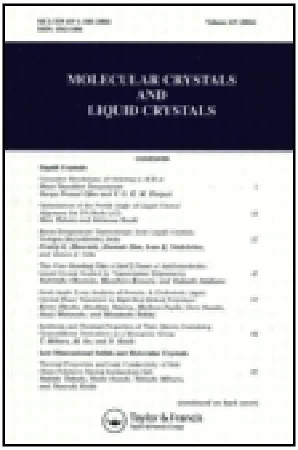

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THE SYNTHESIS AND THERMAL PROPERTIES OF NOVEL HETEROCYCLIC LIQUID CRYSTALLINE MATERIALS

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THE SYNTHESIS AND THERMAL PROPERTIES OF NOVEL HETEROCYCLIC LIQUID CRYSTALLINE MATERIALS

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The synthesis and transition temperatures of a series of novel 2-(4-benzyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidine liquid crystals is described. Using a palladium-catalysed cross-coupling reaction benzyloxyphenylboronic acid was coupled to 5-bromo-2-iodopyrimidine. A second coupling reaction was then performed using a series of 5-alkyl-2-tri-butylstannyl thiophenes to create the title compounds. These compounds exhibit nematic, smectic A, smectic C and smectic C_{alt} phases, and these phases were identified by a combination of differential scanning calorimetry and optical microscopy. The most unusual aspect of these compounds is the appearance of a previously undiscovered achiral version of the ferrielectric chiral smectic C phase. To unambiguously identify this phase, further detailed investigation by X-ray analysis is being undertaken.

Keywords: heterocyclic liquid crystals; thiophene-pyrimidine moiety; palladium catalysed coupling reactions

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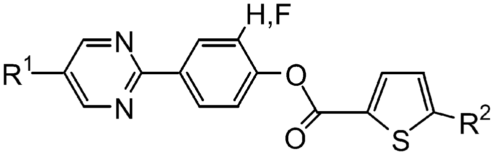
INTRODUCTION

Since the first discovery of the liquid crystalline molecule cholesteryl benzoate by Rhinitzer [1], the overwhelming majority of liquid crystalline research has been concerned with the synthesis of liquid crystalline materials containing mainly non-heterocyclic rings such as phenyl rings, in particular biphenyl and terphenyl molecules, and the cyclohexyl ring. The removal of phenyl rings and the incorporation of the pyrimidine ring, especially in ferro- and antiferro-electric mesogens, awakened the interest in heterocyclic containing mesogens. Compared to nitrogen containing heterocycles there are however, relatively few examples of sulphur containing heterocycles. The use of nitrogen containing heterocyclic rings, such as pyrimidine, in the synthesis of liquid crystalline materials is well known [2–6] and is widely documented in the literature. However, the inclusion of thiophene rings into liquid crystalline materials is comparatively rare [7,8].

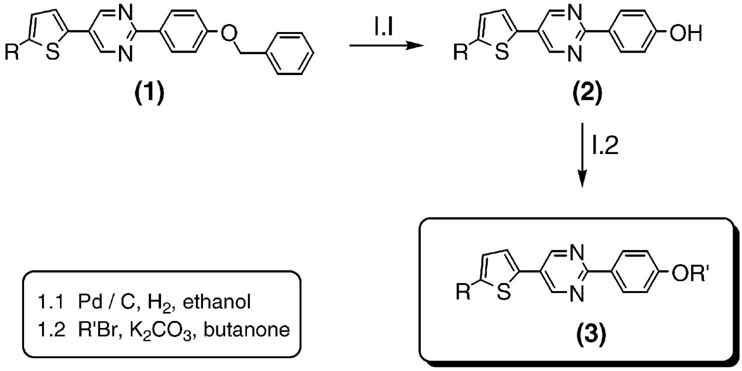
It was Byron *et al.* [9] who first pointed out that the slightly bent nature of the thiophene ring had the desirable effect of lowering the melting points of liquid crystalline materials. Unfortunately it also appears to lower the mesophase stability, in particular, the clearing point of the liquid crystalline materials by a similar amount. It has been demonstrated that the presence of a bent molecular core structure is conducive to the formation of the antiferroelectric liquid crystalline phase [10,11], in which the large negative anisotropy imparted by the presence of the thiophene ring is most beneficial to the application of these phases in display devices. Therefore the synthesis of thiophene containing liquid crystals would seem desirable, as would the combination of thiophene rings with a nitrogen containing heterocycle, such as pyrimidine, which lowers the viscosity of the mesogen.

