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Heterocyclic columnar pyrimidines: synthesis, characterization and mesomorphic properties

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The synthesis, characterization, and mesomorphic properties of two series of heterocyclic compounds derived from a pyrimidine core are reported. These series, **1a** and **1b**, are substituted with a variety of functional groups ($X = NHSO_2CF_3$, F, Cl, Br, I, OCH_3, CH_3, C_2H_5) at the $C^{3'}$ (*meta*)- or $C^{4'}$ (*para*)-position of the terminal phenyl ring, and the substituent effect on mesophase formation was studied. The compounds were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis, and the mesomorphic behavior of the compounds was characterized and studied by differential scanning calorimetry, polarizing optical microscopy and powder X-ray diffraction. Most of the compounds were mesogenic at room temperature, and the mesophases were assigned as lamellar columnar (Col_L) phases, as expected for disk-like molecules. The results also revealed that compounds with a *para*-substituent (**1a**; except for $-OCH_3$) at the $C^{4'}$-position, exhibited higher clearing temperatures and wider temperature mesophase ranges than those of compounds with a *meta*-substituent (**1b**) at the $C^{3'}$-position. The higher clearing temperatures may be attributed to stronger dipolar interactions resulting from a greater resonance effect with the central core for *para*-substitution than for *meta*-substitution. The results also indicated that the columnar mesophases observed show a correlation with the electronic properties of the substituents; compounds containing electron-withdrawing substituents (X = F, Cl, Br, I, $NHSO_2CF_3$) also have higher clearing temperatures than compounds containing electron-donating substituents (X = Me, Et, OMe).

1. Introduction

A wide range of new mesogenic compounds exhibiting columnar phases have been prepared and studied since the discovery of the first thermotropic discotic liquid crystals by Chandrasekhar *et al*. in 1977 [1]. The formation of columnar phases is well known to be dependent on the number of side chains attached around the central core group [2]. A delicate balance between the core size and the number of side chains is critically essential for the formation of columnar mesophases. Most reported columnar mesogens are composed of benzene or fused benzene rings [2]. These types of discotic cores are normally considered as rigid and/or planar structures with a higher rotational symmetry, and these planar structures often result in strong π–π interactions between phenyl rings in the solid state. Thus, the formation of a stable mesophase is often inhibited.

Utilization of unique heterocyclic structures, in which the molecular symmetry of the central core is reduced should lead to a lowering of the melting point due to less favorable packing in the crystal state [3, 4]. Significant numbers of heterocyclic compounds have been found to exhibit mesomorphic properties due to the greater range of structural types [5]. A variety of common phases, including nematic/smectic phases have been observed for rod-like heterocyclic molecules. However, examples of heterocyclics exhibiting columnar phases are relatively limited. Core groups having a six-membered or larger fused ring have been most commonly used. By contrast, examples of discogenic molecules with five-membered rings are rare. Five-membered rings were generally considered less suitable for the formation of mesogenic materials

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than six-membered rings, due to their relatively unfavourable deviation from linearity or planarity [6].

A number of heterocyclic compounds derived from 1,3,4-oxadiazole [7] and 1,2,4-triazole [8], containing an unsaturated five-membered ring have previously been prepared and studied by ourselves. Among these two types of compound, 2,5-bis(3,4,5-trialkoxyphenyl)-1,3,4-oxadiazoles and 4-benzyl-2,5-bis(3,4,5-trialkoxyphenyl)-4H-1,2,4-triazoles, were found to exhibit a hexagonal columnar phase (Col_h) at room temperature. The results suggest that the formation of columnar phases by such heterocyclic structures may probably be attributed to a shape effect caused by a larger exocyclic bond angle. In addition, the formation of liquid crystallinity in such heterocyclic derivatives might be more favoured and facilitated by weak π–π interactions between these aromatic or heterocyclic rings.

In this work, and as part of our continuing research on heterocyclic compounds, a new class of compounds, **1a** and **1b**, derived from a heterocyclic pyrimidine core has been prepared and characterized. These compounds, substituted with a variety of functional groups ($NHSO_2CF_3$, F, Cl, Br, I, OCH_3, CH_3, C_2H_5) at the $C^{3'}$ (*meta*)- or $C^{4'}$ (*para*)-positions of the terminal phenyl, have been prepared, and the substituent effect on the formation of the mesophase studied in detail.

2. Experimental

2.1. *Characterization*

All chemicals and solvents were reagent grades from Acros Chemical Co. or Lancaster Co. ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 instrument. FTIR spectra were obtained using a Nicolet Magna-IR 550 spectrometer. HRMS analysis was performed using a JEOLSA 102A instrument. Differential scanning calorimetry (DSC) was carried out on a Mettler DSC-820 calibrated with a pure indium sample, and all phase transition temperatures and enthalpies were determined at a scan rate of $10.0^\circ C\,min^{-1}$. Polarizing optical microscopy (POM) was carried out on an Olympus BX 50 or Zeiss Axialplan with a Mettler FP90/FP82HT hot stage system. Elemental analysis for carbon, hydrogen and nitrogen was conducted on a Heraeus Vario EL-III elemental analyser at the National Taiwan University. Some compounds used in this work, namely 4-alkoxyacetophenones, 3,4-dialkoxyacetophenones, 3,4-dialkoxybenzaldehydes, 3,4,5-trialkoxybenzoic acids, 3,4,5-trialkoxyacetophenones, 3,4,5-trialkoxybenzyl alcohols and 3,4,5-trialkoxybenzaldehydes, were prepared by literature procedures [6*a*, 7–10].

2.2. *Synthesis*

2.2.1. *3,4,5-Trioctyloxybenzyl alcohol*

White solid; yield 90%. ^1H NMR ($CDCl_3$): δ 0.86 (m, $-CH_3$, 9H), 1.26–1.82 (m, $-CH_2$, 36H,), 3.93 (m, $-OCH_2$, 6H), 4.57 (d, $J = 5.9$ Hz, $-CH_2OH$, 2H), 6.53 (s, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.75, 22.41, 25.90, 29.08, 29.19, 29.22, 29.32, 30.06, 31.60, 31.67, 64.57, 68.62, 73.09, 104.67, 136.35, 152.70, 136.39. IR (melt): 2960, 2926, 2876, 2857, 1592, 1506, 1487, 1471, 1465, 1457, 1442, 1437, 1419, 1394, 1387, 1336, 1232, 1128, 1116 cm^{-1}. HRMS (FAB): calcd for M $C_{31}H_{56}O_4$ 492.4179, found 492.4177.

