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Synthesis and characterization of a range of heterocyclic liquid crystalline materials incorporating the novel thiophene-pyrimidine moiety

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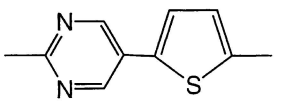
In this structure/property study six 2-(4-alkyloxyphenyl)-5-thiophen-2-ylpyrimidines and thirty-six 2-(4-alkyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines were synthesized to evaluate the effect of the introduction of heterocyclic rings on the liquid crystalline (LC) behaviour of mesogens. The 'bent' nature of the structure of the 2-(4-alkyloxyphenyl)-5-thiophen-2-yl-pyrimidines, due to the presence of the thiophene ring, was further exaggerated in the 2-(4-alkyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines by the incorporation of an alkyl group at the 5-position in the thiophene ring. This simple change in structure led to a remarkable change in the LC behaviour of the mesogens. From a series of mesogens having high melting points and exhibiting monotropic nematic phases, the incorporation of the alkyl group gave a series of three-ring mesogens with relatively low melting points (60–80°C), and exhibiting a range of tilted smectic phases, including SmI, SmC and SmC_{alt} phases.

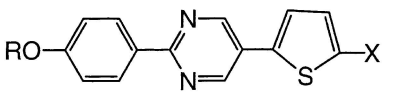
1. Introduction

In previous work on ferro- and antiferro-electric liquid crystal (LC) materials [1], we concentrated on the novel use of the thiophene-pyrimidine moiety, structure 1. Although there are numerous examples in the literature of LC compounds exhibiting ferro- and antiferro-electric chiral smectic C phases, there are very few examples of LC materials incorporating the thiophene ring. This is despite the fact that thiophene-based LC materials (a) have lower melting points than the 1,4-phenylene analogues, (b) promote negative dielectric anisotropy and (c) have a tendency to generate a range of different liquid crystalline phases [2–7]. The pyrimidine ring is used extensively in the synthesis of ferroelectric LC materials exhibiting fast response times and low melting points [8].

Before our initial communication, there had been no reports on the use of the thiophene-pyrimidine moiety in the formation of LC materials. Here, we report recent results on the synthesis, characterization and LC properties of a range of novel LC materials incorporating the thiophene-pyrimidine moiety, structure 1. The materials targeted have the general structure 2, and have been designed to provide an interesting insight into the effect of molecular structure on the LC behaviour of these novel heterocyclic compounds. Full details of synthesis and characterization are given in § 3.



(1)



(2)

X = H or alkyl

R = alkyl

2. Results and discussion

2.1. *2-(4-Alkyloxyphenyl)-5-thiophen-2-ylpyrimidines* ***8–13***

The first series of materials to be synthesized were the 2-(4-alkyloxyphenyl)-5-thiophen-2-ylpyrimidines (structure 2, $X = H$, compounds **8**–**13**). The transition

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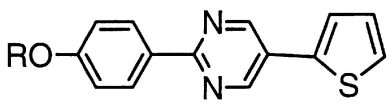
temperatures for these compounds are given in table 1. Interestingly, all six compounds exhibited a short-lived monotropic nematic phase that was identified by the two- and four-brush defects in the nematic schlieren texture.

2.2. *2-(4-Alkyloxyphenyl)-5-(5-alkylthiophen-2-yl)-pyrimidines **14**–**49***

The incorporation of the second terminal alkyl group into structure 2 to yield the 2-(4-alkyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines (structure 2, X = alkyl, compounds **14**–**49**) had a dramatic effect on the LC thermal behaviour of the compounds. The incorporation of the alkyl group exaggerated the 'bent' nature of the molecule caused by the presence of the thiophene ring. This dramatically decreased the melting point of the compounds by 30–40°C and, as we shall see later, reduced the tendency of the compounds to form the nematic phase but enhanced their ability to form smectic phases, especially the tilted SmI and SmC phases. Even in the few 2-(4-alkyloxyphenyl)-5-(5-alkylthiophen-2-yl) that do form the nematic phase (compounds **14**, **20**, **26** and **32**), the N–I transition temperatures are some 40–45°C higher than those found in the 2-(4-alkyloxyphenyl)-5-thiophen-2-ylpyrimidines. This is expected, since the incorporation of an alkyl group will increase the extended nature of the molecule.

A large number of 2-(4-alkyloxyphenyl)-5-(5-alkythiophen-2-yl)pyrimidines were synthesized and their liquid crystalline behaviour investigated by a combination of polarising optical microscopy (POM), differential scanning calorimetry (DSC) and mixture studies. In all, 36 LC compounds were synthesized and these can be divided into six series, each containing six LC compounds. In each series the alkyloxy group of the LC compound (*R*O in structure 2) remains constant within the series, while the alkyl group (X in structure 2) is varied from hexyl to decyl, plus the dodecyl homologue.

Table 1. Structure and transition temperatures (°C) for the 2-(4-alkyloxyphenyl)-5-thiophen-2-ylpyrimidines **8**–**13**.



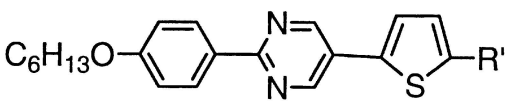
		Transition temperatures (°C)				
Compound	*R*	Cr		N		I
8	6	•	115.1	•	(107.8)	•
9	7	•	104.9	•	(100.5)	•
10	8	•	110.8	•	(107.4)	•
11	9	•	112.2	•	(102.5)	•
12	10	•	107.7	•	(104.9)	•
13	12	•	106.4	•	(106.2)	•

6 = C_6H_{13}, 7 = C_7H_{15} etc.

2.2.1. *Series 1: 2-(4-hexyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **14**–**19***

The structure and transition temperatures for the 2-(4-hexyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines are given in table 2. The series, as a whole, gave a variety of liquid crystalline phases which included crystal (J/G), smectic (SmI, SmC_{alt}, SmC, SmA) and nematic phases. The only phase to be exhibited by all the members of the series studied was the SmC phase. From the data in table 2 it seems that the structure of these LC materials is conducive to the formation of tilted smectic phases, with only the hexyloxy (SmA, nematic) and the heptyloxy homologues (SmA) (compounds **14** and **15** respectively) exhibiting non-tilted smectic or nematic phases. This is not surprising since the incorporation of the 2,5-disubstituted thiophene ring will give rise to a non-linear or slightly

Table 2. Structure and transition temperatures (°C) for the 2-(4-hexyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **14**–**19** (series 1).



		Transition temperatures (°C)															
Compound	*R′*	Cr		J/G		SmI		SmC_{alt}		SmC		SmA		N		I	
14	6	•	75.0							•	145.4	•	149.7	•	153.7	•	
15	7	•	69.5					•	85.6	•	149.1	•	154.7			•	
16	8	•	88.9			•	98.9			•	154.6					•	
17	9	•	61.2	•	64.2	•	104.9			•	154.7					•	
18	10	•	68.2	•	78.1	•	109.0			•	152.6					•	
19	12	•	74.6	•	95.9	•	117.4			•	150.9					•	

C = C_6H_{13}, 7 = C_7H_{15} etc.

bent nature to the structure of the molecule. The core angle of the 2,5-disubstituted thiophene ring is 148° [9] and this, coupled to fact that the thiophene ring is in a lateral position within the structure of the compounds, will give a hockey-stick-like structure to the molecule.

