	6	42	(32)	47	—
57	8	7	33	35	46	—
10	8	8	25	34	46	—
58	8	9	12	30	42	—
59	8	10	22	25	41	—
60	8	11	30	(20)	39	—
61	8	12	32	(14)	41	—
62	9	4	55	—	56	—
63	9	5	48	(25)	55	—
64	9	6	58	(41)	(56)	—
65	9	7	34	45	54	—
17	9	8	24	43	54	—
66	9	9	6	38	51	—
67	9	10	19	34	49	—
68	9	11	26	(24)	47	—
69	9	12	29	(14)	50	—

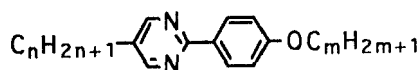
() Represents a monotropic transition temperature.

Table 4. The liquid crystal transition temperatures for the 5-heptyl-, octyl-, and nonyl-2-[(4-*n*-(alkenyloxy)phenyl]pyrimidines 7, 14, 21, 70-96.



<i>n</i>	<i>m</i>	$T_{CS_C/S_A/N/I}/^{\circ}C$	$T_{S_C/S_A}/^{\circ}C$	$T_{S_A/N/I}/^{\circ}C$	$T_{NI}/^{\circ}C$	
70	7	3	44	—	(43)	50
71	7	4	38	—	41	49
72	7	5	46	—	(45)	63
73	7	6	27	—	43	57
74	7	7	56	(34)	(47)	67
7	7	8	36	(33)	48	62
75	7	9	52	(43)	54	67
76	7	10	43	(42)	55	64
77	7	11	49	(46)	59	67
78	7	12	50	(45)	60	65
79	8	3	54	—	(51)	—
80	8	4	34	—	46	—
81	8	5	38	—	54	58
82	8	6	44	—	51	55
83	8	7	37	(30)	58	64
14	8	8	22	34	56	60
84	8	9	27	45	62	66
85	8	10	24	46	60	63
86	8	11	34	52	64	66
87	8	12	36	50	63	64
88	9	3	47	—	59	—
89	9	4	55	—	56	—
90	9	5	40	—	65	—
91	9	6	48	—	62	—
92	9	7	31	—	69	—
21	9	8	37	—	67	—
93	9	9	19	39	71	—
94	9	10	35	45	70	—
95	9	11	32	52	72	—
96	9	12	46	50	70	—

() Represents a monotropic transition temperature.

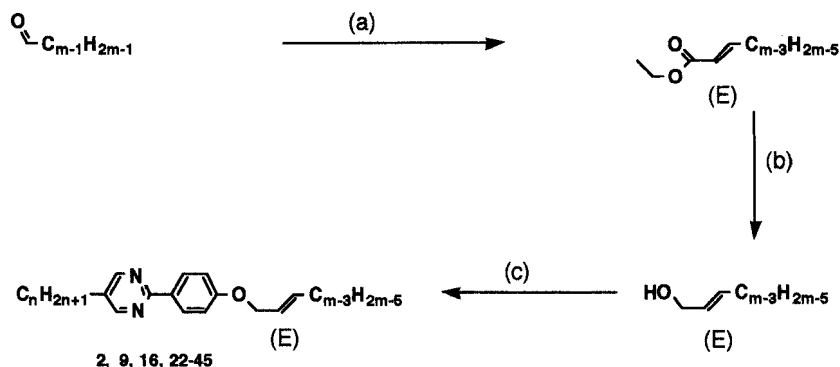
Table 5. The liquid crystal transition temperatures for the 5-heptyl-, octyl-, and nonyl-2-[4-(*n*-alkoxy)phenyl]pyrimidines.

	<i>n</i>	<i>m</i>	$T_{CS_C/S_A/I}/^{\circ}C$	$T_{S_C S_A/N}/^{\circ}C$	$T_{S_A N/I}/^{\circ}C$	$T_{NI}/^{\circ}C$
97	7	3	42	—	44	52
98	7	4	41	—	42	64
99	7	5	49	—	52	66
100	7	6	48	(36)	—	70
101	7	7	39	48	—	68
1	7	8	51	(45)	—	72
102	7	9	48	(47)	—	70
103	7	10	54	55	—	72
104	7	11	55	(54)	63	70
105	7	12	60	(58)	63	71
106	8	3	45	—	50	—
107	8	4	35	—	54	60
108	8	5	38	—	54	58
109	8	6	28	47	59	66
110	8	7	47	49	61	66
8	8	8	34	56	64	70
111	8	9	35	57	65	69
112	8	10	35	61	67	70
113	8	11	45	60	67	69
114	8	12	42	62	69	70
115	9	5	41	—	66	—
116	9	6	33	48	71	72
117	9	7	35	51	72	—
15	9	8	33	61	75	—
118	9	9	36	61	74	—
119	9	10	40	66	76	—

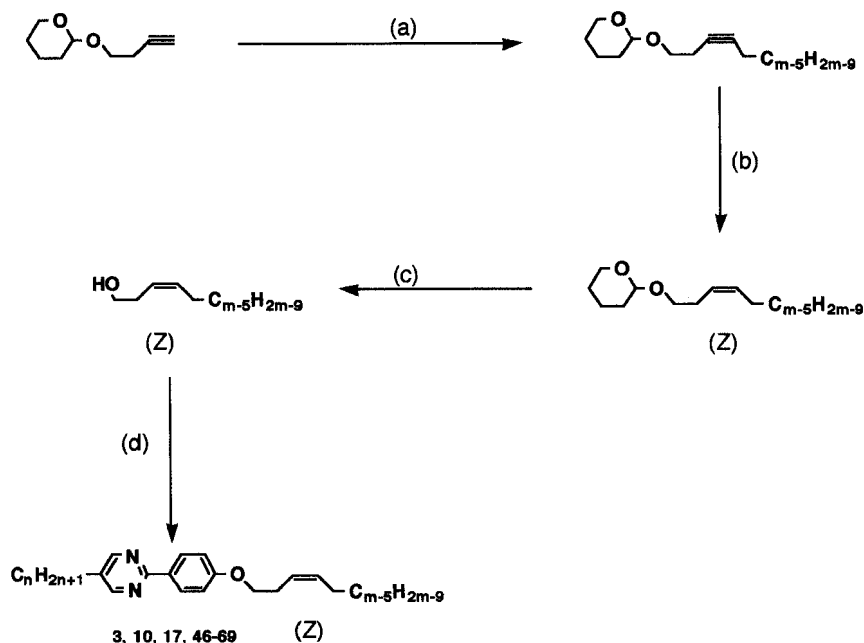
() Represents a monotropic transition temperature.

recrystallization of the desired end product (see Experimental). The structural and isomeric purity was determined by differential thermal analysis and gas capillar chromatography as usual and, where necessary, on liquid crystal packed columns [47].

The reaction pathway leading to the 5-heptyl-, octyl-, and nonyl-2-[4-((*E*)-2-alkenylloxy)phenyl]pyrimidines (**2**, **9**, **16** and **22–45**) is shown in scheme 1. Commercially available alkyl aldehydes are converted in a standard Wittig–Horner reaction [48] to the *trans* acrylates. Reduction of these *trans* acrylates with diisobutylaluminium hydride [49] yielded the corresponding (*E*)-2-alkenyl-1-ols, which were used in a Mitsunobu reaction [50] with the known 5-heptyl-, octyl-, and nonyl-2-[4-(hydroxy)phenyl]pyrimidines [45] to yield the desired ethers (**2**, **9**, **16** and **22–45**). Some