2.2.2. *3,4,5-Trioctyloxybenzaldehyde*

Pale yellow liquid; yield 88%. ^1H NMR ($CDCl_3$): δ 0.86 (m, $-CH_3$, 9H), 1.26–1.85 (m, $-CH_2$, 36H), 4.02 (m, $-OCH_2$, 6H), 7.06 (s, Ar, 2H), 9.81 (s, –CHO, 1H). ^{13}C NMR ($CDCl_3$): δ 13.86, 22.49, 25.90, 29.10, 29.17, 29.31, 30.19, 31.64, 31.72, 68.95, 73.33, 107.55, 131.34, 143.59, 153.32, 190.80. IR (melt): 2958, 2927, 2857, 1703, 1586, 1498, 1465, 1379, 1331, 1229, 1117, 723 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{31}H_{55}O_4$ 491.4100, found 491.4099.

2.2.3. *3,4,5-Trioctyloxybenzonitrile*

The preparation of this compound followed the literature procedures [9, 10]; yellow solid, yield 89%. ^1H NMR ($CDCl_3$): δ 0.86 (m, $-CH_3$, 9H), 1.26–1.81 (m, $-CH_2$, 36H), 3.96 (m, $-OCH_2$, 6H), 6.79 (s, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.88, 22.49, 25.86, 29.03, 29.09, 29.15, 29.18, 29.30, 30.14, 31.65, 31.73, 69.19, 73.46, 106.08, 110.27, 118.96, 142.30, 153.29. IR (melt): 2958, 2930, 2875, 2860, 2229, 1582, 1501, 1469, 1458, 1429, 1386, 1338, 1241, 1118, 833 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{31}H_{54}NO_3$ 488.4103, found 488.4097.

2.2.4. *4-(4-Trifluoromethanesulphonylaminophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

To a solution of 3,4,5-trioctyloxybenzonitrile (4.88 g, 10.0 mmol) dissolved in dried methylene chloride (30 ml) was slowly added trifluoromethane sulphonic anhydride (2.41 g, 8.55 mmol) under nitrogen. The mixture was stirred for 30 min. To this solution, 4-aminoacetophenone (0.811 g, 6.0 mmol) dissolved in dried methylene chloride (10 ml) was added dropwise at room temperature; the solution was then stirred for 48 h. The solution was twice extracted with saturated sodium bicarbonate (50 ml), and the organic layer was collected and dried over anhydrous $MgSO_4$. It was concentrated to give a black paste, and the oily residue was purified by flash chromatography, eluting with hexane/ethyl acetate (10/1). The product was obtained

as a light brown paste after recrystallization from methylene chloride/methanol; yield 20%. ^{1}H NMR ($CDCl_3$): δ 0.86 (m, $-CH_3$, 18H), 1.27–1.89 (m, $-CH_2$, 72H), 4.02–4.14 (m, $-OCH_2$, 12H), 7.20 (s, $-NHSO_2CF_3$, 1H), 7.44 (m, Ar, 4H), 7.79 (s, Ar, 1H), 7.91 (s, Ar, 2H), 8.25 (d, $J=8.6$ Hz, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.04, 22.64, 26.08, 26.15, 26.20, 29.30, 29.36, 29.45, 29.52, 30.30, 31.82, 31.88, 69.08, 69.31, 73.72, 105.91, 106.93, 109.31, 123.08, 128.37, 119.81 (q, $J=320.7$ Hz), 132.22, 133.00, 136.11, 136.48, 140.51, 140.83, 153.07, 153.43, 163.18, 164.06, 164.41. IR (melt): 2959, 2930, 2860, 1575, 1533, 1506, 1470, 1458, 1436, 1416, 1380, 1362, 1216, 1146, 1118, 834, 607 cm^{-1}. MS (FAB): calcd for MH^+ $C_{71}H_{113}F_3N_3O_8S$ 1224.8, found 1225.1. Anal: calcd for $C_{71}H_{112}F_3N_3O_8S$, C 69.63, H 9.22, N 3.43; found C 69.89, H 8.97, N, 3.51%.

2.2.5. *4-(4-Methoxyphenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow solid; yield 24%. ^{1}H NMR ($CDCl_3$): δ 0.87 (m, $-CH_3$, 18H), 1.28–1.90 (m, $-CH_2$, 72H), 3.89 (s, $-OCH_3$, 3H), 4.02–4.15 (m, $-OCH_2$, 12H), 7.06 (d, $J=8.7$ Hz, Ar, 2H), 7.46 (s, Ar, 2H)), 7.78 (s, Ar, 1H), 7.93 (s, Ar, 2H), 8.22 (d, $J=8.7$ Hz, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.03, 22.64, 26.10, 26.15, 26.18, 29.30, 29.36, 29.41, 29.49, 30.35, 31.81, 31.88, 55.29, 69.01, 69.24, 73.42, 73.53, 105.91, 106.96, 108.56, 114.13, 128.66, 129.99, 132.51, 133.18, 140.64, 140.78, 153.02, 153.37, 161.80, 163.79, 163.86, 163.92. IR (melt): 2959, 2929, 2859, 1610, 1573, 1530, 1505, 1469, 1419, 1380, 1362, 1323, 1306, 1251, 1224, 1209, 1175, 1040, 829, 785, 723 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{71}H_{115}N_2O_7$ 1107.8704, found 1107.8685. Anal: calcd for $C_{71}H_{114}N_2O_7$, C 76.99, H 10.37, N 2.53; found C 76.71, H 10.08, N 2.39%.

2.2.6. *4-(3-Trifluoromethanesulphonylaminophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Light brown paste; yield 10%. ^{1}H NMR ($CDCl_3$): 0.86 (m, $-CH_3$, 18H), 1.27–1.89 (m, $-CH_2$, 72H), 4.02–4.13 (m, $-OCH_2$, 12H), 7.15 (s, $-NHSO_2CF_3$, 1H), 7.42 (m, –Ar, 3H), 7.56 (t, $J=8.0$ Hz, 1H), 7.77 (s, Ar, 1H), 7.90 (s, Ar, 2H), 8.06 (d, $J=7.6$ Hz, Ar, 2H), 8.24 (s, Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 14.05, 22.67, 26.12, 26.19, 29.13, 29.33, 29.38, 29.50, 29.53, 30.34, 31.70, 31.86, 31.90, 68.81, 69.00, 73.67, 73.85, 105.22, 106.42, 108.70, 123.60, 125.32, 126.48, 129.46, 120.05 (q, $J=321.8$ Hz), 131.92, 132.69, 138.87, 135.36, 140.27, 140.40, 152.96, 153.25, 162.76, 163.40, 163.69. IR (melt): 2959, 2930, 2859, 1573, 1535, 1505, 1470, 1418, 1380, 1358, 1314, 1304, 1222, 1196, 1148, 1118, 843, 785, 606 cm^{-1}. MS (FAB): calcd for MH^+ $C_{71}H_{113}F_3N_3O_8S$ 1224.8; found 1224.8. Anal: calcd for $C_{71}H_{112}F_3N_3O_8S$, C 69.63, H 9.22, N 3.43; found C 69.91, H 9.43, N 3.38%.