The thermal stability of all the tilted smectic phases increased on increasing the size of the alkyl group *R′*. The only slight exception was found for the SmC phase, where the thermal stability for this phase rose initially, but then levelled off for the octyl/nonyl homologues and began to fall after the nonyl homologue **10**.

The most unusual phase behaviour found in this, and the following series of compounds, is the appearance of the SmC_{alt} phase in all the heptyl homologues (in series 3 both the heptyl and octyl homologues exhibit this phase). This behaviour will be discussed later, but it does seem that the appearance of this phase is due to the presence of the heptyl group in the molecule and is not influenced by the presence or size of the alkyloxy group, even though both groups are in a terminal position in the structure of these heterocyclic LC materials.

2.2.2. *Series 2: 2-(4-heptyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **20**–**25***

The structure and transition temperatures for the 2-(4-heptyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines are given in table 3. The phase sequences for series 2 were very similar to those found for series 1, except that the nonyl homologue **23** did not exhibit the J/G phase. Again, the heptyl homologue **21** exhibited the SmC_{alt} phase, which has a similar transition temperature to the SmC_{alt} phase (and associated enthalpy) to that found for the heptyl homologue in series 1. The thermal stabilities (in terms of the transition temperatures) for the nematic, SmA and SmC phases for series 2 compounds were slightly lower than those found for series 1 compounds, but the thermal stabilities for the more ordered phases, the SmI and J/G phases, were slightly higher. However, all the transition temperatures for the corresponding series 1 and 2 compounds were within 2–3°C of each other.

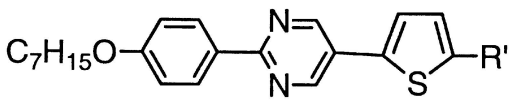
2.2.3. *Series 3: 2-(4-octyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **26**–**31***

The structure and transition temperatures for the 2-(4-octyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines are given in table 4. The phase sequences for the hexyl, heptyl and dodecyl homlogues are similar to those found in series 1 and 2, with again the heptyl homologue **27** exhibiting the SmC_{alt} phase. However, in this series alone, the octyl homologue **28** exhibited the SmC_{alt} phase at the expense of the SmI phase. It seems that in all these compounds either the SmI or SmC_{alt} phase is exhibited, but not both. For the nonyl and decyl homologues in series 3 we see the appearance of the SmF phase, although this and the J/G phase were observed only by POM. It is interesting to note that all the transition temperatures for the corresponding series 1, 2 and 3 compounds are within 2–3°C of each other, with the exception of the J/G–SmI transition.

2.2.4. *Series 4: 2-(4-nonyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **32**–**37***

The structure and transition temperatures for the 2-(4-nonyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines are given in table 5. On changing the alkyloxy group form octyloxy to nonyloxy, both the SmF and J/G phases disappear, and for the octyl homologue **34** the SmC_{alt} phase disappears at the expense of the re-emergence of the SmI phase. The transition temperatures for both the SmC_{alt} and SmI phases are very similar to those found for compounds in series 1, 2 and 3, but there is a decrease in the thermal stabilities of both the SmC and SmA phases, especially for the early members of series 4.

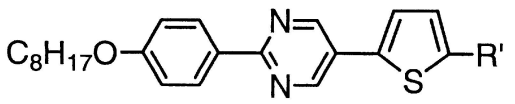
Table 3. Structure and transition temperatures (°C) for the 2-(4-heptyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **20**–**25** (series 2).



		Transition temperatures (°C)															
Compound	*R′*	Cr		J/G		SmI		SmC_{alt}		SmC		SmA		N		I	
20	6	•	76.2							•	141.7	•	149.3	•	150.2	•	
21	7	•	66.2					•	88.1	•	148.9	•	153.6			•	
22	8	•	78.1			•	100.4			•	152.2					•	
23	9	•	63.9			•	105.2			•	153.5					•	
24	10	•	74.6	•	75.1	•	110.8			•	151.3					•	
25	12	•	64.6	•	93.4	•	115.3			•	147.9					•	

6 = C_6H_{13}, 7 = C_7H_{15} etc.

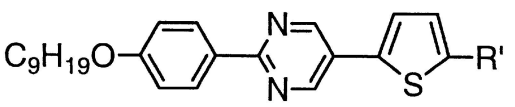
Table 4. Structure and transition temperatures (°C) for the 2-(4-octyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **26**–**31** (series 3).



		Transition temperatures (°C)																					
Compound	R'	Cr		J/G		SmF		SmI		SmC_{alt}		SmC		SmA		N		I					
26	6	•	83.3									•	145.0	•	150.3	•	152.0	•					
27	7	•	86.1							•	88.9	•	150.2*	•	152.7			•					
28	8	•	78.0			•	71.6			•	97.9	•	153.5					•					
29	9	•	68.1	•	91.9*	•	92.3*	•	106.0			•	153.1					•					
30	10	•	79.3	•	91.7	•	92.9	•	110.8			•	151.5					•					
31	12	•	72.6	•	94.6			•	118.4			•	149.6					•					

* denotes that the transition was not detected by DSC.
$6 = C_6H_{13}$, $7 = C_7H_{15}$ etc.

Table 5. Structure and transition temperatures (°C) for the 2-(4-nonyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **32**–**37** (series 4).



		Transition temperatures (°C)															
Compound	R'	Cr		SmI		SmC_{alt}		SmC		SmA		N		I			
32	6	•	65.6					•	138.2	•	147.1	•	147.3	•			
33	7	•	84.2			•	86.1	•	147.7*	•	151.4			•			
34	8	•	81.0	•	99.9			•	150.6					•			
35	9	•	51.4	•	105.6			•	150.8					•			
36	10	•	67.7	•	111.5			•	150.3					•			
37	12	•	71.6	•	117.3			•	147.7					•			

* denotes that the transition was not detected by DSC.
$6 = C_6H_{13}$, $7 = C_7H_{15}$ etc.

2.2.5. *Series 5: 2-(4-decyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **38**–**43***

The structure and transition temperatures for the 2-(4-decyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines are given in table 6.

2.2.6. *Series 6: 2-(4-dodecyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **44**–**49***

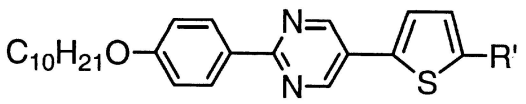
The structure and transition temperatures for the 2-(4-dodecyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines are given in table 7.