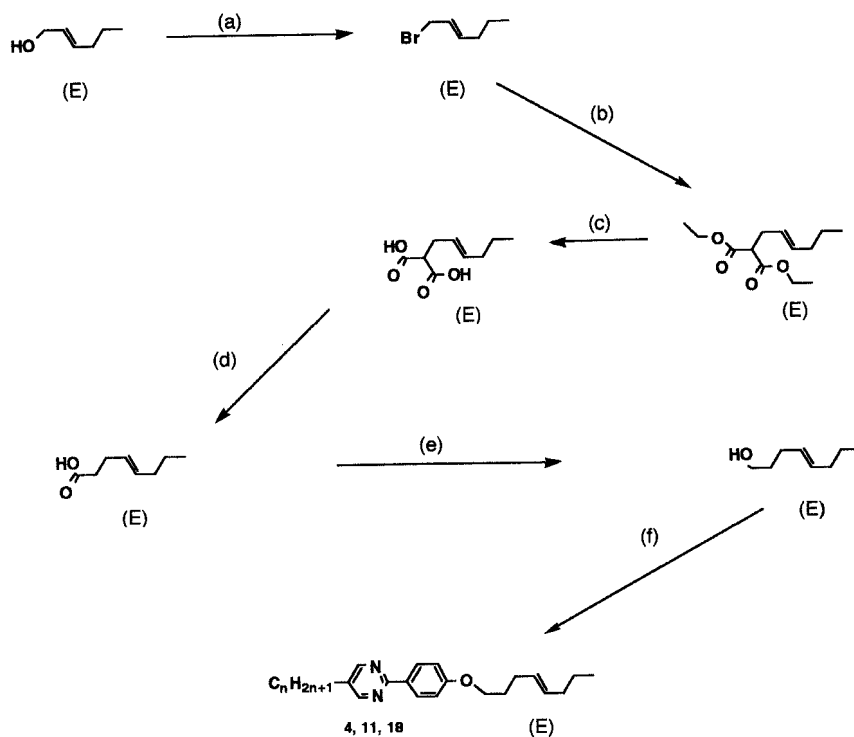
Scheme 1. (a) $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5/\text{K}_2\text{CO}_3/\text{H}_2\text{O}/\text{tetrahydrofuran}$, (b) DIBALH/hexane, (c) DEAD/TPP/tetrahydrofuran/ $\text{C}_n\text{H}_{2n+1}$ -2-[4-(hydroxy)phenyl]pyrimidine



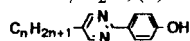
Scheme 2. (a) $\text{C}_4\text{H}_9\text{Li}/\text{BrC}_{m-5}\text{H}_{2m-9}/\text{tetrahydrofuran}$, (b) $\text{H}_2/\text{Lindlar's Catalyst}/\text{HOCH}_2\text{CH}_2\text{SC}_2\text{H}_4\text{SC}_2\text{H}_4\text{OH}/\text{ethyl acetate}$, (c) $((\text{CH}_3)_3\text{Si})_2\text{SO}_2/\text{CH}_3\text{OH}$, (d) DEAD/TPP/tetrahydrofuran/ $\text{C}_n\text{H}_{2n+1}$ -2-[4-(hydroxy)phenyl]pyrimidine

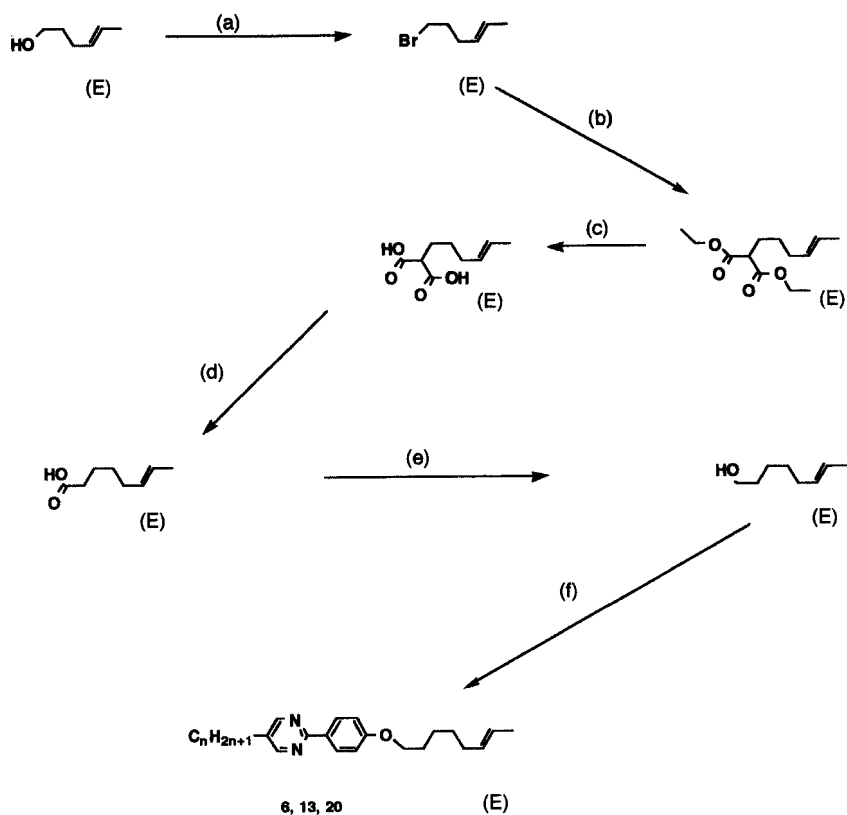
(*E*)-2-alkenyl-1-ols are commercially available. The method of preparation of the 5-heptyl-, octyl-, and nonyl-2-[4-((*Z*)-3-alkenyloxy)phenyl]pyrimidines (**3**, **10**, **17**, **46–69**) is depicted in scheme 2. The commercially available 2-(3-butynyloxy)tetrahydro-2H-pyran is alkylated at -78°C with the appropriate commercially available bromo- or iodo-alkanes [51]. The resultant 2-(3-alkynyl-1-oxy)tetrahydro-2H-pyrans are then hydrogenated using Lindlar's catalyst [52] modified with 1,2-bis(2-hydroxyethylthio)ethane to yield the *cis*-2-[(*Z*)-3-alkenyl-1-oxy]tetrahydro-2H-pyrans with less than 2 per cent of the corresponding *trans* isomer. Deprotection of the tetrahydropyranyl protecting group under mild conditions [53] yielded the (*Z*)-3-alkenyl-1-ols, which were used in a Mitsunobu reaction with the known 5-heptyl-, octyl-, and nonyl-2-(4-(hydroxy)phenyl)pyrimidines to yield the desired ethers (**3**, **10**, **17**, **46–69**).

The synthesis of the 5-heptyl-, octyl-, and nonyl-2-[4(*E*)-octenyloxy]phenyl]pyrimidines (**4**, **11** and **18**) is demonstrated in scheme 3 [54]. The commercially available (*E*)-2-hexen-1-ol is converted by bromination with tetrabromomethane and triphenylphosphine to the corresponding bromide [55], which was condensed with diethyl malonate to yield the diester with eight carbon atoms in the longest chain. Saponification with potassium hydroxide and decarboxylation of the resultant diacid at 150°C led to (*E*)-4-octenoic acid. Reduction with lithiumaluminium hydride yielded the corresponding *trans* alcohol, which was alkylated as above to yield the required ethers (**4**, **11**, and **18**). The *trans* configuration is retained throughout the synthesis.

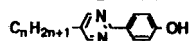


Scheme 3. (a) $\text{CBr}_4/\text{TPP}/\text{dichloromethane}$, (b) $\text{NaOEt}/\text{ethanol}/\text{diethylmalonate}$, (c) (i) $\text{KOH}/\text{H}_2\text{O}$; (ii) HCl , (d) $150^{\circ}\text{C}/-\text{CO}_2$, (e) $\text{LiAlH}_4/\text{ether}$, (f) $\text{DEAD}/\text{TPP}/\text{tetrahydrofuran}/$





Scheme 4. (a) CBr_4 /TPP/dichloromethane, (b) NaOEt/ethanol/diethylmalonate, (c) (i) KOH/ H_2O ; (ii) HCl, (d) $150^\circ C$ / $-CO_2$, (e) $LiAlH_4$ /ether, (f) DEAD/TPP/tetrahydrofuran/



The parallel synthesis of the related 5-heptyl-, octyl-, and nonyl-2-[6-(*E*-octenyloxy)phenyl]pyrimidines (**6**, **13**, and **20**) using the same reaction steps, but starting with (*E*)-4-hexen-1-ol, is depicted in scheme 4.

The 5-heptyl-, octyl-, and nonyl-2-[5-(*Z*-octenyloxy)phenyl]pyrimidines (**5**, **12**, and **19**) were prepared from the known 5-heptyl-, octyl-, and nonyl-2-[4-(hydroxy)phenyl]pyrimidines and the commercially available (*Z*)-5-octen-1-ol as described above.

The ethers (**7**, **14**, **21**, **70–96**) with a carbon-carbon double bond in a terminal position of the alkenyloxy chain were prepared as described above using either commercially available straight chain alkenyl-1-ols or as previously described [43].

3. Mesomorphic properties

The liquid crystal transition temperatures of the 5-heptyl-, octyl-, and nonyl-2-(4-(octyloxy)phenyl)pyrimidines (**1**, **8**, and **15**) and those of the analogous 5-heptyl-, octyl-, and nonyl-2-(4-(alkenyloxy)phenyl)pyrimidines (**2–7**, **9–14**, and **16–21**) 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 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. The width of the smectic C mesophase (i.e. the mesophase type of most direct interest for electrooptic applications based on ferroelectric effects) is recorded in the last column.