2.2.7. *4-(3-Methoxyphenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 42%. ^{1}H NMR ($CDCl_3$): δ 0.86 (m, $-CH_3$, 18H), 1.27–1.90 (m, $-CH_2$, 72H), 3.92 (s, $-OCH_3$, 3H), 4.04–4.15 (m, $-OCH_2$, 12H), 7.07 (dd, $J=2.7$ and 8.3 Hz, Ar, 1H), 7.46 (m, Ar, 3H), 7.79 (m, Ar, 3H), 7.93 (s, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.95, 22.59, 26.13, 29.26, 29.32, 29.40, 29.46, 29.49, 30.34, 31.77, 31.84, 55.02, 68.80, 69.06, 73.29, 73.38, 105.66, 106.74, 109.12, 112.59, 115.95, 119.37, 129.59, 132.09, 132.88, 138.95, 140.55, 140.77, 152.91, 153.27, 159.92, 163.59, 163.82, 163.88. IR (melt): 2959, 2929, 2859, 1594, 1573, 1535, 1505, 1469, 1430, 1414, 1381, 1358, 1303, 1244, 1225, 1209, 1117, 1076, 1053, 1039, 840, 780, 723, 677 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{71}H_{115}N_2O_7$ 1107.8704, found 1107.8723. Anal: calcd for $C_{71}H_{114}N_2O_7$, C 76.99, H, 10.37, N 2.53; found C 76.75, H, 10.41, N, 2.25%.

2.2.8. *4-(4-Fluorophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 28%. ^{1}H NMR (CD_2Cl_2): δ 0.89 (m, $-CH_3$, 12H), 1.31–1.92 (m, $-CH_2$, 72H), 4.02–4.17 (m, $-OCH_2$, 12H), 7.27 (t, $J=8.6$ Hz, –Ar, 2H), 7.52 (s, Ar, 2H), 7.88 (s, –Ar, 1H), 7.95 (s, Ar, 2H), 8.31 (td, $J=2.1$ and 7.2 Hz, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.04, 22.65, 26.11, 26.17, 26.20, 29.31, 29.36, 29.43, 29.49, 30.36, 31.83, 31.89, 69.05, 69.28, 73.46, 73.56, 105.95, 107.00, 109.03, 115.79 (d, $J=21.6$ Hz), 129.22 (d, $J=8.3$ Hz), 132.21, 132.89, 133.74, 140.82, 140.99, 153.08, 153.43, 163.35, 163.94, 164.21, 164.47 (d, $J=249.2$ Hz). IR (melt): 2959, 2929, 2859, 1603, 1575, 1533, 1505, 1470, 1415, 1381, 1361, 1320, 1233, 1210, 1157, 1117, 831, 785 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{70}H_{112}FN_2O_6$ 1095.8504, found 1095.8516. Anal: calcd for $C_{70}H_{112}FN_2O_6$, C 76.74, H 10.21, N, 2.56; found C 76.95, H 10.08, N, 2.56%.

2.2.9. *4-(4-Chlorophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 14%. ^{1}H NMR ($CDCl_3$): δ 0.86 (m, $-CH_3$, 18H), 1.22–1.87 (m, $-CH_2$, 72H), 4.02–4.15 (m, $-OCH_2$, 12H), 7.46 (s, Ar, 2H), 7.52 (d, $J=8.7$ Hz, Ar, 2H), 7.79 (s, –Ar, 1H), 7.91 (s, Ar, 2H), 8.17 (d, $J=8.6$ Hz, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.98, 22.61, 26.09, 26.15, 29.28, 29.34, 29.43, 29.48, 29.51, 30.35, 31.80, 31.86, 68.86, 69.09, 73.36, 73.44, 105.63, 106.72, 108.71, 128.38, 128.84, 131.90, 135.91, 136.62, 132.70,

140.62, 140.83, 152.93, 153.28, 162.90, 163.65, 163.89. IR (melt): 2960, 2929, 2859, 1596, 1579, 1570, 1530, 1505, 1493, 1469, 1410, 1380, 1360, 1318, 1304, 1226, 1211, 1116, 1093, 1015, 827, 784, 724 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{70}H_{112}ClN_2O_6$ 1111.8209, found 1111.8184. Anal: calcd for $C_{70}H_{111}ClN_2O_6$, C 75.60, H, 10.06, N 2.52; found C 75.59, H, 9.92, N 2.73%.

2.2.10. *4-(4-Bromophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 16%. ^1H NMR ($CDCl_3$): δ 0.87 (m, $-CH_3$, 18H), 1.27–1.88 (m, $-CH_2$, 72H), 4.02–4.15 (m, $-OCH_2$, 12H), 7.46 (s, Ar, 2H), 7.68 (d, $J = 8.4$ Hz, Ar, 2H), 7.79 (s, Ar, 1H), 7.91 (s, Ar, 2H), 8.10 (d, $J = 8.6$ Hz, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.05, 22.66, 26.11, 26.17, 26.20, 29.31, 29.36, 29.43, 29.50, 30.36, 31.83, 31.89, 69.04, 69.28, 73.47, 73.57, 105.94, 106.97, 109.06, 128.73, 131.99, 125.19, 132.10, 132.79, 136.52, 140.83, 141.03, 153.06, 153.43, 163.28, 163.98, 164.31. IR (melt): 2959, 2929, 2859, 1593, 1577, 1569, 1530, 1505, 1489, 1470, 1380, 1361, 1318, 1305, 1226, 1211, 1116, 1074, 1011, 824, 784, 723 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{70}H_{112}BrN_2O_6$ 1155.7703, found 1155.7684. Anal: calcd for $C_{70}H_{111}BrN_2O_6$, C 72.69, H, 9.67, N 2.42; found C 72.47, H 9.47, N 2.17%.

2.2.11. *4-(4-Iodophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 22%. ^1H NMR ($CDCl_3$): δ 0.87 (m, $-CH_3$, 18H), 1.27–1.87 (m, $-CH_2$, 72H), 4.02–4.14 (m, $-OCH_2$, 12H), 7.45 (s, Ar, 2H), 7.79 (s, Ar, 1H), 7.89 (m, Ar, 4H), 7.96 (dd, $J = 2.1$ and 8.4 Hz, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.02, 22.64, 26.11, 26.17, 29.30, 29.36, 29.44, 29.50, 30.37, 31.82, 31.88, 68.89, 69.13, 73.38, 73.46, 97.17, 105.70, 106.76, 108.70, 128.74, 137.86, 131.92, 132.69, 137.02, 140.67, 140.90, 152.95, 153.31, 163.17, 163.71, 163.98. IR (melt): 2959, 2928, 2859, 1590, 1576, 1528, 1506, 1487, 1470, 1457, 1409, 1380, 1361, 1227, 1211, 1117, 1007, 821, 784 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{70}H_{112}IN_2O_6$ 1203.7565, found 1203.7537. Anal: calcd for $C_{70}H_{111}IN_2O_6$, C 69.86, H 9.30, N 2.33; found C 69.73, H 9.02, N, 2.13%.