The phase sequences exhibited by series 5 and 6 compounds are very similar, i.e. SmI, SmC_{alt}, SmC and SmA. The nematic phase has disappeared but the two heptyl homologues, **39** and **45**, still exhibit the SmC_{alt} phase. The downward trend of the thermal stabilities of both the SmA and SmC phases continues in series 5 and 6 but the thermal stability for the SmC_{alt} phase has now also decreased. However, the thermal stability of the SmI phase remains fairly constant throughout the six series of compounds.

2.3. *The SmC_{alt} phase*

The SmC_{alt} phase was identified by a combination of optical POM and DSC. We would like to thank Professor J. W. Goodby for his valuable assistance in the identification of the SmC_{alt} phase. 2-(4-Hexyloxyphenyl)-5-(5-heptylthiophen-2-yl)pyrimidine was used for this work. Upon cooling from the isotropic liquid a smectic A phase is formed. The smectic A phase separates from the isotropic liquid in the form of batonnets, which immediately coalesce to form focal-conics (see figure 1).

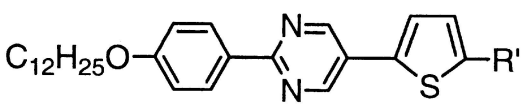
Table 6. Structure and transition temperatures (°C) for the 2-(4-decyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **38**–**43** (series 5).



		Transition temperatures (°C)										
Compound	*R′*	Cr		SmI		SmC_{alt}		SmC		SmA		I
38	6	•	68.1					•	136.5	•	145.8	•
39	7	•	82.2			•	84.7	•	145.6	•	150.8	•
40	8	•	79.5	•	98.6			•	149.4			•
41	9	•	60.1	•	105.3			•	148.7			•
42	10	•	74.5	•	111.3			•	149.0			•
43	12	•	73.5	•	117.9			•	146.7			•

$6 = C_6H_{13}$, $7 = C_7H_{15}$ etc.

Table 7. Structure and transition temperatures (°C) for the 2-(4-dodecyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines **44**–**49** (series 6).



		Transition temperatures (°C)										
Compound	R′	Cr		SmI		SmC_{alt}		SmC		SmA		I
44	6	•	68.5					•	135.2	•	145.2	•
45	7	•	64.9			•	80.1	•	137.4	•	146.7	•
46	8	•	81.9	•	95.4			•	146.9			•
47	9	•	66.5	•	104.5			•	146.2			•
48	10	•	74.4	•	111.2			•	147.0			•
49	12	•	62.0	•	118.0			•	144.2			•

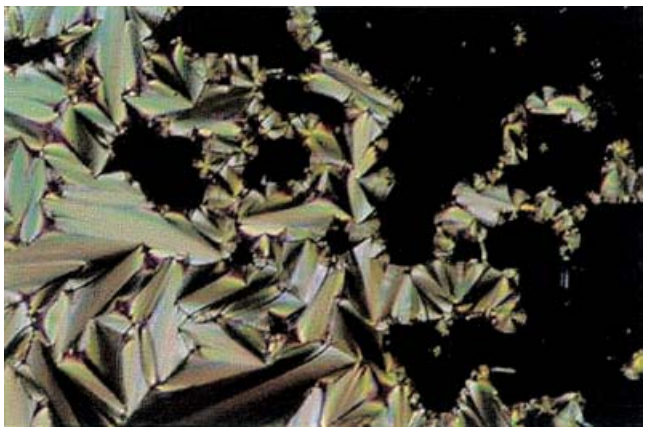


Figure 1. Focal-conic fan texture of the smectic A phase of 2-(4-hexyloxyphenyl)-5-(5-heptylthiophen-2-yl)pyrimidine **15** at 153°C.

The smectic A phase was characterized from its defect texture, which exhibited focal-conic (left-hand side of figure 1) and homeotropic (right-hand side of figure 1) textures. The focal-conic domains were characterized by their elliptical and hyperbolic lines of optical discontinuity. On further cooling the homeotropic texture became schlieren (right-hand side of figure 2), whereas the focal-conic domains became broken and patchy. The schlieren texture exhibited four-brushed singularities but with no two-brush singularities, indicating that the phase was smectic C (see figure 2).

On further cooling the schlieren defects disappeared and returned to a homeotropic texture. However, the focal-conic domains, although becoming less patchy, showed grain boundary lines parallel to the layers, indicating that the phase has long range out-of-plane order (figure 3). Upon cooling this texture the grain boundary lines remained, indicating that they were not transition bars associated with a transition to a crystal B phase. Moreover, the presence of the grain boundaries also indicated that the phase cannot be a hexatic phase as this has a fluid texture and can be defined in three dimensions.

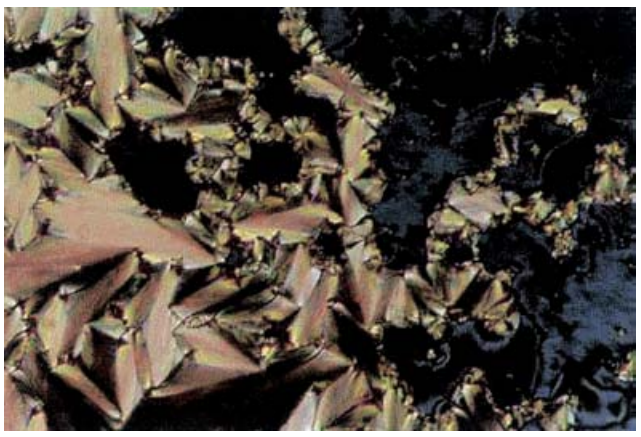


Figure 2. Broken focal-conic fan texture and schlieren texture of the smectic C phase of 2-(4-hexyloxyphenyl)-5-(5-heptylthiophen-2-yl)pyrimidine **15** at 148°C.

The low enthalpy of transition for the SmC_{alt} phase (0.479 J g^{-1}) obtained by DSC, coupled with the presence of grain boundaries and patchy domains in the focal-conic region, indicated that this mesophase cannot be either the crystal B or SmB phases. The mesophase was, therefore, identified to be an alternating smectic C phase [2].

3. Experimental

3.1. *Characterization*

The proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a Jeol JMN-LA 400 FT spectrometer. All NMR spectra were measured in deuterated chloroform as solvent and tetramethylsilane as internal standard. Infrared (IR) spectra were obtained using Perkin-Elmer 487G or 983G spectrophotometers. Samples were prepared as either potassium bromide discs, or if liquid were run on single crystal sodium chloride discs. Mass spectra (MS) were obtained using a Finnigan 1020 GC-MS spectrometer. In the results quoted, M^+ represents the molecular ion and the base peak is represented by (100%). Elemental analysis was carried out on a Fisons EA 1108 CHN instrument.

Differential scanning calorimetry (DSC) thermograms were obtained using a Perkin-Elmer DSC 7, with a TAC 7/PC interface and a controlled cooling accessory. The instrument was calibrated using an indium standard. The heating rate was 10°C min^{-1}. Data analyses were made using Perkin-Elmer Pyris version 3.81 software. Optical microscopy was performed using an Olympus BH-2 polarizing microscope, fitted with a Mettler FP52 hot stage and a Mettler FP5 controller. Samples were prepared as thin films between a glass slide and a glass cover slip.