In this paper we report the synthesis of some novel liquid crystalline materials incorporating a thiophene-pyrimidine moiety. However, it was noted that the intermediate materials possessing a benzyloxy group at one end of the molecular core were liquid crystalline themselves. The original aim of this work was to remove this protecting group in order to synthesise a range of novel dialkyl thiophene-pyrimidine liquid crystalline materials. Herein we report the synthesis and liquid crystalline behaviour of these intermediate materials possessing a benzyloxy terminally positioned end group.

In a previous paper [12], it was shown that only one example of a thiophene/pyrimidine liquid crystal exists [13,14], the structure of which is shown below.



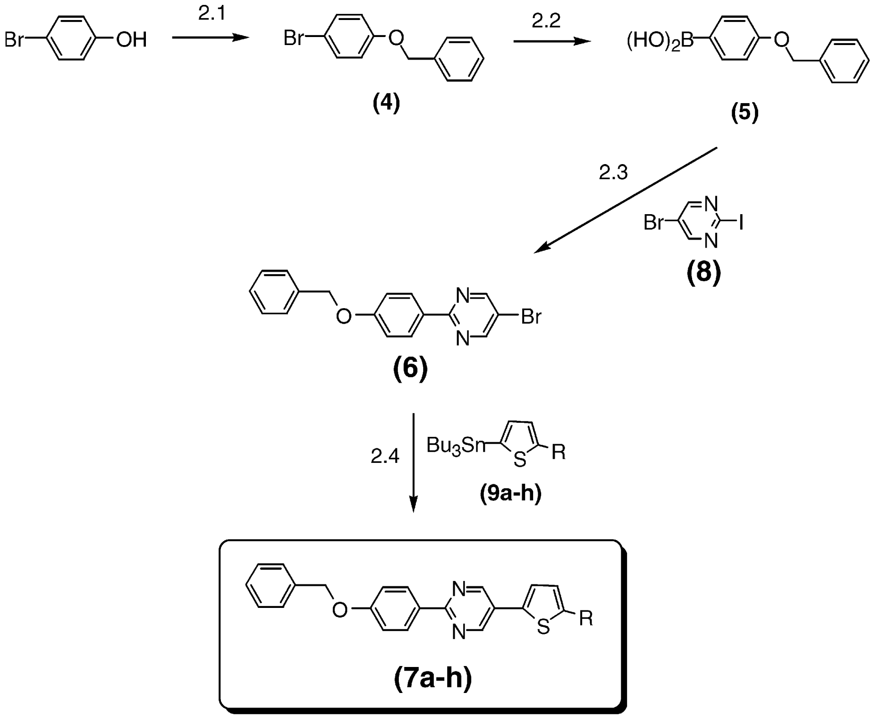
The initial aim of our present work was to produce materials of structure **3** shown in Scheme 1.



The original intention of our work was to remove the benzyloxy protection group from compound **1** to give the phenolic derivative **2**. Using a general literature alkylation method [15], a range of alkyl bromides could be coupled to this molecule, which would enable the whole homologous series of compound **3** to be synthesised both rapidly and efficiently in high yield. As we have stated in our previous publication [12] we believe that this is the first attempt to synthesise terphenyl liquid crystal analogues containing both thiophene and pyrimidine heterocyclic rings. However, it was upon synthesis of the precursor materials **7a–h** (see Scheme 2) that we discovered that these compounds possessed interesting liquid crystalline properties, and these will be discussed in this paper.