The data in the table can be separated into four distinct classes: the standard compounds (**1**, **8**, and **15**) without a double bond in the terminal chains; the materials (**2**, **4**, **6**, **9**, **11**, **13**, **16**, **18**, and **20**) incorporating a *trans* double bond in positions 2, 4 and 6 in the terminal alkenyloxy chain; the substances (**3**, **5**, **10**, **12**, **17**, and **19**) with a *cis* double bond in positions 3 and 5; and those (**7**, **14**, and **21**) with a terminal double bond.

Taken as a whole the substances (**2**, **4**, **6**, **9**, **11**, **13**, **16**, **18**, and **20**) incorporating a *trans* double bond in positions 2, 4 and 6 in terminal alkenyloxy chain exhibit similar melting points (37°C, on average), smectic C temperatures (53°C, on average), smectic A transition temperatures (66°C, on average) and nematic–isotropic transition temperatures (68°C, on average) as those (39°C, 54°C, 70°C, and 71°C, on average, respectively) of their analogues containing no double bond in the alkoxy chain (**1**, **8**, and **15**).

However, these average values mask the rise (+9°C) in the smectic C–smectic A transition temperature for the (*E*)-2-octenyloxy substituted compound (**16**) with a decrease (–3°C) in the smectic A transition temperature resulting in only a narrow smectic A mesophase range (2°C) above the smectic C mesophase. Additionally, a narrow range (1°C) nematic mesophase is observed for the unsaturated compound (**16**) and not for the saturated compound (**15**). Thus the compound (**16**) exhibits the ideal order and range of mesophases for mixtures designed for electrooptic effects based on ferroelectric effects. Although the range of the smectic C mesophase for the unsaturated compound (**16**) is the same as that (18°C) of the corresponding saturated material (**15**), this still represents an improvement in the transition temperatures with regard to electrooptic display device applications based on ferroelectric effects.

A totally different picture appears for the materials (**3**, **5**, **10**, **12**, **17**, and **19**) with a *cis* double bond in positions 3 and 5 compared to the standard compounds. The melting point, smectic C, smectic A and nematic transition temperatures are all lower (–20°C, –16°C, –19°C and –22°C, on average, respectively) 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 (for example **17** and **19**). Several homologues (for example **5** and **12**) exhibit extremely low melting points below room temperature. Decreases in all the liquid crystal transition temperatures of the three compounds (**7**, **14**, and **21**) with a terminal carbon–carbon double bond are also observed. Comparisons are difficult because all three homologues do not always exhibit the same phases. However, the smectic C transition temperature seems to be decreased more (–17°C, on average, for **7** and **14**) than either the melting point (–7°C, on average), the smectic A transition temperature (–8°C, on average, for **14** and **21**) or the nematic–isotropic transition temperature (–10°C, on average) relative to the saturated materials (**1**, **8**, and **15**). Thus, this would seem to be the least attractive position of all the possible positions of the double bond. However, initial measurements of the physical properties of these chosen homologues in a standard chiral smectic C mixture indicated that the electrooptic response offered advantages over the standard materials.

Thus a total of nine homologous series (**2** and **22–29**, **9** and **30–37**, **16** and **38–45**; **3** and **46–53**, **10** and **54–61**, **17** and **62–69**; **7** and **70–78**, **14** and **79–87**, **21** and **88–96**) of these ethers (see tables 2–4 and figures 1–9) were chosen for further study. Three series contained the (*E*)-2-alkenyloxy chain as these seemed the most promising compounds

of all due to their transition temperatures and relative ease of preparation (see table 2 and figures 1–3). Three series incorporating the (*Z*)-3-alkenyloxy chain were prepared (see table 3 and figure 4–6) because of their relatively wide smectic C mesophase and low melting points, fast response times and relative ease of synthesis compared to the very similar (*Z*)-5-alkenyloxy chain (although their physical properties appeared equally attractive). Three series with an alkenyloxy chain with the double bond in a terminal position were also prepared due to their good response times in test mixtures, the absence of isomer problems and the ready availability of appropriate starting materials (see table 4 and figures 6–9).

The liquid crystal transition temperatures of the 5-heptyl-, octyl-, and nonyl-2-[4-((*E*)-2-alkenyloxy)phenyl]pyrimidines (**2** and **22–29**, **9** and **30–37**, **16** and **38–45**, respectively) are recorded in table 2 and plotted against the total number of carbon atoms in the terminal alkenyloxy chain in figures 1–3, respectively. The plots of the nematic–isotropic liquid crystal transition temperature (N–I) against chain length (*m*) of the 5-heptyl-2-[4-((*E*)-2-alkenyloxy)phenyl]pyrimidines (**2** and **22–29**) shown in figure 1 are unusually flat and show a considerable degree of alternation at surprisingly high temperatures (67°C, on average) for two-ring compounds without a polarizable central linkage to increase the length/breadth ratio and the total degree of conjugation. The plots of the smectic C–nematic transition temperature (S_C –N) also show a degree of alternation, although to a lesser extent and at much lower temperatures (40°C, on average). The plots begin at low temperatures (30°C) for the shorter chain lengths (*m* = 5) and rise smoothly to reach the highest values (55°C) for the longest chain studied (*m* = 12) without appearing to reach a maximum as is often the case with smectic series. The plot of the melting point (C– S_C and C–N) is irregular as expected varying greatly with chain length, although starting and ending at relatively high temperatures (52°C and 55°C, respectively) leading to a relatively high average value (42°C). Thus it is not surprising that most of the smectic C–nematic transitions are just monotropic (i.e. below the melting point). There are no other smectic mesophases.

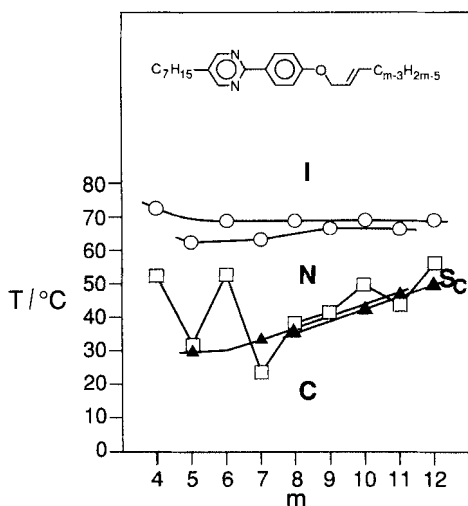


Figure 1. Plots of the transition temperatures against the number of carbon atoms (*m*) in the alkyl chain of the 5-heptyl-2-[4-((*E*)-2-alkenyloxy)phenyl]pyrimidines **2** and **22–29**. (□, crystal–smectic C/nematic transition; ▲, smectic C–nematic transition; ○, nematic–isotropic transition).

The plots of the nematic–isotropic liquid crystal transition temperature (N–I) against chain length (m) of the 5-octyl-2-[4-(*E*)-2-alkenyloxy]phenyl]pyrimidines (**9** and **30–37**) shown in figure 2 are very similar in shape to those of the corresponding heptyl homologues and at almost identical temperatures (66°C, on average). However, while the plots of the smectic C–nematic transition temperature (S_C –N) of the heptyl homologues were concave, the corresponding plots of the octyl homologues are convex and at much higher temperatures (55°C, on average). The plot of the melting point of the octyl homologues shows much less variation than that of the heptyl analogues, beginning and ending at similar temperatures, with a corresponding minimum (24°C) for the octyl analogues for intermediate chain lengths ($m=8$), similar to that of (22°C) of the heptyl materials ($m=7$) resulting in almost the same average values for the heptyl and octyl derivatives (42°C and 38°C, on average, respectively). This results in enantiotropic, relatively wide range smectic C mesophases for most of the octyl homologues (17°C, on average) and for some homologues in particular (for example 32°C for $n=m=8$; **9**).

Addition of one methylene unit ($-\text{CH}_2-$) to octyl derivatives (**9** and **30–37**) to produce the nonyl analogues (**16** and **38–45**) results in the injection of an enantiotropic smectic A mesophase at elevated temperatures (70°C, on average; see figure 3). This causes a reduction (-8°C , on average) in the nematic mesophase range (3°C, on average), although the nematic–isotropic transition temperature is high (73°C, on average). For some homologues ($m=5, 7$) there is no nematic phases at all. The smectic C mesophase now lies underneath a smectic A phase for most of the chain lengths studied ($m=5$ –11). However, the plots of the smectic C transition temperature rises much more steeply for the nonyl derivatives resulting in high values (66°C, on average) and a direct transition (S_C –I) to the isotropic phase for the longest chain lengths investigated ($m=12$).