Column chromatography was carried out using Sorbsil C60 (40–60 µm) as the stationary phase, unless stated otherwise. Thin layer chromatography (TLC) was carried out on aluminium sheets coated in Merck Kieselgel silica gel 60 F_{254}, eluting with dichloromethane. All the compounds in the scheme gave a single spot by TLC.

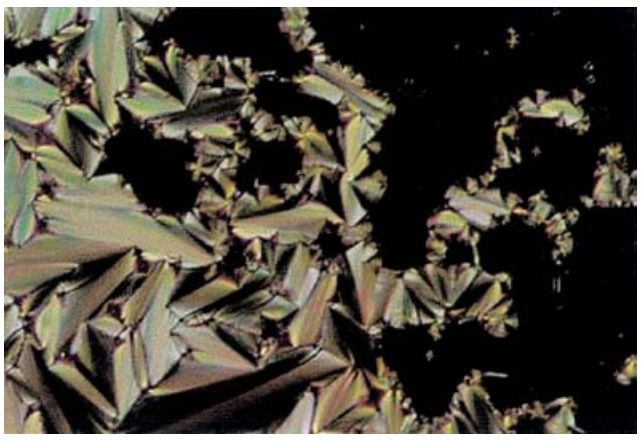


Figure 3. Focal-conic texture of the alternating smectic C phase of 5-(5-heptylthiophen-2-yl)-2-(4-hexyloxyphenyl)pyrimidine **62** at 80°C.

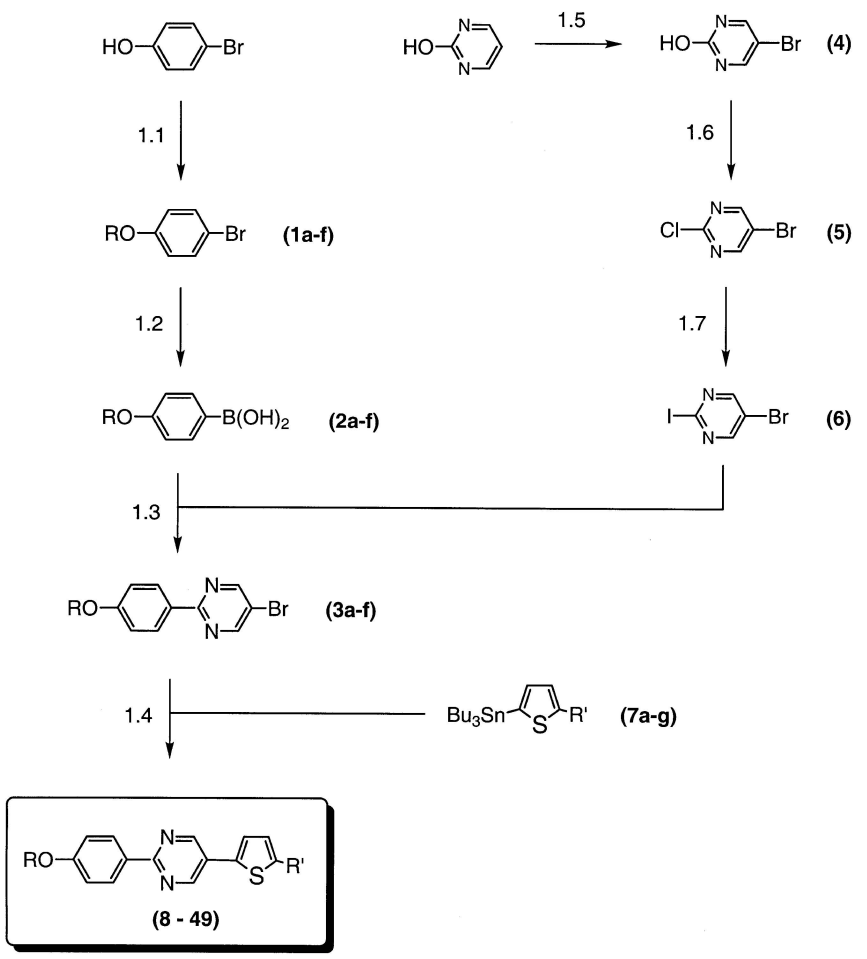
3.2. *Synthesis*

The reaction pathways used to synthesize the liquid crystalline materials are outlined in the scheme. The experimental details for the preparation of 2-(5-alkyl)tributylstannyl thiophenes **7a**–**g** can be found in reference [1]. The methods used to prepare 5-bromo-2-iodopyrimidine **6** are similar to those used by Lewis *et al.* [10].

3.2.1. *1-Bromo-4-hexyloxybenzene **1a***

Anhydrous potassium carbonate (170.0 g, 1.23 mol) was added to a stirred solution of 4-bromophenol (105.5 g, 0.610 mol) and 1-bromohexane (100.0 g, 0.606 mol) in butanone (300 cm^3). The mixture was heated under reflux for 16 h, then allowed to cool to room temperature. It was filtered through Hyflo supercel filter aid to remove inorganic salts and the solvent was removed *in vacuo*. The crude product was distilled under reduced pressure to give 1-bromo-4-hexyloxybenzene **1a** as a clear colourless liquid; 144.1 g (93%), b.p. 168–172°C at 2.5 mm Hg (lit. [10] 100–110°C at 0.1 mm Hg). δ_H (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.28–1.59 (6H, m), 1.75 (2H, quint), 3.88 (2H, t), 6.75 (2H, d), 7.34 (2H, d). IR (thin film) ν_{max} 2938, 2868, 1594, 1492, 1388, 1246, 1073, 822 cm^{-1}. MS *m*/*z* 258 [M^+], 256 [M^+], 174, 172 (100%), 55.

Compounds **1b**–**f** were prepared using the same general procedure as for compound **1a** (yields 86–93%). **1b**–**d** were obtained as clear colourless liquids, while **1e** and **1f** were purified by recrystallization from ethanol to give white crystalline solids [10–12]. The structure of compounds 1b–f were confirmed by ^{1}H NMR, IR and MS.