SYNTHESIS

The synthesis of the compounds is outlined in Scheme 2. The synthesis of two of the intermediates, 5-bromo-2-iodopyrimidine **8** and 5-alkyl-2-tri-butylstannyl thiophene **9a–h**, have been discussed at some length in previous papers [12,21,22] and will not be discussed further here. 4-Bromophenol was treated with benzyl bromide using standard potassium carbonate alkylation conditions [15] to give 1-benzyloxy-4-bromobenzene **4**. Using the method of Grignard [16] magnesium was added to **4**, which was cooled to −78°C and then treated with trimethyl borate. On warming and treatment with dilute acid yielded the corresponding boronic acid **5**. The synthesis of the 2-(4-benzyloxyphenyl)-5-(5-alkylthiopen-2-yl)pyrimidines **7a–h** required two different coupling reactions, the first of which utilizes the selective coupling ability of the starting material 5-bromo-2-iodopyrimidine **8**. The first coupling reaction was *via* the method of Suzuki [17] using the modification of Gronowitz [18]. Compound **8** was coupled to 4-benzyloxyphenylboronic acid **5** to give 2-(4-benzyloxyphenyl)-5-bromopyrimidine **6**. This compound **6** was then reacted further *via* the method of Stille [19] with a range of 5-alkyl-2-tri-butylstannylthiophenes **9a–h** to give the final materials **7a–h** in reasonable yields.



7a, 9a, R = H; 7b, 9b, R = C_5H_{11}; 7c, 9c, R = C_6H_{13}; 7d, 9d, R = C_7H_{15}; 7e, 9e, R = C_8H_{17}
7f, 9f, R = C_9H_{19}; 7g, 9g, R = $C_{10}H_{21}$; 7h, 9h, R = $C_{12}H_{25}$

2.1 benzylbromide, K_2CO_3, butanone
2.2 (i) Mg / THF; (ii) $B(OCH_3)_3$ / THF, - 78 °C; (iii) H^+, RT
2.3 $Pd(PPh_3)_4$, Na_2CO_3, DME / H_2O
2.4 $PdCl_2(PPh_3)_2$, DMF

Nuclear magnetic resonance spectra (^1H NMR) were carried out on a Jeol JMN-LA 400 FT spectrometer. All NMR spectra were carried out in deuterated chloroform as a solvent and tetramethylsilane as the internal standard. The following notations denoted the peak types in the spectra: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q) and multiplet (m). Infrared spectra (ir) were obtained using a Perkin Elmer 983 G spectrophotometer. Samples were prepared as potassium bromide discs. Mass spectra (ms) were obtained using a Finnigan 1020 GCMS spectrometer. Results are quoted where M^+ represents the molecular ion and the base peak represented by (100%). Elemental analysis was carried out on a Fisions 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 (mp 156.6°C, ΔH 28.45 $J.g^{-1}$). Heating rate was 10°C min^{-1}. Calculations were made using a Perkin Elmer Pyris version 3.81 software. Optical microscopy was performed using an Olympus BH-2 polarising 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. Thin layer chromatography (TLC) was carried out on aluminium sheets coated in Merck Kieselgel silica gel 60 F_{254}, eluting with dichloromethane.