2.2.12. *4-(4-Ethylphenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 33%. ^1H NMR ($CDCl_3$): δ 0.87 (m, $-CH_3$, 18H), 1.27–1.90 (m, $-CH_2$, 75H), 2.74 (q, $J = 7.5$ Hz, $-ArCH_2CH_3$), 2H), 4.01–4.15 (m, $-OCH_2$, 12H), 7.38 (d, $J = 8.1$ Hz, Ar, 2H), 7.46 (s, Ar, 2H), 7.81 (s, Ar, 1H), 7.93 (s, Ar, 2H), 8.15 (d, $J = 8.3$ Hz, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.03, 15.39, 22.64, 26.10, 26.15, 26.18, 28.78, 29.30, 29.36, 29.41, 29.48, 30.34, 31.82, 31.88, 69.03, 69.26, 73.44, 73.54, 105.96, 107.00, 109.24, 127.23, 128.34, 132.48, 133.14, 135.13, 140.68, 140.85, 153.04, 153.40, 147.21, 163.90, 164.04, 164.52. IR (melt): 2960, 2929, 2859, 1571, 1530, 1505, 1469, 1416, 1380, 1362, 1319, 1306, 1225, 1117, 1064, 1050, 1020, 832, 785, 723 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{72}H_{117}N_2O_6$ 1105.8911, found 1105.8889. Anal: calcd for $C_{72}H_{116}N_2O_6$, C 78.21, H, 10.57, N 2.53; found C 78.03, H 10.45, N 2.24%.

2.2.13. *4-(4-Methylphenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 39%. ^1H NMR ($CDCl_3$): δ 0.87 (m, $-CH_3$, 18H), 1.27–1.88 (m, $-CH_2$, 72H), 2.45 (s, $-ArCH_3$, 3H), 4.02–4.15 (m, $-OCH_2$, 12H), 7.35 (d, $J = 8.1$ Hz, Ar, 2H), 7.46 (s, Ar, 2H), 7.81 (s, Ar, 1H), 7.93 (s, Ar, 2H), 8.13 (d, $J = 8.3$ Hz, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.06, 21.43, 22.66, 26.11, 26.17, 26.20, 29.19, 29.31, 29.38, 29.43, 29.49, 30.36, 31.84, 31.90, 69.08, 69.32, 73.48, 73.59, 106.02, 107.05, 109.24, 127.14, 129.57, 132.52, 133.16, 134.88, 140.72, 140.96, 153.07, 153.43, 140.88, 163.96, 164.11, 164.50. IR (melt): 2959, 2928, 2859, 1571, 1531, 1505, 1470, 1458, 1437, 1413, 1380, 1362, 1320, 1305, 1224, 1208, 1117, 1020, 819, 785, 755, 723 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{71}H_{115}N_2O_6$ 1091.8755, found 1091.8807. Anal: calcd for $C_{71}H_{114}N_2O_6$, C 78.11, H 10.53, N, 2.57; found C 77.94, H, 10.59, N, 2.33%.

2.2.14. *4-(3-Fluorophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow solid; yield 19%. ^1H NMR (CD_2Cl_2): δ 0.89 (m, $-CH_3$, 18H), 1.31–1.92 (m, $-CH_2$, 72H), 4.02–4.17 (m, $-OCH_2$, 12H), 7.27 (td, $J = 1.8$ and 8.5 Hz, Ar, 1H), 7.56 (m, Ar, 3H), 7.90 (s, Ar, 1H), 7.95 (s, Ar, 2H), 8.04 (m, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.02, 22.64, 26.11, 26.18, 29.29, 29.36, 29.42, 29.49, 30.36, 31.81, 31.88, 69.03, 69.24, 73.44, 73.53, 105.90, 106.98, 109.34, 114.14 (d, $J = 20.6$ Hz), 117.37 (d, $J = 21.4$ Hz), 122.71 (d, $J = 2.1$ Hz), 130.26 (d, $J = 8.2$ Hz), 132.03, 132.74, 140.00 (d, $J = 7.2$ Hz), 140.87, 141.05, 153.08, 153.43, 163.06, 164.00, 164.35, 163.23 (d, $J = 245.0$ Hz). IR (melt): 2959, 2929, 2859, 1594, 1575, 1535, 1506, 1470, 1411, 1405, 1380, 1360, 1315, 1225, 1117, 841, 781, 670 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{70}H_{112}FN_2O_6$ 1095.8504, found 1095.8516. Anal: calcd for $C_{70}H_{111}FN_2O_6$, C 76.74, H 10.21, N, 2.56; found C 76.52, H, 9.98, N 2.41%.

2.2.15. *4-(3-Chlorophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 29%. ^{1}H NMR ($CDCl_3$): δ 0.87 (m, $-CH_3$, 18H), 1.27–1.90 (m, $-CH_2$, 72H), 4.02–4.16 (m, $-OCH_2$, 12H), 7.48 (m, Ar, 4H), 7.79 (s, –Ar, 1H), 7.92 (s, Ar, 2H), 8.11 (dd, $J=3.4$ and 8.5 Hz, Ar, 1H), 8.21 (s, Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.67, 26.11, 26.17, 29.32, 29.38, 29.43, 29.47, 29.55, 30.36, 31.84, 31.90, 69.08, 69.30, 73.50, 73.60, 105.94, 106.98, 109.55, 125.35, 127.39, 130.09, 130.55, 132.11, 134.97, 139.51, 132.76, 140.85, 141.02, 153.12, 153.47, 163.13, 164.12, 164.53. IR (melt): 2959, 2929, 2859, 1570, 1532, 1505, 1470, 1425, 1413, 1404, 1379, 1359, 1315, 1226, 1210, 1117, 1080, 841, 782, 723, 668 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{70}H_{112}ClN_2O_6$ 1111.8209, found 1111.8214. Anal: calcd for $C_{70}H_{111}ClN_2O_6$, C 75.60, H 10.06, N 2.52; found C 75.36, H 9.98, N 2.27%.

2.2.16. *4-(3-Bromophenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 23%. ^{1}H NMR ($CDCl_3$): δ 0.84 (m, $-CH_3$, 18H), 1.26–1.89 (m, $-CH_2$, 72H), 4.01–4.14 (m, $-OCH_2$, 12H), 7.42 (m, Ar, 3H), 7.64 (d, $J=7.4$ Hz, Ar, 1H), 7.77 (s, Ar, 1H), 7.90 (s, Ar, 2H), 8.13 (d, $J=8.0$ Hz, Ar, 1H), 8.35 (d, $J=1.2$ Hz, Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 14.05, 22.66, 26.11, 26.18, 29.31, 29.37, 29.42, 29.50, 29.53, 30.36, 31.83, 31.90, 69.12, 69.36, 73.50, 73.59, 106.08, 107.10, 109.50, 125.79, 130.32, 133.45, 123.10, 132.11, 132.75, 139.79, 140.96, 141.15, 153.12, 153.48, 163.02, 164.13, 164.54. IR (melt): 2959, 2928, 2859, 1576, 1569, 1532, 1505, 1470, 1422, 1413, 1379, 1359, 1315, 1307, 1294, 1226, 1210, 1117, 1070, 841, 781, 723, 667 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{70}H_{112}BrN_2O_6$ 1155.7703, found 1155.7692. Anal: calcd for $C_{70}H_{111}BrN_2O_6$, C 72.69, H 9.67, N 2.42; found C 72.39, H 9.59, N 2.17%.