1.1 RBr, K_2CO_3, butanone
1.2 (i) Mg, THF; (ii) trimethyl borate; (iii) aq. HCl
1.3 $Pd(PPh_3)_4$, DME, aq. Na_2CO_3
1.4 $Pd(PPh_3)_2Cl_2$, DMF
1.5 Br_2, water
1.6 phosphoryl chloride, *N,N*-dimethylaniline
1.7 hydriodic acid, DCM

1a, **2a**, **3a**, $R = C_6H_{13}$; **1b**, **2b**, **3b**, $R = C_7H_{15}$; **1c**, **2c**, **3c**, $R = C_8H_{17}$; **1d**, **2d**, **3d**, $R = C_9H_{19}$; **1e**, **2e**, **3e**, $R = C_{10}H_{21}$; **1f**, **2f**, **3f**, $R = C_{12}H_{25}$.
7a, $R' = C_6H_{13}$; **7b**, $R' = C_7H_{15}$; **7c**, $R' = C_8H_{17}$; **7d**, $R' = C_9H_{19}$; **7e**, $R' = C_{10}H_{21}$; **7f**, $R' = C_{12}H_{25}$; **7g**, $R' = H$.
8, $R = C_6H_{13}$, $R' = H$; **9**, $R = C_7H_{15}$, $R' = H$; **10**, $R = C_8H_{17}$, $R' = H$; **11**, $R = C_9H_{19}$, $R' = H$; **12**, $R = C_{10}H_{21}$, $R' = H$; **13**, $R = C_{12}H_{25}$, $R' = H$.

Series 1 compounds, $R = C_6H_{13}$
14, $R' = C_6H_{13}$; **15**, $R' = C_7H_{15}$; **16**, $R' = C_8H_{17}$; **17**, $R' = C_9H_{19}$; **18**, $R' = C_{10}H_{21}$; **19**, $R' = C_{12}H_{25}$.

Series 2 compounds, $R = C_7H_{15}$
20, $R' = C_6H_{13}$; **21**, $R' = C_7H_{15}$; **22**, $R' = C_8H_{17}$; **23**, $R' = C_9H_{19}$; **24**, $R' = C_{10}H_{21}$; **25**, $R' = C_{12}H_{25}$.

Series 3 compounds, $R = C_8H_{17}$
26, $R' = C_6H_{13}$; **27**, $R' = C_7H_{15}$; **28**, $R' = C_8H_{17}$; **29**, $R' = C_9H_{19}$; **30**, $R' = C_{10}H_{21}$; **31**, $R' = C_{12}H_{25}$.

Series 4 compounds, $R = C_9H_{19}$
32, $R' = C_6H_{13}$; **33**, $R' = C_7H_{15}$; **34**, $R' = C_8H_{17}$; **35**, $R' = C_9H_{19}$; **36**, $R' = C_{10}H_{21}$; **37**, $R' = C_{12}H_{25}$.

Series 5 compounds, $R = C_{10}H_{21}$
38, $R' = C_6H_{13}$; **39**, $R' = C_7H_{15}$; **40**, $R' = C_8H_{17}$; **41**, $R' = C_9H_{19}$; **42**, $R' = C_{10}H_{21}$; **43**, $R' = C_{12}H_{25}$.

Series 6 compounds, $R = C_{12}H_{25}$
44, $R' = C_6H_{13}$; **45**, $R' = C_7H_{15}$; **46**, $R' = C_8H_{17}$; **47**, $R' = C_9H_{19}$; **48**, $R' = C_{10}H_{21}$; **49**, $R' = C_{12}H_{28}$.

Scheme. Synthesis of 2-(4-alkyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines.

3.2.2. *4-Hexyloxyphenylboronic acid* ***2a***

About 20% of a solution of compound **1a** (20.00 g, 77.8 mmol) in dry THF (150 cm^3) was added to ground magnesium turnings (2.10 g, 87.5 mmol) and a few crystals of iodine added to activate the reaction. The reaction mixture was heated under reflux in an atmosphere of dry nitrogen. The remainder of the THF solution was added and the reaction mixture heated under reflux for a further 45 min. The resulting Grignard reagent was cooled to $-78^{\circ}C$ (cardice/acetone), and trimethyl borate (16.47 g, 0.158 mol) was added dropwise, maintaining the temperature below $-70^{\circ}C$. After the addition the temperature was kept below $-60^{\circ}C$ for 1 h. After allowing to warm to room temperature overnight, the mixture was acidified with water (100 cm^3) and aqueous hydrochloric acid (10%, 100 cm^3) and was stirred for 1 h. Organic material was extracted into ether (3×100 cm^3) and the combined ethereal extracts were washed with water (50 cm^3) and dried ($MgSO_4$). The crude product was stirred in hexane (300 cm^3) for 1 h; it was then filtered off and dried *in vacuo* to give 4-hexyloxyphenylboronic acid **2a** as a white solid; 12.9 g (74%). δ_H (400 MHz, DMSO) 0.84 (3H, t), 1.26–1.49 (6H, m), 1.68 (2H, quint), 3.94 (2H, t), 6.81 (2H, d), 7.65 (2H, d), 7.74 (2H, s). IR (KBr) ν_{max} 3600–3200, 2939, 2865, 1607, 1356, 1250, 833 cm^{-1}.

Compounds **2b**–**f** were prepared using the same general procedure as that described for compound **2a** (yields 76–80%). Structure of compounds **2b**–**f** were confirmed by ^1H NMR and IR.

3.2.3. *5-Bromopyrimidin-2-ol hydrochloride/hydrobromide* ***4***

Bromine (120.9 g, 0.757 mol) was added dropwise to a stirred solution of 2-hydroxpyrimidine hydrochloride (100.0 g, 0.752 mol) in water (700 cm^3). After the addition the solution was stirred for 1 h. The solvent was removed *in vacuo* and the orange powder dried *in vacuo* overnight. The crude material was used in the next step without further purification. IR (KBr) ν_{max} 3600–3000, 1728, 1397, 1211, 804 cm^{-1}.

3.2.4. *5-Bromo-2-chloropyrimidine* ***5***

Phosphoryl chloride (500 cm^3) and *N*,*N*-dimethylaniline (50 cm^3) were added to the crude compound **4**. The mixture was heated to reflux under anhydrous conditions until the mixture became a dark brown solution (5 h). The reaction mixture was allowed to cool to room temperature before being carefully poured, in small portions, onto ice (2 dm^3) with stirring. The product was extracted into ether (3×500 cm^3), and the combined ethereal extracts were dried ($MgSO_4$). The crude product was purified by recrystallization (ethanol) to give 5-bromo-2-chloropyrimidine **5** as colourless crystals; 101.3 g (69%), m.p. 77–78°C (lit. [13] 79°C). δ_H (400 MHz, $CDCl_3$) 8.69 (2H, s). IR (KBr) ν_{max} 3033, 1535, 1397, 1360, 1164, 1008, 631, 505 cm^{-1}. MS *m*/*z* 196 [M^+], 194 [M^+] (100%), 192, 106, 104, 86, 77.

3.2.5. *5-Bromo-2-iodopyrimidine* ***6***

Cold hydriodic acid (57% w/w) (333.4 g, 2.60 mol) was added to a cooled ($-5^{\circ}C$) rapidly stirred solution of compound **5** (101.0 g, 0.521 mol) in DCM (300 cm^3). The mixture was stirred at 0°C for 5 h, then neutralized carefully with solid potassium carbonate and decolourized with solid sodium metabisulphite. Water was added until a solution formed. The product was extracted into DCM (3×200 cm^3) and the combined extracts dried ($MgSO_4$). The resulting product was recrystallized (60–80°C petroleum ether) to give 5-bromo-2-iodopyrimidine **6** as colourless needles; 126.1 g (85%), m.p. 98–99°C (lit. [13] 101–102°C). δ_H (400 MHz, $CDCl_3$) 8.53 (2H, s). IR (KBr) ν_{max} 3007, 1516, 1375, 1131, 1002, 747, 622 cm^{-1}. MS *m*/*z* 286 [M^+], 284 [M^+], 178, 159, 157 (100%), 141, 127, 105, 77.