SCHEME 2

1-Benzyloxy-4-bromobenzene (4)

Anhydrous potassium carbonate (162.00 g, 1.170 mol) was added to a stirred solution of 4-bromophenol (101.19 g, 0.585 mol) and benzyl bromide (100.00 g, 0.585 mol) in butanone (400 cm^3). The stirred mixture was heated under reflux for 16 h. The reaction was allowed to cool to room temperature, filtered through Hyflo supercel filter-aid to remove any inorganic salts and the solvent was removed *in vacuo*. The resulting solid was dissolved in ether (300 cm^3) and was washed consecutively with 5% sodium hydroxide solution (3×100 cm^3) and water (3×100 cm^3). The combined ethereal extracts were dried ($MgSO_4$). The residue was recrystallised (ethanol) to give 1-benzyloxy-4-bromobenzene **(4)** as a white solid, 136.2 g (88%), mp 57–58°C (Lit[23], mp 59–60°C). δ_H (400 MHz, $CDCl_3$) 5.03 (2H, s), 6.84 (2H, d), 7.25–7.42 (7H, m); ir (KBr) ν_{max}: 3039, 2895, 1584, 1490, 1453, 1379, 1286, 1071, 825, 734, 693 cm^{-1}; ms *m/z*: 264 [M^+], 262 [M^+], 91 (100%), 65.

4-Benzyloxyphenylboronic acid (5)

About 20% of compound **4** (20.00 g, 76.0 mmol), dissolved in dry THF (150 cm^3) was added to ground magnesium turnings (2.00 g, 83.3 mmol) and a few crystals of iodine present to activate the reaction. The reaction was heated under reflux in an atmosphere of dry nitrogen. The remainder of the THF solution was added and the stirred reaction mixture was heated under reflux for a further 45 minutes. The Grignard reagent was cooled to –78°C (cardice/acetone) and trimethyl borate (17.5 cm^3, 16.01 g, 0.154 mol) was added dropwise maintaining the temperature below −70°C. After the addition the temperature was kept below −60°C for 1 h. The reaction was allowed to warm to room temperature overnight. The mixture was acidified with 50 : 50 hydrochloric acid (200 cm^3) and was stirred for 1 h. Any organic material was extracted into ether ($3 \times 100\,cm^3$) 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, and the purified product was filtered off and dried *in vacuo* to give 4-benzyloxyphenylboronic acid **(5)** as a white solid, 14.9 g (86%). δ_H (400 MHz, $CDCl_3$) 5.10 (2H, s), 6.94 (2H, d), 7.31–7.45 (5H, m), 7.71 (2H, d), 7.77 (2H, s); ir (KBr) ν_{max}: 3600–3200, 1610, 1382, 1253, 1112, 826 cm^{-1}.

2-(4-Benzyloxyphenyl)-5-bromopyrimidine (6)

Tetrakis(triphenylphosphine)palladium(0) (1.22 g, 1.06 mmol) in DME (25 cm^3) was added to a rapidly stirred mixture of compound **8** (10.00 g, 0.0351 mol) in DME (75 cm^3) and 2 mol dm^{-3} sodium carbonate solution (100 cm^3), which was heating under reflux in an atmosphere of nitrogen. A solution of compound **5** (10.00 g, 35.1 mmol) in DME (100 cm^3) was added dropwise to the stirred mixture. The mixture was heated under reflux until TLC analysis revealed a complete reaction (16 h). The reaction was allowed to cool to room temperature. Water (100 cm^3) was added and the product was extracted into DCM ($3 \times 100\,cm^3$) and the combined DCM extracts were dried ($MgSO_4$). The crude product was purified by column chromatography (DCM) and recrystallisation (ethanol) to give 2-(4-benzyloxyphenyl)-5-bromopyrimidine **(6)** as a white solid, 6.3 g (53%); mp: 152–153°C. δ_H (400 MHz, $CDCl_3$): 5.14 (2H, s), 7.06 (2H, d), 7.32–7.47 (5H, m), 8.35 (2H, d), 8.77 (2H, s); ir (KBr) ν_{max}: 3035, 1607, 1529, 1424, 1381, 1255, 1032, 791 $cm^{-1;}$ ms *m/z*: 342 [M^+], 340 [M^+], 206, 91 (100%).