The liquid crystal transition temperatures of the 5-heptyl-, octyl-, and nonyl-2-[4-(*Z*)-3-alkenyloxy]phenyl]pyrimidines (**3** and **46–53**, **10** and **54–61**, **17** and **62–69**,

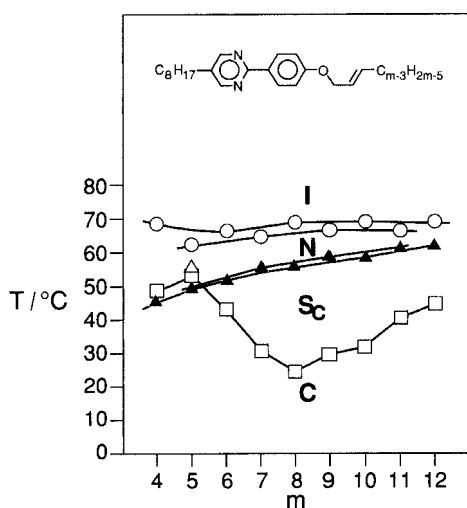


Figure 2. Plots of the transition temperatures against the number of carbon atoms (m) in the alkyl chain of the 5-octyl-2-[4-(*E*)-2-alkenyloxy]phenyl]pyrimidines **9** and **30–37**. (□, crystal–smectic C/smectic A/nematic transition; ▲, smectic A–nematic transition; ○, nematic–isotropic transition).

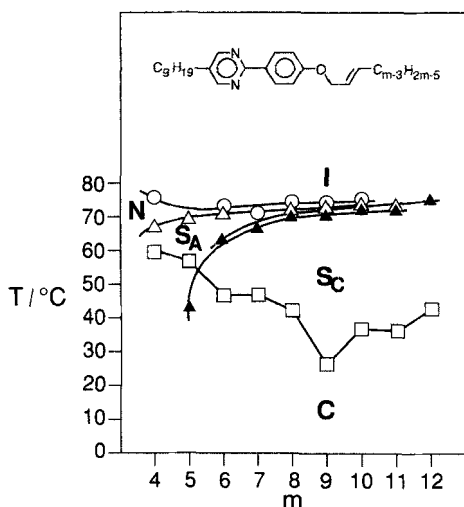


Figure 3. Plots of the transition temperatures against the number of carbon atoms (m) in the alky chain of the 5-nonyl-2-[4-((*E*)-2-alkenyloxy)phenyl]pyrimidines **16** and **38–45**. (\square , crystal-smectic C/smectic A/nematic transition; \blacktriangle , smectic C-smectic A/isotropic transition; \triangle , smectic A-nematic/isotropic transition; \circ , nematic-isotropic transition).

respectively) are recorded in table 3 and plotted against the total number of carbon atoms (m) in the terminal alkenyloxy chain in figures 4–6. The most salient feature of the plots of the liquid crystal transition temperatures of the 5-heptyl-2-[4-((*Z*)-3-alkenyloxy)phenyl]pyrimidines (**3** and **46–53**) is the total absence of a smectic C mesophase (see figure 4). Compared to the corresponding 5-heptyl-2-[4-((*E*)-2-alkenyloxy)phenyl]pyrimidines (**2** and **22–29**) a primarily monotropic smectic C mesophase has been transformed into an enantiotropic smectic A mesophase at moderately elevated temperatures (41°C, on average). The melting point (32°C, on average) and nematic-isotropic transition temperature (45°C, on average) are lower (–10°C and –22°C, on average, respectively) for the materials incorporating the *cis* instead of the *trans* double bond. Thus, the similarities between the two series are minimal.

The addition of one methylene unit (–CH₂–) to the heptyl derivatives (**3** and **46–53**) to produce the octyl analogues (**10** and **54–61**) results in the disappearance of the nematic phase and the appearance of a smectic C mesophase around room temperature (24°C, on average; see figure 5). The melting point (25°C, on average) decreases (–7°C, on average), while the smectic A transition temperature (44°C, on average) increases marginally (+3°C, on average) compared to the heptyl homologues. The plot of the smectic C transition temperature rises steeply for short chain lengths ($m=4, 5$), reaches a maximum for intermediate chain lengths ($m=7$) and decreases gradually to monotropic values below room temperature for the longest chain lengths studied ($m=11, 12$). The plot of the melting point is similar to those of the corresponding materials containing a *trans* double bond, beginning and ending at high values and showing a minimum for intermediate chain lengths ($m=9$), although at a much lower value (12°C) for the material (**58**) containing the *cis* double bond than that (24°C) observed for the corresponding homologue (**9**) for a slightly different chain length ($m=9$) of the analogous series with a *trans* double bond.

The plots of the melting point, smectic C and smectic A transition temperatures of the 5-nonyl-2-[4-((Z)-3-alkenyloxy)phenyl]pyrimidines (**17** and **62–69**) are very similar to those of the corresponding octyl homologous series, although at consistently higher temperatures (31°C, 34°C and 52°C, on average, respectively; see figure 6). However, the minimum for the melting point plot is at a lower temperature (6°C), although for the same homologue ($m=9$), while the smectic C transition temperature (38°C) is somewhat higher (+8°C) leading to a wider (+14°C) smectic C mesophase range (32°C). Three homologues (**17**, **66** and **67**) exhibit enantiotropic smectic C mesophases at room temperature.

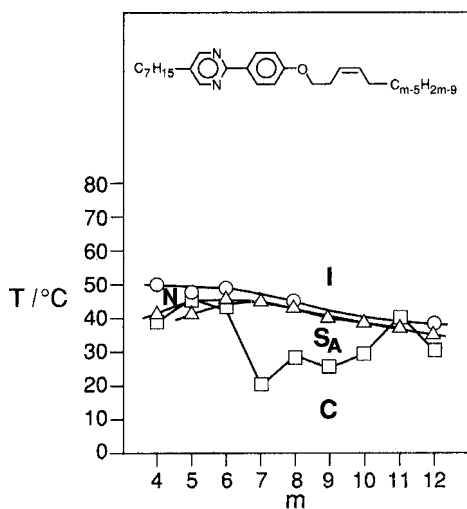


Figure 4. Plots of the transition temperatures against the number of carbon atoms (m) in the alkyl chain of the 5-heptyl-2-[4-((Z)-3-alkenyloxy)phenyl]pyrimidines **3** and **46–53**. (□, crystal-smectic A/nematic/isotropic transition; Δ, smectic A–nematic/isotropic transition; ○, nematic–isotropic transition).

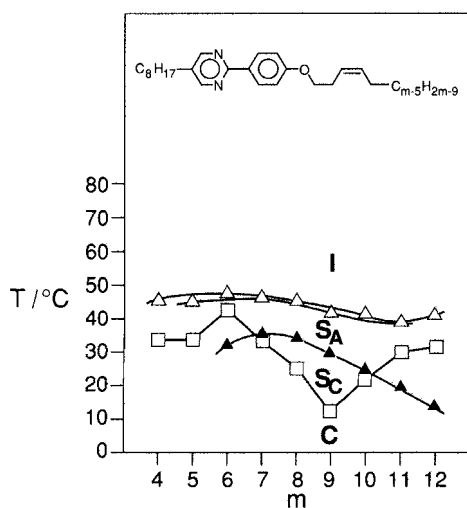


Figure 5. Plots of the transition temperatures against the number of carbon atoms (m) in the alkyl chain of the 5-octyl-2-[4-((Z)-3-alkenyloxy)phenyl]pyrimidines **10** and **54–61**. (□, crystal-smectic C/smectic A transition; ▲, smectic C–smectic A; Δ, smectic A–isotropic transition).

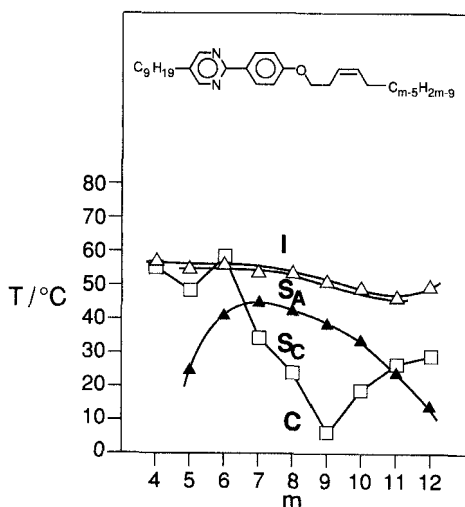


Figure 6. Plots of the transition temperatures against the number of carbon atoms (m) in the alky chain of the 5-nonyl-2-[4-((*Z*-3-alkenyloxy)phenyl)pyrimidines **17** and **62–69**. (□, crystal–smectic C/smectic A/isotropic transition; ▲, smectic C–smectic A; △, smectic A–isotropic transition).