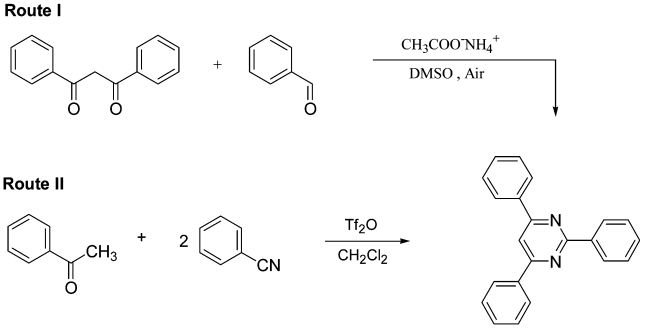
2.2.17. *4-(3-Methylphenyl)-2,6-bis(3,4,5-trioctyloxyphenyl)pyrimidine*

Yellow paste; yield 40%. ^{1}H NMR ($CDCl_3$): δ 0.86 (m, $-CH_3$, 18H), 1.27–1.90 (m, $-CH_2$, 72H), 2.48 (s, $ArCH_3$ 3H), 4.02–4.15 (m, $-OCH_2$, 12H), 7.34 (d, $J=7.6$ Hz, Ar, 1H, 7.44 (m, Ar, 3H), 7.82 (s, Ar, 1H), 8.00 (s, Ar, 2H), 8.01 (m, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.04, 21.54, 22.64, 26.11, 26.15, 26.18, 29.30, 29.36, 29.41, 29.48, 29.53, 30.35, 31.82, 31.88, 69.09, 69.32, 73.46, 73.57, 106.06, 107.10, 109.67, 124.41, 127.86, 128.73, 131.39, 132.46, 133.11, 138.47, 137.67, 140.76, 140.93, 153.08, 153.43, 164.00, 164.17, 164.77. IR (melt): 2959, 2928, 2859, 1572, 1534, 1506, 1469, 1380, 1360, 1225, 1117, 843, 782 cm^{-1}. HRMS (FAB): calcd for MH^+ $C_{71}H_{115}N_2O_6$ 1091.8755, found 1091.8749. Anal: calcd for $C_{71}H_{114}N_2O_6$, C 78.11, H 10.53, N, 2.57; found C 78.35, H 10.81, N 2.51%.

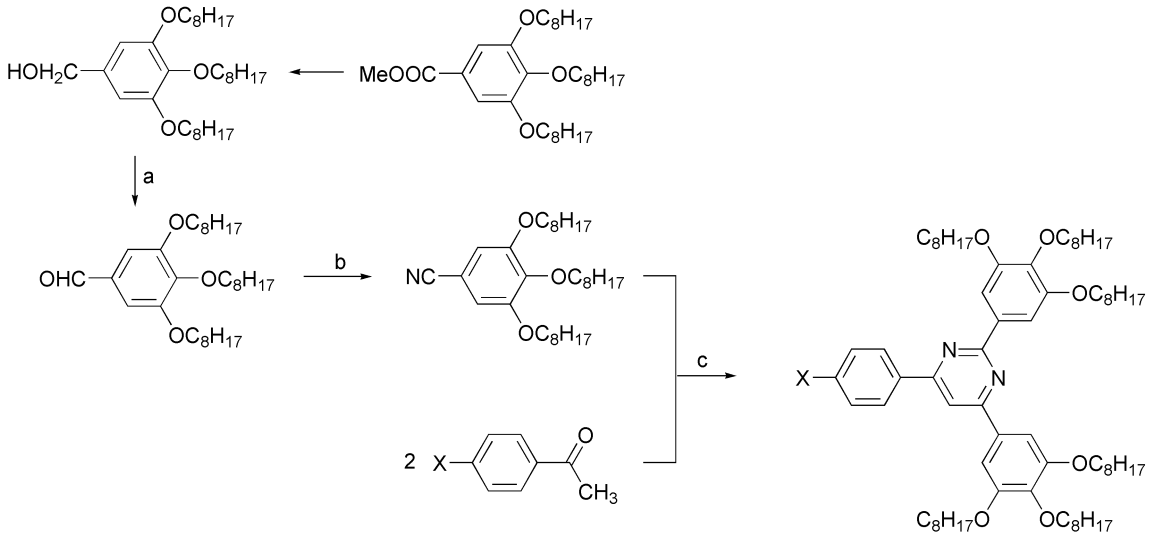
3. Results and discussion

3.1. *Synthesis and characterization*

Typical syntheses of pyrimidyl derivatives as reported in the literature [11] were followed and may be summarized by either Route I or Route II. However, the synthetic preparation by either route was found to be quite sensitive to the electronic and/or steric properties of the substituents on the phenyl rings.

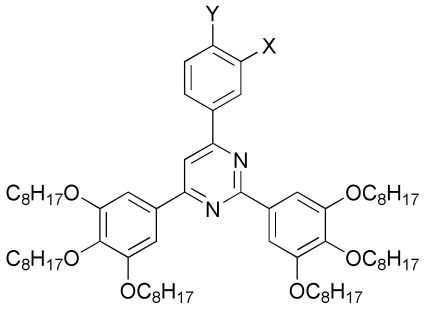


In our previous paper [9] we described the preparation and mesomorphic characterization of a new type of similar pyrimidyl derivatives **2a**–**2d** and **3a**–**3c**; these discotic molecules were found to exhibit hexagonal columnar (Col_h) phases. Interestingly the synthetic preparation of these pyrimidyl derivatives [11 *b*] was found to be unsuccessful if prepared by Route I using substituted β-diketones and benzaldehydes in the presence of sodium hydride and ammonium acetate with oxygen bubbling. However, these compounds were successfully prepared and isolated by Route II. In addition, the pyrimidyl derivatives prepared by Route II were found to be dependent on the number of alkoxy chains on the phenyl rings of the reactants used. For example, the reactions of 4-alkoxyacetophenones with 4-alkoxybenzonitriles, or 3,4-dialkoxyacetophenones with 3,4-dialkoxybenzonitriles, led completely to the final products isolated as 2,4,6-tri(4-alkoxy phenyl)-pyrimidines **2a** or 2,4,6-tri(3,4-dialkoxyphenyl)-pyrimidines **2b**, respectively, as the major products. Nevertheless, as the numbers of alkoxy chains on both reactants increased to two or three, the yields of the isolated pyrimidines **2a**–**2d** were dramatically decreased, and 2,4,6-tri(3,4,5-trialkoxyphenyl)triazines **4** were also isolated as minor products. The ratio of these two products (i.e. pyrimidines **2**/triazines **4**) obtained also varied with the carbon length of the alkoxy chains and the reaction conditions. However, the mixtures were easily separated and purified by flash chromatography. Nevertheless, 2,4,6-tri(3,4,5-trialkoxyphenyl)triazines **4**, not the expected products, 2,4,6-tri(3,4,5-trialkoxy-phenyl)pyrimidines **2** were in fact isolated as the

