Synthesis and mesomorphic studies on the series of 2-(4-alkoxyphenyl)-5-phenylpyridines and 2-(6-alkoxynaphthalen-2-yl)-5-phenylpyridines

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Two homologous series of pyridine-containing liquid crystalline compounds, 2-(4-alkoxyphenyl)-5-phenylpyridines (nO-PPyP, n = 3–7) and 2-(6-alkoxynaphthalen-2-yl)-5-phenylpyridines (mO-NpPyP, m = 3–7), were synthesised. The preparation of compounds of nO-PPyP and mO-NpPyP was completed in a short two-step reaction with overall yields of about 71–80% and 36–40%, respectively. Spectral analyses were in accordance with the expected structures. Their thermotropic behaviours were studied using polarising optical microscopy (POM) and further confirmed by differential scanning calorimetry (DSC). Experimental evidence shows that compounds in the mO-NpPyP series with a slightly tilted hard core display greater nematic tendency than those in the nO-PPyP series with a straight hard core.

Keywords: synthesis; pyridine-containing compounds; liquid crystals; thermal analysis

1. Introduction

Many nitrogen-containing heteroaromatic mesogenic compounds have been studied in the past [1–14]. Due to the difficulties in synthesis, detailed comparisons of trends within homologous series of pyridine-containing liquid crystalline compounds were rarely investigated [11–14]. The synthesis of pyridine-containing liquid crystals was usually carried out by a cyclisation reaction, such as by reacting an enamine with an appropriate vinyl ketone to give a dihydropyran, which then reacts with hydroxylamine hydrochloride to provide a pyridine [14], or else by a varied procedure [10].

Recently, pyridine-containing liquid crystals have been studied extensively [15–20]. Some were prepared by the cross coupling of arylboronic acids with halopyridines in the presence of a palladium complex [12, 20], whereas others were synthesised by the reaction of 2,2-dichloro-1-(4-methylphenyl)cyclopropanecarbaldehyde and 4-n-alkoxybenzylamine at a high temperature [17–19]. Although these methods are of great value for constructing important heterocyclic systems, most suffer from limited scope of the method applied, a large number of synthetic steps, need an expensive catalyst and have relatively low yields.

Pyridine-containing liquid crystalline compounds were known for their good thermal stability and good miscibility with other mesogenic partners. Compounds containing pyridyl rings appear to favour smectic behaviour and usually have reduced crystal thermal stabilities [11, 15–20]. It was further indicated that the lone pair of electrons on the nitrogen atoms act to broaden the molecule and also introduce attractive forces, which aid smectic phase formation [21].

Previously, we successfully applied the regioselective addition of organometallic reagents to 1-acylpyridinium salts for the preparation of some pyridine-containing compounds [22–24]. Recently, we reported the novel synthesis of some homologous series of pyridine-containing liquid crystalline compounds [25–28]. As a continuation of our research, the present work reports the syntheses and thermotropic behaviour of two novel homologous series of 2-(4-alkoxyphenyl)-5-phenylpyridines (nO-PPyP) and 2-(6-alkoxynaphthalen-2-yl)-5-phenylpyridines (mO-NpPyP), in which both n and m varied from propyl to heptyl for comparing the structure–property relationships. The structures of the target materials are as follows:

nO-PPyP (n = 3–7)

and

mO-NpPyP (m = 3–7).
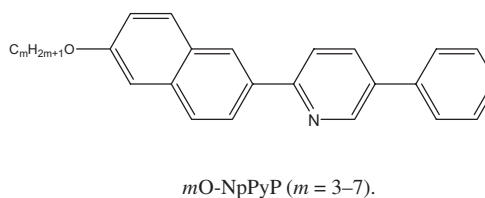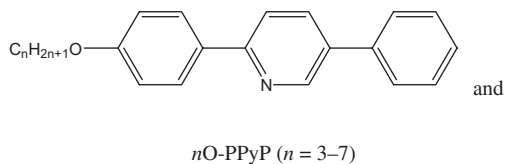
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2. Experimental

2.1 Characterisation

The chemical structures of the compounds were analysed by [1]H- and ^{13}C-nuclear magnetic resonance (NMR) spectra using a Bruker AC 300 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 Series spectrometer. The purity of the compounds was checked by thin-layer chromatography and further confirmed by elemental analysis.