2-(4-Benzyloxyphenyl)-5-thiophen-2-ylpyrimidine (7a)

Compound **6** (2.00 g, 5.87 mmol) and 2-(tri-butylstannylthiophene (**9a**) (2.41 g, 6.46 mmol) were added to anhydrous DMF (50 cm^3) under an atmosphere of dry nitrogen. The stirred mixture was heated to 100°C and bis(triphenylphosphine)palladium(II) chloride (0.12 g, 0.171 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 and then the solvent was removed *in vacuo*. The crude product was purified by column chromatography (DCM) and recrystallisation (hexane) to give 2-(4-benzyloxyphenyl)-5-thiophen-2-ylpyrimidine **(7a)** as a white solid, 1.4 g (70%). Calc. for $C_{21}H_{16}ON_2S$: C 73.23%, H 4.68%, N 8.13%; found C 73.06%, H 4.65%, N 8.04%. δ_H (400 MHz, $CDCl_3$): 5.16 (2H, s), 7.08 (2H, d), 7.17 (1H, dd), 7.34–7.48 (7H, m), 8.41 (2H, d), 8.96 (2H, s); IR (KBr) ν_{max}: 2922, 2858, 1605, 1579, 1524, 1447, 1338, 1247, 1161, 798 $cm^{-1;}$ ms *m/z*: 344 [M^+], 253, 91 (100%).

2-(4-Benzyloxyphenyl)-5-(5-pentylthiophen-2-yl) pyrimidine (7b)

Compound **6** (1.00 g, 2.93 mmol) and 2-(tri-butylstannyl)-5-pentylthiophene (**9b**) (1.43 g, 3.22 mmol) were added to anhydrous DMF (50 cm^3) under an atmosphere of dry nitrogen. The stirred mixture was heated to 100°C and bis(triphenylphosphine)palladium(II) chloride (0.06 g, 0.086 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 and then the solvent was removed *in vacuo*. The crude product was purified by column chromatography (DCM) and recrystallisation [petroleum ether (bp 100–120°C)] to give 2-(4-benzyloxyphenyl)-5-(5-pentylthiophen-2-yl)pyrimidine **(7b)** as a white solid, 0.92 g (76%). Calc. for $C_{26}H_{26}ON_2S$: C 75.33%, H 6.33%, N 6.76%; found C 75.45%, H 6.48%, N 6.69%. δ_H (400 MHz, $CDCl_3$): 0.92 (3H, t), 1.36–1.40 (4H, m), 1.69–1.76 (2H, m), 2.85 (2H, t), 5.15 (2H, s), 6.82 (1H, d), 7.08 (2H, d), 7.22 (1H, d), 7.32–7.47 (5H, m), 8.39 (2H, d), 8.90 (2H, s); ir (KBr) ν_{max}: 2933, 2865, 1605, 1580, 1522, 1483, 1425, 1384, 1242, 1169, 798 cm^{-1}; ms *m/z*: 414 [M^+], 323, 266, 238, 121, 91 (100%).

The following 2-(4-benzyloxyphenyl)-5-(5-alkylthiophen-2-yl)pyrimidines (**7c–7h**) were prepared using the same general procedure to that described for the preparation of compound **7b**. The IR and ^1H NMR spectra for compounds **7c–7h** were found to be consistent with the structure of the compound and similar to that obtained for compound **7b**, except that in the case of the ^1H NMR spectra, the integration of the multiplet at 1.30–1.40 reflected the additional methylene (-CH_2-) groups.

2-(4-Benzyloxyphenyl)-5-(5-hexylthiophene-2-yl) pyrimidine (7c)

2-(4-Benzyloxyphenyl)-5-(5-hexylthiophene-2-yl)pyrimidine **(7c)** was obtained as a white solid, 1.01 g (81%). Calc. for $C_{27}H_{28}ON_2S$: C 75.67%, H 6.58%, N 6.54%; found C 75.38%, H 6.82%, N 6.58%. Ms *m/z*: 428 [M^+], 337, 91 (100%).