An interesting feature of the transition temperatures of the 5-heptyl-, octyl-, and nonyl-2-[4-((*Z*-3-alkenyloxy)phenyl)pyrimidines **3** and **46–53**, **10** and **54–61**, **17** and **62–69**) is that although the first homologue (**46**, **54** and **62**) of each series ($n = 7–9$; $m = 4$) does not incorporate a *cis* carbon–carbon double bond, but a terminal one, they still continue the plots of the smectic A and nematic phases for the remaining eight homologues with a *cis* carbon–carbon double bond (i.e. $m = 5–12$). This is most unusual and is not valid for any of the other homologous series studied (i.e. the ethers **22–45**) or for a shorter alkenyloxy chain (i.e. $m = 3$; allyloxy, see table 4).

The liquid crystal transition temperatures of the 5-heptyl-, octyl-, and nonyl-2-[4-(alkenyloxy)phenyl]pyrimidines (**7** and **70–78**, **14** and **79–87**, **21** and **88–96**, respectively) with a terminal carbon–carbon double bond are recorded in table 4 and plotted against the total number of carbon atoms (m) in the terminal alkenyloxy chain in figures 7–9. The most obvious feature of the plots of the melting point, smectic C and smectic A and nematic transition temperatures of the 5-heptyl-2-[4-(alkenyloxy)phenyl]pyrimidines (**7** and **70–78**) shown in figure 7 is the presence of broad smectic A and nematic mesophases for the complete homologous series at elevated temperatures (50°C and 61°C, on average, respectively). The plots of the nematic–isotropic liquid crystal transition temperature (N–I) against chain length (m) are convex, while the plot of the smectic A–nematic transition temperature (S_A –N) are concave. Both series of plots show a regular degree of alternation. This applies to the plot of the melting point across almost the whole homologous series. The melting point is relatively high (44°C, on average). Thus, several of the smectic A mesophases (i.e. for the compounds **70**, **72** and **74**) and all the smectic C mesophases are monotropic (41°C, on average). Only those homologues with relatively long chains ($m = 7–12$) show a smectic C mesophase.

The smectic C and smectic A mesophase transition temperatures for the corresponding octyl derivatives (**14** and **79–87**) are higher (+7°C for both, comparing identical homologues for both series) than those of the corresponding heptyl substances (see figure 8). However, the melting point is lower (–7°C, on average). This

results in the appearance of enantiotropic, relatively wide range smectic C and A mesophases, although the smectic C mesophase is still only observed for longer chain lengths ($m = 7-12$). The nematic transition temperatures remain more or less constant (61°C , on average) and, thus, the nematic mesophase range becomes narrower (5°C , on average).

The addition of one methylene unit ($-\text{CH}_2-$) to the octyl derivatives (**14** and **79-87**) to produce the nonyl analogues (**21** and **88-96**) results in the disappearance of the

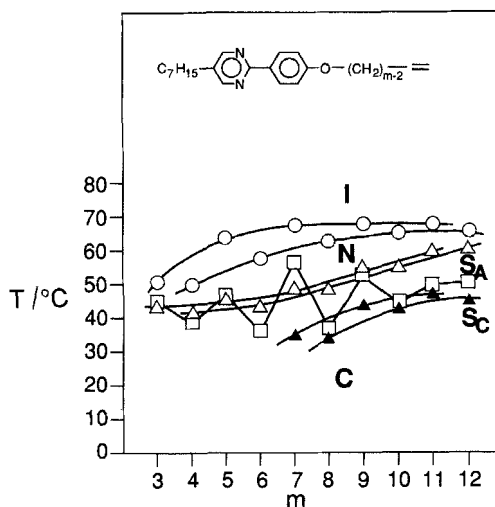


Figure 7. Plots of the transition temperatures against the number of carbon atoms (m) in the alkyl chain of the 5-heptyl-2-[4-(alkenyloxy)phenyl]pyrimidines **7** and **70-78**. (\square , crystal-smectic A/nematic transition; \blacktriangle , smectic C-smectic A transition; \triangle , smectic A-nematic transition; \circ , nematic-isotropic transition).

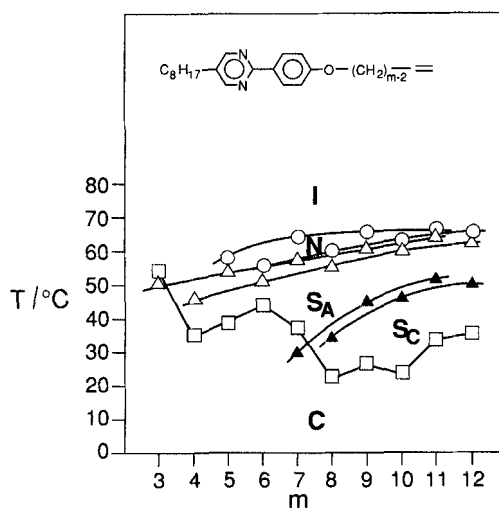


Figure 8. Plots of the transition temperatures against the number of carbon atoms (m) in the alkyl chain of the 5-octyl-2-[4-(alkenyloxy)phenyl]pyrimidines **14** and **79-87**. (\square , crystal-smectic C/smectic A/isotropic transition; \blacktriangle , smectic C-smectic A transition; \triangle , smectic A-nematic/isotropic transition; \circ , nematic-isotropic transition).

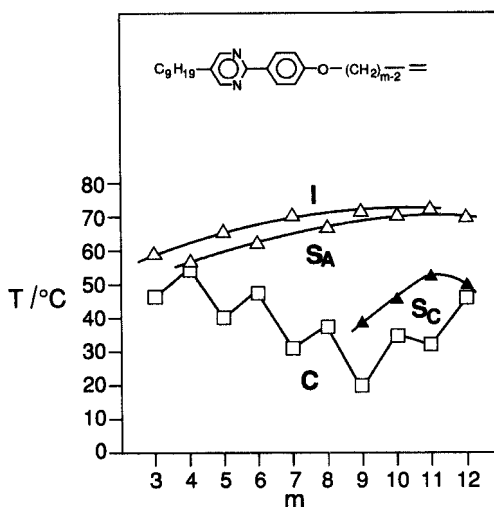


Figure 9. Plots of the transition temperatures against the number of carbon atoms (m) in the alkyl chain of the 5-nonyl-2-[4-(alkenyloxy)phenyl]pyrimidines **21** and **88–96**. (□, crystal-smectic C/smectic A transition; ▲, smectic C–smectic A transition; △, smectic A–isotropic transition).

nematic phase and a substantial rise (+11°C) in the smectic A transition temperatures (S_A –I), while the smectic C transition temperatures remain more or less constant (–1°C on average, comparing the same homologues; $m=9$ –12); see figure 9. This is unusual. The melting point shows a surprising degree of alternation.

4. Discussion

Since the introduction of an unsaturated carbon–carbon double bond into an alkyl/alkoxy chain of such a large molecular model system changes the mesomorphic properties significantly the differences in the chain conformation must also be large (although the geometry at only two carbon atoms from more than fifteen in the two chains is changed). The size of the changes are commensurate with that observed for analogous nematic systems [56–67], but the type of change is different.

Analogous to the situation for nematics, it may be assumed that the preferred arrangement for both terminal alkyl chains is a linear conformation. This may be either the most efficient way of filling space in a layered, ordered system with tilted molecules and/or lead to the greatest degree of inter-molecular attraction [46].

It may be supposed that the double bond at position 2 in the terminal alkenyloxy chain leads to the reduction in the (already small) number of non-linear conformations possible for the first four atoms in the chain. This change in the molecular shape could also result in a stronger interaction between the chains and the aromatic core of adjacent molecules. Whichever of these two effects may be dominant an increase in the smectic and nematic transition temperatures would be expected. This is reflected in the high liquid crystal transition temperatures of most of these compounds (see table 2).

The degree of chain-stiffening (i.e. the reduction in the number of non-preferred, antiperiplanar, zig-zag conformations) could be expected to decrease directly with the distance of the *trans* double bond from the core of the molecule. Thus, the effect on the

liquid crystal transition temperatures can be expected to decrease as the *trans* double bond moves from position 2 to 4 and then to 6. This is observed to be the case for the nonyl homologues, but not always for the heptyl and octyl materials (see table 1). This serves to demonstrate the complexity of the molecular situation. A double bond seems to be detrimental to mesophase formation near to the end of the chain, perhaps due to induced dipole–dipole interactions between adjacent chains (see the general decreases in the liquid crystal transition temperatures of the ethers containing a carbon–carbon double bond in a terminal position of the alkenyloxy chain). This is difficult to explain on steric grounds.