3.2.6. *5-Bromo-2-(4-hexyloxyphenyl)pyrimidine* ***3a***

Tetrakis(triphenylphosphine)palladium(0) (1.22 g, 1.06 mmol) in DME (25 cm^3) was added to a rapidly stirred mixture of compound **6** (10.00 g, 35.1 mmol) in DME (75 cm^3) and sodium carbonate solution (2M, 100 cm^3), which was heated under reflux in an atmosphere of nitrogen. A solution of compound **2a** (7.79 g, 35.1 mmol) in DME (100 cm^3) was added dropwise to the mixture, which was then heated under reflux for 16 h (monitored by TLC). The reaction mixture was allowed to cool to room temperature; water (100 cm^3) was added and the product extracted into DCM (3×100 cm^3). The combined DCM extracts were dried ($MgSO_4$), and the crude product was purified by column chromatography (DCM) and recrystallization (ethanol) to give 5-bromo-2-(4-hexyloxyphenyl)pyrimidine **3a** as a white solid; 7.3 g (62%), m.p. 92–93°C. δ_H (400 MHz, $CDCl_3$) 0.91 (3H, t), 1.34–1.52 (6H, m), 1.81 (2H, quint), 4.03 (2H, t), 6.98 (2H, d), 8.34 (2H, d), 8.76 (2H, s). IR (KBr) ν_{max} 2956, 2871, 1609, 1526, 1422, 1259, 1165, 1059, 790 cm^{-1}. MS *m*/*z* 336 [M^+], 334 [M^+], 252 (100%), 250, 119.

Compounds **3b**–**3f** were prepared using the same general procedure as that for compound **3a** (yields 55–62%). In each case, 35.1 mmol of compound **6** and 35.1 mmol of the appropriate alkyloxyphenylboronic acid **2b**–**2f** were used. Structure of compounds **3b**–**f** confirmed by ^1H NMR, IR and MS.

3.2.7. *2-(4-Hexyloxyphenyl)-5-thiophen-2-ylpyrimidine* ***8***

5-Bromo-2-(4-hexyloxyphenyl)pyrimidine **3a** (2.00 g, 5.97 mmol) and 2-(tributylstannyl)thiophene (2.45 g, 6.57 mmol) were added to anhydrous DMF (50 cm^3) under

an atmosphere of dry nitrogen. The mixture was heated to 100°C and bis(triphenylphosphine)palladium(II) chloride (0.13 g, 0.185 mmol) was added, once a solution had formed. The black reaction mixture was maintained at 100°C for 16 h before being allowed to cool to room temperature. The solvent was removed by distillation under reduce pressure. The crude product was purified by column chromatography (DCM) and recrystallization (hexane) to give 2-(4-hexyloxyphenyl)-5-thiophen-2-yl-pyrimidine **8** as a white powder; 1.5 g (74%). Calc. for $C_{20}H_{22}ON_2S$ C 70.98, H 6.56, N 8.28; found C 70.80, H 6.79, N 8.16%. δ_H (400 MHz, $CDCl_3$) 0.92 (3H, t), 1.31–1.52 (6H, m), 1.82 (2H, quint), 4.03 (2H, t), 6.99 (2H, d), 7.15 (1H, dd), 7.40–7.41 (2H, m), 8.38 (2H, d), 8.95 (2H, s). IR (KBr) ν_{max} 2927, 2857, 1609, 1584, 1518, 1449, 1250, 1169, 844 cm^{-1}. MS *m/z* 338 [M^+], 254 (100%), 108.

Compounds **9**–**13** were prepared using the same general procedure to that described for the preparation of compound **8** and obtained as white powders (yields 70–77%). In each case, 5.97 mmol of the appropriate 5-bromo-2-(4-alkyloxyphenyl)pyrimidine **3b**–**f** and 6.57 mmol of 2-(tributylstannyl)thiophene was used.

9. Calc. for $C_{21}H_{24}ON_2S$ C 71.56, H 6.87, N 7.95; found C 71.78, H 6.92, N 7.88%. δ_H (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.29–1.51 (8H, m), 1.82 (2H, quint), 4.04 (2H, t), 6.99 (2H, d), 7.16 (1H, dd), 7.40–7.42 (2H, m), 8.39 (2H, d), 8.95 (2H, s). IR (KBr) ν_{max} 2922, 2851, 1580, 1425, 1331, 1250, 1155, 786 cm^{-1}. MS *m/z* 352 [M^+], 254 (100%), 108.

10. Calc. for $C_{22}H_{26}ON_2S$ C 72.09, H 7.15, N 7.64; found C 71.97, H 7.32, N 7.55%. δ_H (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.30–1.36 (8H, m), 1.48 (2H, quint), 1.81 (2H, quint), 4.03 (2H, t), 6.99 (2H, d), 7.15 (1H, dd), 7.40–7.41 (2H, m), 8.39 (2H, d), 8.95 (2H, s). IR (KBr) ν_{max} 2927, 2854, 1609, 1517, 1449, 1336, 1248, 1169, 791 cm^{-1}. MS *m/z* 366 [M^+], 254 (100%), 108.

11. Calc. for $C_{23}H_{28}ON_2S$ C 72.59, H 7.42, N 7.36; found C 72.74, H 7.58, N 7.34%. δ_H (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.29–1.51 (12H, m), 1.82 (2H, quint), 4.04 (2H, t), 6.99 (2H, d), 7.17 (1H, dd), 7.41–7.42 (2H, m), 8.40 (2H, d), 8.96 (2H, s). IR (KBr) ν_{max} 2926, 2854, 1610, 1518, 1450, 1339, 1252, 1172, 793 cm^{-1}. MS *m/z* 380 [M^+], 254 (100%), 108.

12. Calc. for $C_{24}H_{30}ON_2S$ C 73.06, H 7.66, N 7.10; found C 72.87, H 7.92, N 7.15%. δ_H (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.28–1.52 (14H, m), 1.82 (2H, quint), 4.04 (2H, t), 7.01 (2H, d), 7.17 (1H, dd), 7.41–7.42 (2H, m), 8.40 (2H, d), 8.96 (2H, s). IR (KBr) ν_{max} 2927, 2854, 1610, 1519, 1450, 1392, 1339, 1252, 1172, 793 cm^{-1}. MS *m/z* 394 [M^+], 271, 254 (100%), 215, 108, 94.