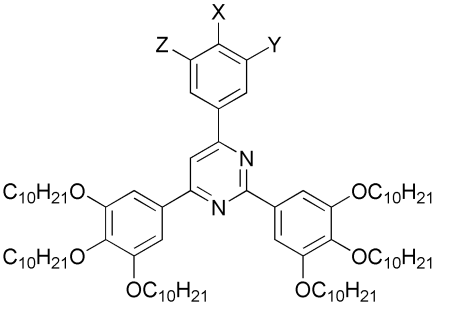


1a X = H, $NHSO_2CF_3$, F, Cl, Br, I, OCH_3, CH_3, C_2H_5

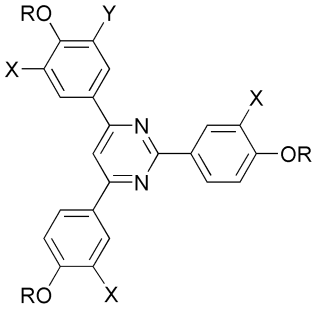
Scheme 1. Conditions and reagents (a) pyridinium chlorochromate (2.0 eq), stirred at rt in CH_2Cl_2, 3 h, 75–85%; (b) pyridine hydrochloride (1.5 eq), reflux in nitroethane, 12 h 78–86%; (c) trifluoromethane sulphonic anhydride (1.1 eq), stirred in CH_2Cl_2, at rt, 48 h 46–65%.



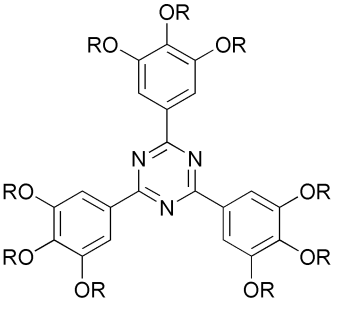
1a X = H; Y = H, $NHSO_2CF_3$, F, Cl, Br, I, OCH_3, CH_3, C_2H_5
1b Y = H; X = $NHSO_2CF_3$, F, Cl, Br, OCH_3, CH_3



2a X = Y = Z = H
2b X = $OC_{10}H_{21}$; Y = Z = H
2c X = Y = $OC_{10}H_{21}$; Z = H
2d X = Y = Z = $OC_{10}H_{21}$



R = $(CH_2)_nH$
3a X = Y = H
3b X = OR; Y = H
3c X = Y = OR



4 R = $(CH_2)_nH$

major products prepared by Route II, when 3,4,5-trialkoxyacetophenes and 3,4,5-trialkoxybenzonitriles were reacted under similar conditions. The yield of the isolated product was also found to be strongly dependent on the electronic properties of the substituents. Strong electron-donating properties of the alkoxy groups apparently influenced the activity and/or stability of the reaction intermediate, consequently leading to the products by different pathways.

All compounds **1a** and **1b** reported in this work were prepared by Route II. The reaction yields, ranging from 41–65%, generally depended on the different reaction conditions used; the synthetic procedures giving the highest yields are described in the experimental section. These were the preparations by the condensation reaction of substituted acetophenones, two equivalents of benzonitriles and trifluoromethanesulphonic anhydride in dried nitroethane or methylene chloride for 48 h, as shown in Scheme 1. Attempts to prepare the derivatives with a nitro group ($X = NO_2$) were all failed by either Route I or II. All compounds **1a**, **1b** were characterized by ^1H and ^{13}C NMR, high resolution MS and elemental analysis.

3.2. *Mesomorphic properties*

The formation of columnar phases is well known to be strongly dependent on the number of side chains (i.e. side chain density) attached to the central core. This general principle is often applied to discotic molecules; consequently, more flexible side chains are often needed for larger cores. However, for non-discotic molecules exhibiting columnar phases, fewer side chains are possibly needed, since correlated columnar phases are generally organized with an antiparallel arrangement within the columns for this type of molecule. On the other hand, the degree of rigidity resulting from the central core may be reduced by the use of heterocyclic molecules. Compounds composed of a heterocyclic core with a reduced molecular symmetry should probably lead to a lowering of melting points, resulting from less favourable packing in the crystal state. The formation of columnar phases was generally found to be critically dependent on the side chain density, and most columnar mesogens reported have at least six side chains appended around the core. In our previous paper we found that in total six side chains around the central pyrimidyl core are at least required for the formation of stable columnar phases.

3.2.1. *Derivatives of para-substituted pyrimidines* ***1a***

The introduction of various substituents at the $C^{3'}$(*meta*)- or $C^{4'}$(*para*)-positions of the phenyl ring allows for systematic studies of the substituent effect on mesophase formation in this system. The terminal phenyl ring was substituted with fluoro, chloro, bromo, iodo, methyl, ethyl, trifluoromethanesulphonylamino and methoxy groups. The liquid crystalline behaviour of these compounds **1a** and **1b** was studied using a DSC and POM. The phase transition temperatures and associated thermodynamic data of compounds **1a** are

Table 1. Phase behaviour of compounds **1a**. Cr_1, Cr_2 = crystal phases; Col_L = lamellar columnar phase; I = isotropic. The transition temperature (^0C) and enthalpies (in parenthesis, $J\,g^{-1}$) are determined by DSC at a scan rate of $10.0\,^0C\,min^{-1}$.

Y = H	Cr_1	29.8 (2.08) / -0.36 (30.5)	Cr_2	38.9 (39.2)	Col_L	90.5 (3.70) / 87.8 (3.80)	I
$NHSO_2CF_3$			Cr	30.0 (6.60) / 14.2 (3.54)	Col_L	148.4 (5.15) / 143.7 (4.88)	I
F	Cr_1	9.96 (22.8) / -19.5 (20.0)	Cr_2	21.4 (1.31)	Col_L	128.2 (5.67) / 125.8 (5.50)	I
Cl	Cr_1	1.66 (15.7) / -35.2 (11.4)	Cr_2	13.9 (6.85)	Col_L	140.9 (6.55) / 138.6 (6.35)	I
Br	Cr_1	-3.00 (8.74) / -39.4 (7.08)	Cr_2	9.39 (1.16)	Col_L	144.4 (6.58) / 142.3 (6.45)	I
I			Cr	7.23 (14.7) / -39.8 (4.75)	Col_L	138.0 (5.89) / 136.2 (5.76)	I
OCH_3			Cr	36.4 (46.1) / -37.1 (13.0)	Col_L	104.5 (4.65) / 102.2 (4.54)	I
CH_3			Cr	-2.89 (14.1)	Col_L	104.9 (5.13) / 102.2 (4.99)	I
C_2H_5			Cr	12.5 (29.3) / -35.9 (12.5)	Col_L	101.5 (5.17) / 99.5 (5.08)	I

summarized in table 1.