2-(4-Benzyloxyphenyl)-5-(5-heptylthiophen-2-yl) pyrimidine (7d)

2-(4-Benzyloxyphenyl)-5-(5-heptylthiophene-2-yl)pyrimidine (**7d**) was obtained as a white solid, 0.90 g (69%). Calc. for $C_{28}H_{30}ON_2S$: C 75.98%, H 6.84%, N 6.33%; found C 75.89%, H 7.10%, N 6.39%. Ms *m/z*: 442 [M^+], 390, 351, 91 (100%), 65.

2-(4-Benzyloxyphenyl)-5-(5-octylthiophene-2-yl) pyrimidine (7e)

2-(4-Benzyloxyphenyl)-5-(5-octylthiophene-2-yl)pyrimidine (**7e**) was obtained as a white solid, 0.94 g (70%). Calc. for $C_{29}H_{32}ON_2S$: C 76.28%, H 7.06%, N 6.13%; found C 76.58%, H 7.35%, N 6.10%. Ms *m/z*: 456 [M^+], 365, 266, 238, 91 (100%).

2-(4-Benzyloxyphenyl)-5-(5-nonylthiophen-2-yl) pyrimidine (7f)

2-(4-Benzyloxyphenyl)-5-(5-nonylthiophene-2-yl)pyrimidine (**7f**) was obtained as a white solid, 0.98 g (71%). Calc. for $C_{30}H_{34}ON_2S$: C 76.56%, H 7.29%, N 5.96%; found C 76.68%, H 7.43%, N 5.99%. Ms *m/z*: 470 [M^+], 379, 91 (100%).

2-(4-Benzyloxyphenyl)-5-(5-decylthiophen-2-yl) pyrimidine (7g)

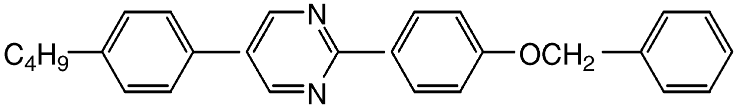
2-(4-Benzyloxyphenyl)-5-(5-decylthiophene-2-yl)pyrimidine (**7g**) was obtained as a white solid, 1.11 g (78%). Calc. for $C_{31}H_{36}ON_2S$: C 76.82%, H 7.49%, N 5.78%; found C 76.83%, H 7.75%, N 5.60%. Ms *m/z*: 484 [M^+], 408, 393, 91 (100%).

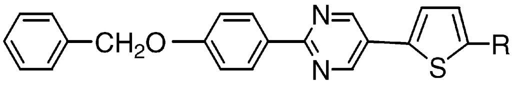
2-(4-Benzyloxyphenyl)-5-(5-dodecylthiophen-2-yl) pyrimidine (7h)

2-(4-Benzyloxyphenyl)-5-(5-dodecylthiophene-2-yl)pyrimidine (**7h**) was obtained as a white solid, 1.16 g (77%). Calc. for $C_{33}H_{40}ON_2S$: C 77.30%, H 7.87%, N 5.47%; found C 77.45%, H 8.17%, N 5.40%. Ms *m/z*: 512 [M^+], 421, 266, 238, 91 (100%).

RESULTS AND DISCUSSION

The transition temperatures and yields for compounds **7a–h** are given in Table 1.





Cmpd		Transition Temperatures (°C)										
No	R	Cr		SmC_{alt}		SmX		SmC		N		Iso
7a	0	■	185.6									■
7b	5	■	133.5					■	154.7	■	169.6	■
7c	6	■	122.5	■		■	107.0	■	160.7	■	165.8	■
7d	7	■	132.9	■	111.6	■	118.6	■	165.8	■	166.7	■
7e	8	■	123.2	■	102.1	■	125.9	■	166.5			■
7f	9	■	121.3	■	121.9	■	131.3	■	168.2			■
7g	10	■	118.2	■	121.3	■	133.2	■	166.4			■
7h	12	■	107.1	■	119.5	■	138.6	■	166.3			■

Optical microscopy readily identified the nematic, smectic A, smectic C and the alternating smectic C (SmC_{alt}) transitions exhibited by compounds **7a–h**. These transitions temperatures were verified by differential scanning calorimetry (DSC) where the enthalpy of the transitions obtained by DSC was very useful in phase identification, especially in the case of the alternating smectic C phase. The presence of the smectic C phase in these materials, where one end of the mesogen is a benzyloxy group and therefore 'blunt ended', is very unusual and rare. Only one previous example of a material of this type exhibiting the smectic C phase is known [20] (see Structure 1).