13 Calc. for $C_{26}H_{34}ON_2S$ C 73.89, H 8.11, N 6.63; found C 73.77, H 8.38, N 6.46%. δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22–1.51 (16H, m), 1.47 (2H, quint), 1.81 (3H, quint), 4.03 (2H, t), 6.99 (2H, d), 7.16 (1H, t), 7.41 (2H, m), 8.39 (2H, d), 8.95 (2H, s). IR (KBr) ν_{max} 2926, 2857, 1610, 1518, 1452, 1342, 1258, 1169, 1023, 795 cm^{-1}. MS *m/z* 422 [M^+], 254 (100%), 108.

3.2.8. *Series 1: compounds **14**–**19***

*2-(4-Hexyloxyphenyl)-5-(5-hexylthiophen-2-yl)pyrimidine **14***. 5-Bromo-2-(4-hexyloxyphenyl)pyrimidine **3a** (1.00 g, 2.99 mmol) and 2-hexyl-5-(tributylstannyl)-thiophene **7a** (1.50 g, 3.28 mmol) were added to anhydrous DMF (50 cm^3) under an atmosphere of dry nitrogen. The mixture was heated to 100°C and bis(triphenylphosphine)-palladium(II) chloride (0.06 g, 0.185 mmol) was added, once a solution had formed. The black reaction mixture was maintained at 100°C for 16 h before being allowed to cool to room temperature. The solvent was removed by distillation under reduced pressure. The crude product was purified by column chromatography (DCM) and recrystallization (hexane) to give 2-(4-hexyloxyphenyl)-5-(5-hexylthiophen-2-yl)pyrimidine **14** as a white solid; 0.89 g (71%). Calc. for $C_{26}H_{34}ON_2S$ C 73.89, H 8.12, N 6.63; found C 74.19, H 8.28, N 6.63%. δ_H (400 MHz, $CDCl_3$) 0.88–0.93 (6H, m), 1.30–1.52 (12H, m), 1.71 (2H, quint), 1.81 (2H, quint), 2.85 (2H, t), 4.03 (2H, t), 6.81 (1H, d), 6.98 (2H, d), 7.21 (1H, d), 8.37 (2H, d), 8.90 (2H, s). IR (KBr) ν_{max} 2931, 2859, 1609, 1581, 1523, 1489, 1425, 1252, 1168, 799 cm^{-1}. MS *m/z* 422 [M^+], 338, 267, 238, 121, 83 (100%).

The following 2-(4-alkyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines (**15**–**49**) were prepared using the same general procedure as that described for compound **14**, i.e. using 1.00 g of the appropriate 5-bromo-2-(4-alkyloxyphenyl)pyrimidine **3a**–**f** and the corresponding number of moles of the 2-alkyl-5-(tributylstannyl)thiophene **7a**–**f**. Each homologue was obtained as a white solid (yields 67–82%). The IR and ^1H NMR spectra were found to be consistent with the structure of each compound and similar to that obtained for compound **14**, except that in the case of the ^1H NMR spectra, the integration of the appropriate multiplets reflected the additional methylene ($-CH_2-$) groups.

15. Calc. for $C_{27}H_{36}ON_2S$ C 74.27, H 8.32, N 6.42; found C 74.22, H 8.29, N 6.41%. MS *m/z* 436 [M^+], 352, 267 (100%).

16. Calc. for $C_{28}H_{38}ON_2S$ C 74.62, H 8.51, N 6.22; found C 74.34, H 8.50, N 6.21%. MS *m/z* 450 [M^+], 366, 351, 267 (100%), 238, 121.

17. Calc. for $C_{29}H_{40}ON_2S$ C 74.95, H 8.68, N 6.03; found C 74.65, H 8.90, N 6.04%. MS *m/z* 464 [M^+], 380, 351, 267 (100%), 238, 121.

18. Calc. for $C_{30}H_{42}ON_2S$ C 75.27, H 8.85, N 5.86; found C 74.97, H 8.85, N 5.82%. MS *m/z* 478 [M^+] (100%), 394, 351, 267, 238, 121.

19. Calc. for $C_{32}H_{46}ON_2S$ C 75.84, H 9.16, N 5.53; found C 75.79, H 9.33, N 5.55%. MS *m/z* 506 [M^+] (100%), 422, 351, 267, 238, 121.

3.2.9. *Series 2: compounds **20–25***

20. Calc. for $C_{27}H_{36}ON_2S$ C 74.27, H 8.32, N 6.42; found C 73.97, H 8.33, N 6.24%. MS *m/z* 436 [M^+], 338, 267, 238, 121, 83 (100%).

21. Calc. for $C_{28}H_{38}ON_2S$ C 74.62, H 8.51, N 6.22; found C 74.62, H 8.73, N 6.28%. MS *m/z* 450 [M^+], 365, 352, 267 (100%), 238, 121, 83, 69.

22. Calc. for $C_{29}H_{40}ON_2S$ C 74.95, H 8.68, N 6.03; found C 74.75, H 8.66, N 5.93%. MS *m/z* 464 [M^+], 366, 267 (100%), 238, 121, 83, 69.

23. Calc. for $C_{30}H_{42}ON_2S$: C 75.27, H 8.85, N 5.86; found C 75.12, H 8.98, N 5.77%. MS *m/z* 478 [M^+] (100%), 380, 365, 267, 238, 121.

24. Calc. for $C_{31}H_{44}ON_2S$ C 75.56, H 9.01, N 5.69; found C 75.84, H 9.13, N 5.70%. MS *m/z* 492 [M^+] (100%), 267.

25. Calc. for $C_{33}H_{48}ON_2S$ C 76.10, H 9.30, N 5.38; found C 76.08, H 9.32, N 5.33%. MS *m/z* 520 [M^+] (100%), 267.

3.2.10. *Series 3: compounds **26–37***

26. Calc. for $C_{32}H_{46}ON_2S$ C 74.62, H 8.51, N 6.22; found C 74.50, H 8.67, N 6.00%. MS *m/z* 450 [M^+] (100%), 338, 267.

27. Calc. for $C_{29}H_{40}ON_2S$ C 74.95, H 8.68, N 6.03; found C 74.89, H 8.91, N 6.01%. MS *m/z* 464 [M^+] (100%), 352, 267.

28. Calc. for $C_{30}H_{43}ON_2S$ C 75.11, H 9.03, N 5.84; found C 75.37, H 8.94, N 5.78%. MS *m/z* 478 [M^+] (100%), 267.

29. Calc. for $C_{31}H_{44}ON_2S$ C 75.56, H 9.01, N 5.69; found C 75.81, H 8.86, N 5.71. MS *m/z* 492 [M^+], 379, 267, 238, 121, 71.

30. Calc. for $C_{32}H_{46}ON_2S$ C 75.84, H 9.16, N 5.53; found C 75.94, H 9.14, N 5.50. MS *m/z*: 506 [M^+] (100%), 394, 379, 267, 238, 121, 71.

31. Calc. for $C_{34}H_{50}ON_2S$ C 76.35, H 9.43, N 5.24; found C 76.40, H 9.28, N 5.22%. MS *m/z* 534 [M^+] (100%), 422, 379, 267, 238, 121, 71.