All compounds **1a** formed columnar phases, and in fact are all room temperature liquid crystals. All compounds **1a** exhibited enantiotropic behaviour. The DSC traces show that all the compounds exhibit two transitions, crystal–columnar and columnar–isotropic (Cr→Col→I). An additional crystal–crystal transition ($Cr_1 \rightarrow Cr_2$) was also observed for compounds with an electron-withdrawing group (X=F, Cl, Br, I, $NHSO_2CF_3$) at lower temperatures. The recrystallization temperature of the ($X=CH_3$) derivative on cooling was not detected at temperatures down to −60°C. Crystal–mesophase transitions of compounds **1a** were observed in the range −2.89–36.4°C, and the mesophase–isotropic transitions were observed at higher temperatures and in the range 101.5–148.4°C. All compounds containing a substituent have a higher clearing temperature than that of the compound containing no substituent (X=H), by *c.* 11–58°C depending on the electronic properties of the substituent. This increase in clearing temperatures may be attributed to stronger dipolar interactions due to the presence of a polar substituent. The DSC data also indicate that the observed columnar mesophases show a correlation with the electronic properties of the substituents, compounds containing electron-withdrawing substituents (X=F, Cl, Br, I, $NHSO_2CF_3$) having a higher clearing temperature than those of compounds containing electron-donating substituents (X=Me, Et, OMe). Specifically, compounds containing electron-withdrawing substituents have clearing temperatures higher by *c.* 37.7–57.9°C than that of the compound without a substituent (**1a**; X=H); whereas, the increase in clearing temperatures decreased to *c.* 11.0–14.0°C for compounds containing electron-donating substituents. Molecular interactions were enhanced by the presence of a polar substituent near close to the central core, and the temperature range of the columnar phase also increased dramatically. In addition, all compounds **1a** with substituents have a wider range of mesophase temperature (68.1–135°C on heating) than that (51.6°C on heating) of the compound **1a**; X=H. Halogen-substituted compounds have higher clearing temperatures (128.2–144.4°C) than those of non halogen-substituted compounds (90.5–104.9°C). These dramatic increased both in the clearing temperatures and mesophase ranges may be attributed to stronger dipolar interactions. The derivative **1a** ($X=OCH_3$) was found to have the smallest temperature range (68.1°C on heating) for the mesophase.

The mesophase was identified as columnar (Col) based on the characteristic optical textures observed. A focal-conic texture (see figure 1) with linear birefrigent defects was obtained on slowly cooling from the isotropic liquid, as is often observed for discotic molecules. A large homeotropic area was also observed. All these compounds **1a** were also studied using a variable temperature powder X-ray diffractometer to confirm the structures of the mesophase. A summary of the diffraction peaks for compounds **1a** is given in table 2. A diffraction pattern consisting of a strong peak and a weak peak (see figure 2) corresponding to the Miller indices (1 0) and (2 0) at lower angles, characteristic of Col_L phases with a *d*-spacing ratio of 1/1 and 1/2, is observed throughout the series. However, others diffraction peaks corresponding to (3 0), (4 0), (5 0), and higher indices, which may normally be detected in lamellar mesophases, were not observed in our system. These diffraction patterns

Figure 1. Optical textures observed for compound **1a** (X=F) at 120°C (top) and **1b** ($X=OCH_3$) at 100°C (bottom).

Table 2. Variable temperature XRD data for compounds **1a**.

Substituent	Mesophase	Obsd (calcd) spacing/Å	Miller indices
$NHSO_2CF_3$	Col_L at 100°C	22.34 (22.34)	(1 0 0)
		11.22 (11.17)	(2 0 0)
F	Col_L at 100°C	20.98 (20.98)	(1 0 0)
		10.61 (10.49)	(2 0 0)
Cl	Col_L at 100°C	21.26 (21.26)	(1 0 0)
		10.72 (10.63)	(2 0 0)
Br	Col_L at 100°C	21.16 (21.16)	(1 0 0)
		10.68 (10.58)	(2 0 0)
I	Col_L at 100°C	21.22 (21.22)	(1 0 0)
		10.69 (10.61)	(2 0 0)
H	Col_L at 60°C	20.97 (20.97)	(1 0 0)
C_2H_5	Col_L at 70°C	20.79 (20.79)	(1 0 0)
		10.49 (10.40)	(2 0 0)
CH_3	Col_L at 70°C	20.85 (20.85)	(1 0 0)
		10.51 (10.43)	(2 0 0)
OCH_3	Col_L at 70°C	21.07 (21.07)	(1 0 0)
		10.64 (10.54)	(2 0 0)

are typically characteristic of the lamellar columnar (Col_L) phase. A broad diffuse band, which arises from alkyl chains and is normally seen at 4.0–5.0 Å in the wide angle was barely observed.

3.2.2. *Derivatives of meta substituted pyrimidines* ***1b***

The compounds **1b**, containing a variety of substituents at the $C^{3'}$(*meta*)-position of the phenyl ring, were also studied; the phenyl ring was only substituted with fluoro, chloro, bromo, methyl, trifluoromethanesulphonylamino and methoxy groups. The mesomorphic properties observed for these two types of derivatives, i.e. *para*- (**1a**) and *meta*- (**1b**), were used to establish the substituent effects on the formation of mesophases. The phase transitions and thermodynamic data are summarized in table 3.

The compounds **1b** exhibited mesomorphic behaviour similar to compounds **1a**. However, compounds **1b** have clearing temperatures lower than those of compounds **1a** by *c*. 8.4–47.2°C except for $X=OCH_3$ (higher by *c*. 7.0°C). In addition, the temperature ranges of the columnar mesophases for compounds **1b** were relatively smaller than those of compounds **1a**. This lowering both of the clearing temperatures and temperature ranges of the mesophase may be attributed to weaker dipolar interactions by a reduced resonance effect in the *meta*-substituted compounds. The derivative with $-OCH_3$ substituent is the only one for which the opposite effect is seen. The exact cause of this observation is not clear, and steric factors may play an important role. A summary of the diffraction peaks for compounds **1b** is given in table 4. The diffraction data of compounds **1b** showed similar patterns and lattice constants to compounds **1a**, indicating that these two types of compound probably exhibit similar mesophase structures.