Compound **7a** does not exhibit any mesophases. Presumably this compound is too rigid to display mesomorphic behaviour as it does not have a terminal alkyl or alkoxy group. The other members of the series were all found to show mesophases. Compound **7b** exhibited a nematic and a smectic C phase, whereas compound **7c** was also shown to exhibit an additional phase, the unidentified SmX phase. The next member of the series, compound **7d**, shows similar mesomorphic properties to compound **7c**, except now we see the appearance of the alternating smectic C (SmC_{alt}) phase. From compounds **7e** to **7h** the nematic phase are lost and all these compounds exhibit smectic C, smectic X and alternating smectic C phases. From the data presented in table 1 it seems that increasing the length of the alkyl chain is conducive to the formation of smectic phases, especially tilted smectic phases such as the SmC and SmC_{alt} phases. This is not surprising since the incorporation of the 2,5-disubstituted thiophene ring will give rise to a non-linear or slightly bent nature to the structure of the molecule. The core angle of the 2,5-disubstituted thiophene ring [24] is 148° and this, coupled to fact that the thiophene ring is in a lateral position within the structure of the compounds, will give the molecule a hockey-stick-like structure. By increasing the length of the alkyl chain will exaggerate the bent-like nature of the molecule and hence the formation of tilted smectic phases.

In addition to the nematic, smectic C and alternating smectic C phases formed by this particular series, compounds **7d** to **7h** were also found to exhibit an unidentified phase, which we have denoted as SmX. This phase was identified by optical polarising microscope investigation to be a previously undiscovered phase [2]. The characteristics of the SmX phase include the fact that it always appears to exist between the smectic C and alternating smectic C phases. The phase also has a very small enthalpy associated with is formation from the smectic C phase. Furthermore, the texture of the phase shows fluctuations in the ***schlieren***, as well as the focal-conic domains having patches and characteristic striations. Overall, the texture is very similar in appearance to a ferrielectric chiral smectic C phase.

In view of all of the evidence available, the previously unidentified phase appears to be an achiral form of the ferrielectric chiral smectic C phase. This means that the benzyl groups some how result in the arrangement of the compounds in such a way as to form this SmX phase. To unambiguously identify this phase, however, requires further detailed investigations in the form of X-ray analysis. At present, a X-ray diffraction study is being undertaken. It is interesting to note that if this phase is indeed an achiral version of the ferrielectric chiral smectic C phase, then this and the alternating smectic C phase were both discovered after their chiral analogues.

CONCLUSIONS

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 55 – 70°C, (b) reduced the tendency of the compounds to form the nematic phase and (c) enhanced the tendency of the compounds to form tilted smectic phases, especially the tilted smectic phases SmC and $\mathrm{SmC_{alt}}$. It seems that the alkyl group in the 5-position in the thiophene ring is very important in the formation of tilted smectic phases, especially the SmC and $\mathrm{SmC_{alt}}$ phases.

The presence of the novel heterocyclic moiety, 5-alkyl-2-pyrimidylthiophene, has given rise to some very interesting liquid crystalline materials that exhibit the $\mathrm{SmC_{alt}}$ phase and especially, an achiral form of the ferrielectric chiral smectic C phase; a new liquid and previously undiscovered liquid crystalline phase. To unambiguously identify this phase, however, further detailed investigations in the form of X-ray analysis are being carried out.

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