3.2.11. *Series 4: compounds **32–37***

32. Calc. for $C_{29}H_{40}ON_2S$ C 74.95, H 8.68, N 6.03; found C 75.03, H 8.70, N 6.11%. MS *m/z* 464 [M^+], 394, 338, 267, 254 (100%), 121, 108.

33. Calc. for $C_{30}H_{42}ON_2S$ C 75.27, H 8.85, N 5.86; found C 74.99, H 8.77, N 5.77%. MS *m/z* 478 [M^+] (100%), 352, 267.

34. Calc. for $C_{31}H_{44}ON_2S$ C 75.56, H 9.01, N 5.69; found C 75.86, H 9.30, N 5.64%. MS *m/z* 492 [M^+] (100%), 366, 267.

35. Calc. for $C_{32}H_{46}ON_2S$ C 75.84, H 9.16, N 5.53; found C 75.54, H 9.12, N 5.47%. MS *m/z* 506 [M^+] (100%), 393, 380, 267, 238, 121, 71.

36. Calc. for $C_{33}H_{48}ON_2S$ C 76.10, H 9.30, N 5.38; found C 76.21, H 9.48, N 5.39%. MS *m/z* 520 [M^+] (100%), 394, 267.

37. Calc. for $C_{35}H_{52}ON_2S$ C 76.59, H 9.56, N 5.11; found C 76.36, H 9.72, N 5.10%. MS *m/z* 548 [M^+] (100%), 422, 267.

3.2.12. *Series 5: compounds **38–43***

38. Calc. for $C_{30}H_{40}ON_2S$ C 75.27, H 8.84, N 5.85; found C 75.11, H 8.86, N 5.83%. MS *m/z* 478 [M^+], 337, 267 (100%), 238, 183, 121, 83.

39. Calc. for $C_{31}H_{44}ON_2S$ C 75.56, H 9.01, N, 5.69; found C 75.38, H 8.71, N 5.67%. MS *m/z* 492 [M^+] (100%), 352, 267.

40. Calc. for $C_{32}H_{46}ON_2S$ C 75.84, H 9.15, N 5.53; found C 75.87, H 9.30, N 5.49%. MS *m/z* 507 [M^+], 366, 267, 199, 121, 111, 97, 83 (100%), 71.

41. Calc. for $C_{33}H_{48}ON_2S$ C 76.10, H 9.30, N 5.38; found C 75.83, H 9.46, N 5.40%. MS *m/z* 520 [M^+] (100%), 380, 352, 267, 238, 121.

42. Calc. for $C_{34}H_{50}ON_2S$ C 76.35, H 9.43, N 5.24; found C 76.47, H 9.57, N 5.20%. MS *m/z* 534 [M^+], 407, 394, 267 (100%), 238, 121, 69.

43. Calc. for $C_{36}H_{54}ON_2S$ C 76.81, H 9.68, N 4.98; found C 76.70, H 9.47, N 4.96%. MS *m/z* 562 [M^+] (100%), 267.

3.2.13. *Series 6: compounds **44–49***

44. Calc. for $C_{32}H_{46}ON_2S$ C 75.84, H 9.15, N 5.53; found C 75.57, H 9.45, N 5.34%. MS *m/z* 506 [M^+] (100%), 267.

45. Calc. for $C_{33}H_{48}ON_2S$ C 76.10, H 9.30, N 5.38; found C 76.08, H 9.52, N 5.36%. MS *m/z* 520 [M^+] (100%), 352, 267.

46. Calc. for $C_{34}H_{50}ON_2S$ C 76.35, H 9.42, N 5.24; found C 76.43, H 9.65, N 5.15%. MS *m/z* 534 [M^+] (100%), 267, 147.

47. Calc. for $C_{35}H_{52}ON_2S$ C 76.59, H 9.56, N 5.11; found C 76.29, H 9.60, N 5.00%. MS *m/z* 548 [M^+] (100%), 380, 267.

48. Calc. for $C_{36}H_{54}ON_2S$ C 76.81, H 9.68, N 4.98; found C 76.90, H 9.56, N 4.97%. MS *m/z* 562 [M^+] (100%), 394, 267, 238, 121, 91, 71.

49. Calc. for $C_{38}H_{58}ON_2S$ C 77.23, H 9.90, N 4.74; found C 77.12, H 10.20, N 4.74%. MS *m/z* 590 [M^+] (100%), 435, 422, 267.

4. Conclusions

The 2-(4-alkyloxyphenyl)-5-thiophen-2-ylpyrimidines exhibited a monotropic nematic phase, but the incorporation of a second terminal alkyl group into the structure

to yield the 2-(4-alkyloxyphenyl)-5-(5-alkythiophen-2-yl)-pyrimidines dramatically affected the LC thermal behaviour of the compounds. We believe that the incorporation of the alkyl group has exaggerated the 'bent' nature of the molecule caused by the presence of the thiophene ring and has dramatically (a) decreased the melting point of the compounds by 30–40°C, (b) reduced the tendency of the compounds to form the nematic phase and (c) enhanced the tendency of the compounds to form smectic phases, especially the tilted smectic phases SmI and SmC. It seems that the alkyl group in the 5-position of the thiophene ring is very important in the formation of these tilted smectic phases.

For the 2-(4-alkyloxyphenyl)-5-(5-alkythiophen-2-yl)-pyrimidines, an increase in the chain length of either the alkoxy or alkyl group from hexyl to dodecyl generally leads to small changes in the thermal stabilities of the nematic, SmA, SmC and SmC_{alt} phases exhibited by these compounds, of between 5 and 10°C. One interesting observation concerned the SmI phase. Although increasing the size of the alkyl chain enhanced the thermal stability of this phase, the chain length of the alkoxy group had little effect. For example, the change in thermal stabilities from the nonyl to the dodecyl homologues for each series of compounds was from around 105 to 118°C, but for the nonyl homologues in series 1–6 the thermal stabilities of the SmI phases were in the range 104.5–106.0°C. This was also typical for both the decyl and dodecyl homologues.

One of the most unusual aspects of this study was the SmC_{alt} phase exhibited by the 2-(4-alkyloxyphenyl)-5-(5-heptylthiophen-2-yl)pyrimidines, although the octyl homologue in series 3 also exhibited this phase.

The melting points of the 2-(4-alkyloxyphenyl)-5-(5-octylthiophen-2-yl)pyrimidines were relative low, ranging from 88.9°C for the 2-(4-hexyloxyphenyl)-5-(5-octylthiophen-2-yl)pyrimidine to 56.0°C for the 2-(4-nonyloxyphenyl)-5-(5-nonylthiophen-2-yl)pyrimidine, although the majority of the melting points lay in the range 60–80°C. Such low melting points are unusual for mesogens containing three rings. The low melting points and high SmC/SmC_{alt} thermal stabilities of these compounds could make some of these compounds useful host materials for both ferro- and antiferro-electric mixtures.

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