The effect of the *cis* double bond can be assumed to be to deform the linear conformation. This has been clearly demonstrated in the accompanying publication [46]. This should decrease the smectic C transition temperature as well as all the other liquid crystal transition temperatures (as is indeed observed to be the case). The enlarged degree of asymmetry should also lead to a lower melting point.

With respect to the melting point, there are parallels with natural products. For example, the melting point of a fat or oil depends on the presence, number and type of carbon–carbon double bonds in the alkyl chain. If all the alkyl groups of the fatty acid portion of the molecule are saturated, the chains can align themselves in a regular pattern, with staggered zig-zag conformations along the chain. Molecules of this type can pack reasonably regularly on a crystal lattice (due to the high degree of symmetry and uniformity) and, therefore, they usually form solids at room temperature. The introduction of a *cis* double bond in the alkyl group of fatty acids (the double bonds of most naturally occurring fatty acids are *cis*) prevents such even packing of the chains and lowers the melting point (for example consider the three unsaturated fatty acids: *cis*:-oleic acid, mp 13°C; *cis*-, *cis*-linoleic acid, mp – 5°C; *cis*-, *cis*-, *cis*-linolenic acid, mp – 11°C). Thus, in general, naturally occurring oils (liquids) contain a higher percentage of unsaturated alkyl groups (with *cis* double bonds) than fats (solids) do. However, no naturally occurring straight chain fatty acid is mesomorphic, thus, confirming that a fully-extended zig-zag conformation of the chain is not conducive to mesophase formation.

A *cis* double bond in nematic systems has so far been seen to lead to large depressions in the nematic–isotropic transition temperatures compared to the corresponding systems with a carbon–carbon single bond [59]. This is in contrast to the nematic mesophases at relatively elevated temperatures (see table 3) for some of the materials reported here (where a predominantly linear conformation of the chain is postulated).

Although such arguments may be useful as models in order to better understand the observed changes in the liquid crystal transition temperatures of the alkenyloxy ethers 1–96, they are necessarily somewhat simplistic in comparison to the complex intra/inter-molecular attractions actually responsible for them. The situation with regard to the trends in the observed liquid crystals is also extremely complicated and average values have been quoted in order to be able to comment at all on such a large number of data. The observed effects seem to be more pronounced as the length of the chain attached to the pyrimidine ring increases (i.e. from heptyl to octyl and then nonyl). There are a number of individual deviations from these general trends (especially for the *trans*-substituted members of the heptyl series) evident from reference to tables 1–5. In order to facilitate an independent interpretation of the large number of data collated in tables 1–4, the liquid crystal transition temperatures of the analogous *n*-alkyl/alkoxy chain parent compounds (1, 8, 15 and 97–119, i.e. those without an

additional carbon-carbon double bond in the terminal alkoxy chain) have also been listed in table 5. The author's own values have been quoted where possible as these are in general higher than those found in the literature [45].

5. Experimental

The liquid crystal transition temperatures of the compounds prepared recorded in tables 1-5 were determined by optical microscopy using a Leitz Otholux II POL BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All the monotropic liquid crystal phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. When necessary the Mettler stage could be cooled (-50°C) by allowing nitrogen gas, cooled by liquid nitrogen, 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 capillar chromatograph equipped with a 25 m OV 61 column and GP-100 graphics printer was used. TLC plates (4 cm \times 8 cm) coated with SiO_2 SIL/G/UV₂₅₄ (Machery-nagel, Düren, Germany) were utilized. The purity of the final liquid crystalline products (1-119) 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.

5.1. 5-Heptyl-2-[4-(octyloxy)phenyl]pyrimidine (1)

A mixture of 1-bromooctane (Fluka) (8.6 g, 0.044 mol), 4-(5-heptyl-2-pyrimidinyl)phenol [45] (10.0 g, 0.037 mol), potassium carbonate (1.02 g, 0.0074 mol) and *N,N*-dimethylformamide (500 ml) was stirred at room temperature overnight, then filtered to remove inorganic material. The filtrate was diluted with water (1000 ml) and then extracted into diethyl ether (3 \times 100 ml). The combined organic extracts were washed with water (2 \times 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 (13.2 g, 94 per cent), $T_{\text{CN}} = 51^{\circ}\text{C}$; ($T_{\text{SCN}} = 45^{\circ}\text{C}$); $T_{\text{NI}} = 72^{\circ}\text{C}$. IR (KBr) ν_{max} : 923, 2851, 1582, 1543, 1513, 1426, 1254, 1025, 847, 790 cm^{-1} . MS m/z : 382 (M^+), 270 ($\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}^+$); 185 ($\text{C}_{11}\text{H}_9\text{N}_2\text{O}^+$). ^1H NMR (CDCl_3): 0.88-0.89 (6H, overlapping peaks), 1.29 (18 H, overlapping peaks), 1.62 (2 H, overlapping peaks), 2.60 (2 H, t), 4.02 (2 H, t), 6.96-7.00 (2 H, d), 8.32-8.36 (2 H, d), 8.57 ppm (2 H, s). The liquid crystal transition temperatures of this ether (1) and similar ethers (8, 15 and 97-119) prepared using this general method are collated in the tables 1 and 5.

5.2. 5-Heptyl-2-[4-((E)-2-octenyloxy)phenyl]pyrimidine (2)

A solution of (*E*)-2-octen-1-ol (Johnson Matthey) (0.35 g, 0.0019 mol), 4-(5-heptyl-2-pyrimidinyl)phenol [45] (0.5 g, 0.0019 mol), diethyl azodicarboxylate (0.32 g, 0.0019 mol), triphenylphosphine (0.49 g, 0.0019 mol) and tetrahydrofuran (25 ml) was stirred at room temperature overnight and then evaporated down. The solid residue

was taken up in warm hexane (25 ml), filtered to remove precipitate ($\text{P}(\text{Ph}_3)\text{O}$) 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 (0.37 g, 53 per cent), $T_{\text{CN}} = 38^\circ\text{C}$; ($T_{\text{ScN}} = 35^\circ\text{C}$); $T_{\text{NI}} = 68^\circ\text{C}$. IR (KBr) ν_{max} : 2955, 2926, 1655, 1583, 1429, 1248, 1005, 971, 847, 797 cm^{-1} . MS m/z : 380 (M^+), 270 ($\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}^+$), 185 ($\text{C}_{11}\text{H}_9\text{N}_2\text{O}^+$). $^1\text{H NMR}$ (CDCl_3): 0.86–0.91 (6 H, overlapping peaks), 1.28–1.44 (14H, overlapping peaks), 1.64 (2H, t), 2.05–2.13 (2 H, q), 2.56–2.62 (2 H, t), 4.53–4.55 (2 H, t), 5.68–5.93 (2 H, overlapping peaks), 6.98–7.26 (2 H, d), 8.32–8.36 (2 H, d), 8.57 ppm (2 H, s). The liquid crystal transition temperatures of this ether (**2**) and similar ethers (**9**, **16** and **22–45**) prepared using this general method are recorded in tables 1 and 2.

5.3. 5-Heptyl-2-[4-((Z)-3-octenyloxy)phenyl]pyrimidine (**3**)

A solution of (Z)-3-octen-1-ol (K and K Laboratories) (0.35 g, 0.0019 mol), 4-(5-heptyl-2-pyrimidinyl)phenol [45] (0.5 g, 0.0019 mol), diethyl azodicarboxylate (0.32 g, 0.0019 mol), triphenylphosphine (0.49 g, 0.0019 mol) and tetrahydrofuran (25 ml) was stirred at room temperature overnight and then worked up and purified as described above to yield the pure ether (0.36 g, 52 per cent), $T_{\text{CSA}} = 28^\circ\text{C}$; $T_{\text{SAN}} = 43^\circ\text{C}$; $T_{\text{NI}} = 44^\circ\text{C}$. IR (KBr) ν_{max} : 2956, 2926, 1655, 1608, 1584, 1542, 1431, 1248, 847, 796 cm^{-1} . MS m/z : 380 (M^+), 270 ($\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}^+$), 185, ($\text{C}_{11}\text{H}_9\text{N}_2\text{O}^+$). $^1\text{H NMR}$ (CDCl_3): 0.88 (3 H, overlapping peaks), 1.28–1.44 (12 H, overlapping peaks), 2.08 (2 H, t), 2.56–2.62 (2 H, t), 4.00–4.06 (2H, t), 5.48–5.53 (2 H, overlapping peaks), 6.96–7.00 (2 H, d), 8.32–8.36 (2 H, d), 8.57 ppm (2 H, s). The liquid crystal transition temperatures of this ether (**3**) and similar ethers (**10**, **17** and **46–69**) prepared using this general method are collated in tables 1 and 3.