In our previous paper [12], the correlation of columnar phases with the steric factors of substituents in β-diketonate metallomesogens was studied. The formation of a given columnar phase was dependent on the steric factor; the complexes containing a substituent with an A value [13] >7.11 (for example, $A=7.27$ for $-CH_3$, $A=7.48$ for $-C_2H_5$), exhibited rectangular columnar phases, whereas others containing a substituent with A value <3.34, (i.e. $-OCH_3$,

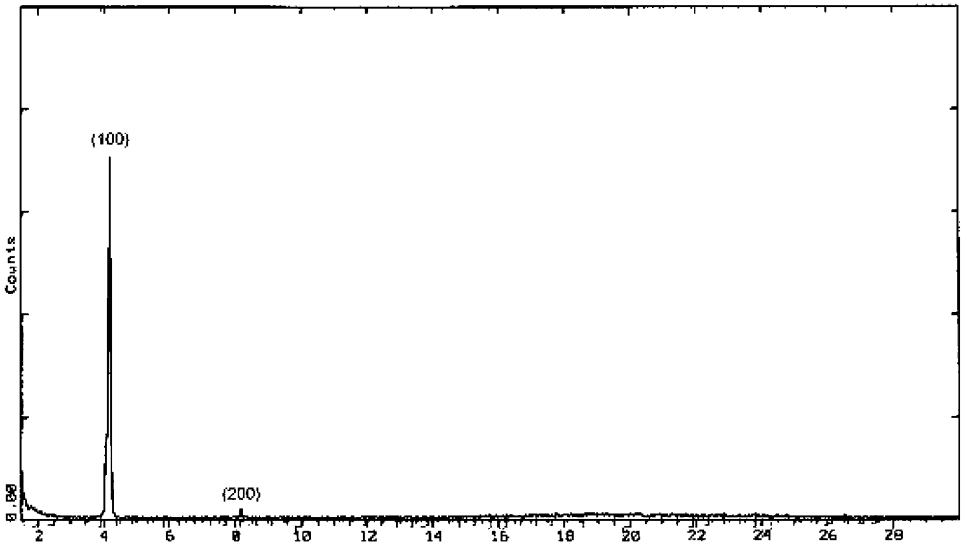


Figure 2. Powder XRD pattern of compound **1a** ($X=NHSO_2CF_3$) at 70°C.

Table 3. Phase behaviour of compounds **1b**. Col_L = lamellar columnar phase; I = isotropic. The transition temperature (^0C) and enthalpies (in parenthesis, $J\,g^{-1}$) are determined by DSC at a scan rate of $10.0^0C\,min^{-1}$.

$X = NHSO_2CF_3$					Col_L	101.2 (1.33) / 91.3 (1.27)	I
F		Cr	27.3 (27.3) / -16.6 (19.8)		Col_L	119.8 (5.52) / 117.3 (5.34)	I
Cl		Cr	5.23 (3.74) / 1.94 (4.37)		Col_L	119.0 (5.28) / 116.1 (4.90)	I
Br		Cr	19.4 (6.13) / 13.1 (5.92)		Col_L	117.0 (5.06) / 114.5 (4.89)	I
OCH_3		Cr	18.2 (41.2) / -39.2 (10.4)		Col_L	111.5 (5.70) / 109.3 (5.55)	I
CH_3	Cr_1	-16.3 (9.13) / -22.4 (10.0)	Cr_2	13.3 (0.71)	Col_L	88.9 (4.49) / 86.8 (4.41)	I

Table 4. Variable temperature XRD data for compounds **1b**.

Substituent	Mesophase	Obsd (calcd) spacing/Å	Miller indexes
$NHSO_2CF_3$	Col_L at 70°C	21.13 (21.13)	(1 0 0)
		10.81 (10.57)	(2 0 0)
F	Col_L at 80°C	21.02 (21.02)	(1 0 0)
		10.57 (10.51)	(2 0 0)
Cl	Col_L at 80°C	20.88 (20.88)	(1 0 0)
		10.53 (10.44)	(2 0 0)
Br	Col_L at 80°C	20.96 (20.96)	(1 0 0)
		10.55 (10.48)	(2 0 0)
CH_3	Col_L at 50°C	20.71 (20.71)	(1 0 0)
		10.43 (10.36)	(2 0 0)
OCH_3	Col_L at 70°C	20.79 (20.79)	(1 0 0)
		10.50 (10.40)	(2 0 0)

$A = 3.14$; I, $A = 2.55$), showed hexagonal columnar phases. However, such a correlation was not observed here case. In addition, it is interesting to note that a non-linear plot of the clearing temperatures and Hammett σ_p constants of different substituents in **1a** and **1b** was obtained, see figure 3. However, a more linear relationship with a correlation coefficient of 0.9499 for *para*-derivatives over 0.8632 for *meta*-derivatives was in fact observed. This result indicated that the mesomorphic properties observed by these compounds were not directly correlated with the electronic properties of the substituents.

4. Conclusions

Examples of a new class of heterocyclic compounds derived from pyrimidine were prepared and all showed room temperature mesophases. Higher clearing temperatures and wider ranges of phase temperatures were observed by the incorporation of various substituents in the terminal phenyl ring of these pyrimidines, and this enhanced effect was attributed to stronger dipolar

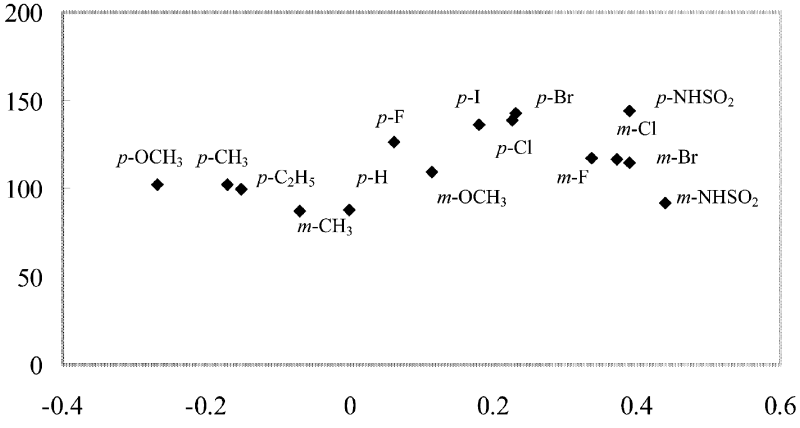


Figure 3. The plot of clearing temperature (°C) with Hammett σ constants of substituents in **1a** and **1b**.

interactions. This effect is more clearly observed in compounds with electron-withdrawing substituents than in those with electron-donating substituents. In addition, this effect is also better observed in compounds substituted in the *para*-position (**1a**) than the *meta*-position (**1b**). Derivatives containing the $X=-OCH_3$ group show the opposite trend. Among these new compounds the *para*-bromo derivative (**1a**; $X=Br$) exhibited a widest mesophase temperature range of 181.7°C on cooling and 135.0°C on heating.

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