5.4. 5-Heptyl-2-[4-((E)-4-octenyloxy)phenyl]pyrimidine (**4**)

A solution of (E)-4-octen-1-ol [53] (0.35 g, 0.0019 mol), 4-(5-heptyl-2-pyrimidinyl)phenol [45] (0.5 g, 0.0019 mol), diethyl azodicarboxylate (0.32 g, 0.0019 mol), triphenylphosphine (0.49 g, 0.0019 mol) and tetrahydrofuran (25 ml) was stirred at room temperature overnight and then worked up and purified as described above to yield the pure ether (0.28 g, 40 per cent), $T_{\text{CSc}} = 39^\circ\text{C}$; $T_{\text{ScN}} = 45^\circ\text{C}$; $T_{\text{NI}} = 65^\circ\text{C}$. IR (KBr) ν_{max} : 2956, 2927, 1600, 1584, 1542, 1431, 1256, 1167, 967, 848 cm^{-1} . MS m/z : 380 (M^+), 270 ($\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}^+$), 185, ($\text{C}_{11}\text{H}_9\text{N}_2\text{O}^+$). $^1\text{H NMR}$ (CDCl_3): 0.85–0.91 (6 H, overlapping peaks), 1.28 (10 H, overlapping peaks), 1.64 (2 H, t), 1.84–1.98 (4 H), 2.18 (2 H, t), 2.56–2.62 (2 H, t), 4.00–4.06 (2 H, t), 5.37 5.56 (2 H, overlapping peaks), 6.95–7.00 (2 H, d), 8.32–8.36 (2 H, d), 8.57 ppm (2 H, s). The liquid crystal transition temperatures of this ether (**4**) and similar ethers (**11** and **18**) prepared using this general method are given in table 1.

5.5. 5-Heptyl-2-[4-((Z)-5-octenyloxy)phenyl]pyrimidine (**5**)

A solution of (Z)-5-octen-1-ol (K and K Laboratories) (0.35 g, 0.0019 mol), 4-(5-heptyl-2-pyrimidinyl)phenol [45] (0.5 g, 0.0019 mol), diethyl azodicarboxylate (0.32 g, 0.0019 mol), triphenylphosphine (0.49 g, 0.0019 mol) and tetrahydrofuran (25 ml) was stirred at room temperature overnight and then worked up and purified as described above to yield the pure ether (0.14 g, 20 per cent), $T_{\text{CSc}} = 2^\circ\text{C}$; $T_{\text{ScSA}} = 24^\circ\text{C}$; $T_{\text{SAN}} = 47^\circ\text{C}$; $T_{\text{NI}} = 53^\circ\text{C}$. IR (KBr) ν_{max} : 2955, 2927, 1608, 1584, 1542, 1431, 1248, 1168, 846, 796 cm^{-1} . MS m/z : 380 (M^+), 270 ($\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}^+$), 185, ($\text{C}_{11}\text{H}_9\text{N}_2\text{O}^+$). $^1\text{H NMR}$ (CDCl_3): 0.85–1.00 (6 H, overlapping peaks), 1.27–1.31 (8 H, overlapping

peaks), 1.51–1.61 (4 H, overlapping peaks), 1.79–1.86 (2 H, overlapping peaks), 2.03–2.13 (4 H, overlapping peaks), 2.56–2.62 (2 H, t), 4.00–4.06 (2 H, t), 5.36–5.38 (2 H), 6.96–7.00 (2 H, d), 8.32–8.36 (2 H, d), 8.57 ppm (2 H, s). The liquid crystal transition temperatures of this ether (5) and similar ethers (12 and 19) prepared using this general method are given in table 1.

5.6. 5-Heptyl-2-[4-((E)-6-octenyloxy)phenyl]pyrimidine (6)

A solution of (E)-6-octen-1-ol [53] (0.35 g, 0.0019 mol), 4-(5-heptyl-2-pyrimidinyl)phenol [45] (0.5 g, 0.0019 mol), diethyl azodicarboxylate (0.32 g, 0.0019 mol), triphenylphosphine (0.49, 0.0019 mol) and tetrahydrofuran (25 ml) was stirred at room temperature overnight and then worked up and purified as described above to yield the pure ether (0.28 g, 40 per cent), $T_{CN} = 53^{\circ}\text{C}$; $T_{NI} = 72^{\circ}\text{C}$. IR (KBr) ν_{max} : 2927, 2852, 1607, 1583, 1543, 1428, 1252, 1167, 967, 847, 797 cm^{-1} . MS m/z : 380 (M^+), 270 ($\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}^+$), 185, ($\text{C}_{11}\text{H}_9\text{N}_2\text{O}^+$). $^1\text{H NMR}$ (CDCl_3): 0.88 (3 H, overlapping peaks), 1.28–1.31 (12 H, overlapping peaks), 1.64–1.65 (5 H, overlapping peaks), 1.81 (2 H, overlapping peaks), 2.01 (2 H, overlapping peaks), 2.56–2.62 (2 H, t), 4.00–4.04 (2 H, t), 5.42–5.45 (2 H, overlapping peaks), 6.95–7.00 (2 H, d), 8.32–8.36 (2 H, d), 8.57 ppm (2 H, s). The liquid crystal transition temperatures of this ether (6) and similar ethers (13 and 20) prepared using this general method are recorded in table 1.

5.7. 5-Heptyl-2-[4-(7-octenyloxy)phenyl]pyrimidine (7)

A mixture of 7-bromo-1-octene (Aldrich) (0.35 g, 0.0019 mol), 4-(5-heptyl-2-pyrimidinyl)phenol [45] (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), $T_{CSA} = 36^{\circ}\text{C}$; ($T_{SCSA} = 33^{\circ}\text{C}$); $T_{SAN} = 48^{\circ}\text{C}$; $T_{NI} = 62^{\circ}\text{C}$. IR (KBr) ν_{max} : 2927, 2851, 1641, 1607, 1584, 1543, 1428, 1253, 917, 851, 790 cm^{-1} . MS m/z : 380 (M^+), 270 ($\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}^+$), 185, ($\text{C}_{11}\text{H}_9\text{N}_2\text{O}^+$). $^1\text{H NMR}$ (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 ppm (2 H, s). The liquid crystal transition temperatures of this ether (7) and similar ethers (14, 21 and 70–96) prepared using this general method are collated in tables 1 and 4.

The author expresses his gratitude to Mr C. Haby for technical assistance in the preparation of the compounds. Dr W. Arnold (NMR), Mr W. Meister (MS), Dr M. Grosjean (IR), Mr F. Wild and Mr B. Halm (DTA) are thanked for the measurement and interpretation of the required spectra.

References

- [1] DEMUS, D., DEMUS, H., and ZASCHKE, H., 1974, *Flüssige Kristalle in Tabellen* Vol. I, (Deutscher Verlag für Grundstoff Industrie, Leipzig).
- [2] DEMUS, D., and ZASCHKE, H., 1984, *Flüssige Kristalle in Tabellen*, Vol. II, (Deutscher Verlag für Grundstoff Industrie, Leipzig).
- [3] SMITH, K., 1985, *Electronics*, p. 26.
- [4] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.
- [5] CLARK, N. A., HANSCHY, M. A., and LAGERWALL, S. T., 1983, *Molec. Crystals liq. Crystals*, **94**, 213.

- [6] BERESNEV, L. A., CHIGRINOV, V. G., DERGACHEV, D. I., POSHIDAEV, E. P., FÜNFSCHILLING, J., and SCHADT, M., 1989, *Liq. Crystals*, **5**, 1171.
- [7] FÜNFSCHILLING, J., and SCHADT, M., 1989, *J. appl. Phys.*, **66**, 3877.
- [8] FÜNFSCHILLING, J., and SCHADT, M., 1990, *Proc. SID*, **31**, 119.
- [9] FÜNFSCHILLING, J., and SCHADT, M., 1990, *S.I.D. 90 Digest*, 106.
- [10] FÜNFSCHILLING, J., and SCHADT, M., 1991, *Jap. J. appl. Phys.*, **30**, 741.
- [11] FÜNFSCHILLING, J., 1992, *Proc. 21st Freiburger Arbeitstagung Flüssigkristalle*.
- [12] SCHADT, M., 1993, *Liq. Crystals*, **14**.
- [13] CHANDANI, A. D. L., HAGIWARA, T., SUZUKI, Y., OUCHI, Y., TAKEZOE, H., and FUKADA, A., 1988, *Jap. J. appl. Phys.*, **27**, L729.
- [14] JOHN, M., CHANDANI, A. D. L., LEE, J., OUCHI, Y., TAKEZOE, H., FUKADA, A., ITOH, K., and KITAZUME, T., 1989, *Proc. Japan Display*, p. 22.
- [15] REIFENRATH, V., KRAUSE, J., PLACH, H.-J., and WEBER, G., 1989, *Liq. Crystals*, **5**, 159.
- [16] CHAN, L. K. M., GRAY, G. W., and LACEY, D. L., 1985, *Molec. Crystals liq. Crystals*, **123**, 185.
- [17] GRAY, G. W., HIRD, M., LACEY, D. L., and TOYNE, K. J., 1989, *J. chem. Soc. Perkin Trans. II*, p. 2041.
- [18] KELLY, S. M., BUCHECKER, R., SCHADT, M., and FROMM, H.-J., 1988, *Ferroelectrics*, **85**, 385.
- [19] KELLY, S. M., and BUCHECKER, R., 1988, *Helv. chim. Acta*, **71**, 451; *Ibid*, **71**, 461.
- [20] KELLY, S. M., 1989, *Liq. Crystals*, **5**, 171.
- [21] KELLY, S. M., 1990, *Helv. chim. Acta*, **72**, 594.
- [22] KELLY, S. M., LEENHOUTS, F., and FÜNFSCHILLING, J., 1991, *Liq. Crystals*, **10**, 243.
- [23] LE PESANT, J. P., MOUREY, B., HARENG, M., DECOBERT, G., and DUBOIS, J. C., 1984, *Proc. Paris Display*, p. 217.
- [24] GOODBY, J. W., 1986, *Science, N.Y.*, **231**, 350.
- [25] GOODBY, J. W., and LESLIE, T., 1984, *Molec. Crystals liq. Crystals*, **110**, 175.
- [26] GOODBY, J. W., 1983, *Ferroelectrics*, **49**, 275.
- [27] BONE, M. F., COATES, D., GRAY, G. W., LACEY, D. L., TOYNE, K. J., and YOUNG, D. J., 1986, *Molec. Crystals liq. Crystal Lett.*, **3**, 189.
- [28] BONE, M. F., BRADSHAW, M. J., CHAN, L. K. M., COATES, D., CONSTANT, J., GEMMEL, P. A., GRAY, G. W., LACEY, D. L., and TOYNE, K. J., 1988, *Molec. Crystals liq. Crystals*, **164**, 117.
- [29] BRADSHAW, M. J., BRIMMEL, V., and RAYNES, P., 1987, *Liq. Crystals*, **2**, 107.
- [30] BAHR, C., and HEPPKE, P., 1987, *Molec. Crystals liq. Crystals*, **148**, 29.
- [31] SAKURAI, T., MIKAMI, N., HIGUCHI, R., HONMA, M., OZAKI, M., and YOSHINO, K., 1986, *J. chem. Soc. chem. Commun.*, p. 978.
- [32] INUKAI, T., SAITOH, S., INOUE, H., MIYAZAWA, K., TERASHIMA, K., and FURUKAWA, K., 1986, *Molec. Crystals liq. Crystals*, **141**, 251.
- [33] KODEN, M., KURATATE, T., FUNADA, F., SAKAGUCHI, K., TAKEHIRA, Y., and KITAMURA, Y., 1989, *Proc. Japan Display*, p. 34.
- [34] GEELHAAR, T., KURMEIER, H.-A., and WÄCHTLER, A. E. F., 1989, *Liq. Crystals*, **4**, 1269.
- [35] BOEMELBERG, J., HEPPKE, P., and RANFT, A., 1989, *Z. Naturf. (b)*, **44**, 1127.
- [36] BUCHECKER, R., KELLY, S. M., and FÜNFSCHILLING, J., 1990, *Liq. Crystals*, **8**, 217.
- [37] HIGASHII, T., MINAI, M., KURIMOTO, I., TODA, S., TANI, T., SEKINE, C., and FUJISAWA, K., 1991, EPA 0435632.
- [38] JANULIS, E. P., NOVACK, J., PAPAPOLYMEROU, G. A., TRISTANI-KENDRA, M., and HUFFMAN, W. A., 1988, *Ferroelectrics*, **85**, 375.
- [39] HEMMERLING, W., MÜLLER, I., and WINGEN, R., 1988, *Ferroelectrics*, **85**, 393.
- [40] ESCHER, C., HEMMERLING, W., ILLIAN, G., MÜLLER, I., WEGENER, P., and WINGEN, R., 1990, *13th International Liquid Crystal Conference*, Vancouver, BC, Canada.
- [41] WALBA, D. M., and CLARK, N., 1988, *Ferroelectrics*, **84**, 65.
- [42] KELLY, S. M., BUCHECKER, R., and SCHADT, M., 1988, *Liq. Crystals*, **3**, 1115; 1988, *Ibid*, **3**, 1125.
- [43] KELLY, S. M., and VILLIGER, A., 1988, *Liq. Crystals*, **3**, 1173.
- [44] FÜNFSCHILLING, J., and KELLY, S. M., 1991, *Proc. 20th Freiburger Arbeitstagung Flüssigkristalle*.
- [45] ZASCHKE, H., 1975, *J. pract. Chem.*, **9**, 1173.
- [46] FÜNFSCHILLING, J., KELLY, S. M., and VILLIGER, A., 1993, *Liq. Crystals*, **14**.
- [47] ÖSTERHELD, G., MARUGG, P., RÜHER, R., and GERMAN, A., 1982, *J. Chrom.*, **234**, 99.
- [48] TEXTIER-BOULLET, F., and FOUCAUD, A., 1979, *Synthesis*, p. 884.

- [49] MILLER, A. E. G., BISS, J. W., and SCHWARTZMANN, L. H., 1959, *J. org. Chem.*, **24**, 627.
- [50] MITSUNOBU, O., 1981, *Synthesis*, p. 1.
- [51] CARVALHO, J. F., and PRESTWICH, G. D., 1984, *J. org. Chem.*, **49**, 1251.
- [52] RAPHAEL, R. A., and ROXBURGH, C. M., 1952, *J. chem. Soc.*, p. 3875.
- [53] MORIZAWA, Y., MORI, I., HIYAMA, T., and NOZAKI, H., 1981, *Synthesis*, p. 899.
- [54] JACOBSON, M., KEISER, I., CHAMBERS, D. L., MIYASHITA, D. H., and HARDING, C., 1970, *J. med. Chem.*, **14**, 236.
- [55] APPEL, R., 1975, *Angew. Chem.*, **87**, 863.
- [56] SCHADT, M., and PETRZILKA, M., 1984, *Proc. Paris Display*, p. 53.
- [57] GOODBY, J. W., LESLIE, T., CLADIS, P. E., and FINN, P. L., 1984, *Liquid Crystals and Ordered Fluids*, Vol. 4 (Plenum), p. 89.
- [58] SCHADT, M., PETRZILKA, M., GERBER, P., and VILLIGER, A., 1985, *Molec. Crystals liq. Crystals*, **122**, 241.
- [59] PETRZILKA, M., 1985, *Molec. Crystals liq. Crystals*, **131**, 109.
- [60] SCHADT, M., BUCHECKER, R., VILLIGER, A., LEENHOUTS, F., and FROMM, J., 1986, *I.E.E.E. Trans. Electron Dev.*, **33**, 1187.
- [61] PETRZILKA, M., BUCHECKER, R., LEE-SCHMIEDERER, S., SCHADT, M., and GERMANN, A., 1987, *Molec. Crystals liq. Crystals*, **148**, 123.
- [62] BUCHECKER, R., and SCHADT, M., 1987, *Molec. Crystals liq. Crystals*, **149**, 359.
- [63] SCHADT, M., BUCHECKER, R., and MÜLLER, K., *Liq. Crystals*, **5**, 293.
- [64] SCHADT, M., BUCHECKER, R., and VILLIGER, A., 1990, *Liq. Crystals*, **7**, 519.
- [65] FRECH, C. B., FUNG, B. M., and SCHADT, M., 1988, *Liq. Crystals*, **3**, 713.
- [66] FRECH, C. B., FUNG, B. M., and SCHADT, M., 1989, *S.P.I.E. Proc.*, **1080**, 215.
- [67] RICHTER, W., FUNG, B. M., and SCHADT, M., 1990, *Liq. Crystals*, **8**, 63.