Mesophases were chiefly identified by the microscopic texture of samples sandwiched between two glass plates under a polarising optical microscope (Olympus BH-2) equipped with a Mettler FP90/FP82HT hot stage. Phase transition temperatures and their corresponding transition enthalpies were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 calorimeter at a scanning rate of 5 r min^{-1}.

2.2 Synthesis

The starting materials, bromoalkane, 4-bromophenol, phenyl chloroformate and 3-phenylpyridine, were purchased from the Aldrich Chemical Co. and distilled under reduced pressure before use. Silica gel (MN Kieselgel 60, 70–230 mesh) was used for the column chromatography. Anhydrous organic solvents, toluene and tetrahydrofuran (THF), were purified by treatment with sodium and distilled before use. The syntheses of the target materials were carried out as outlined in Scheme 1.
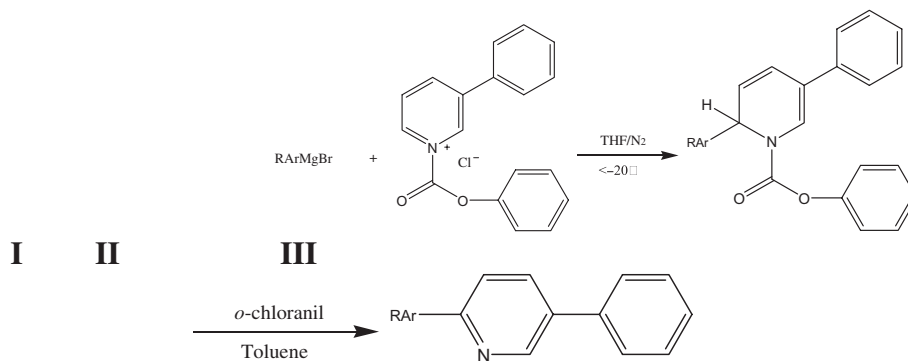
2.2.1 Syntheses of 2-(4-alkoxyphenyl)-5-phenylpyridines (nO-PPyP, n = 3–7)

The *n*O-PPyP were synthesised according to Scheme 1. The entire synthetic procedures were completed in a short two-step process with overall yields in the range of 71–80% (Table 1). For 4O-PPyP in **III**: to a solution of 1-bromo-4-butoxybenzene (10 mmol) in THF (20 ml) was added freshly dried magnesium granules (11 mmol) under an inert atmosphere for about half an hour. The Grignard solution **I** was then slowly added by a syringe into a preformed solution of 3-phenylpyridinium chloride **II**, which was prepared from phenyl chloroformate (10 mmol) and 3-phenylpyridine (10 mmol) in dry THF (20 ml) at –20°C for half an hour. The resulting solution was heated slowly to room temperature and stirred for another eight hours. After evaporating the THF, the residue was extracted with Et$_2$O. The organic layer was further washed once with 20% NH$_4$Cl solution and twice with distilled water and brine and dried with magnesium sulfate. For 4O-PPyP in **IV**: to a solution of dry toluene (20 ml) and compound **III** (10 mmol) was added about 1.5 eq. *o*-chloranil. The reaction mixture was heated to reflux for about three hours under an inert atmosphere and then quenched by adding 1N NaOH (25 ml) and Et$_2$O (25 ml), and then filtered through Celite. A normal aqueous work up and isolation with column chromatography (methylene chloride: hexane = 2:1) affords an overall two-step reaction with a good yield of 2-(4-butoxyphenyl)-5-phenylpyridine (**IV**) (74%). The crude products **IV** were further purified by re-crystallisation from ethyl acetate. The other *n*O-PPyP homologues were synthesised essentially by the same procedure as described above for the *n* = 4 homologue. All compounds gave satisfactory ^{1}H-NMR, ^{13}C-NMR, IR and elemental analysis results as discussed in the following.

2-(4-propoxyphenyl)-5-phenylpyridine (3O-PPyP). ^{1}H-NMR (CDCl$_3$): δ 8.90 (dd, 1H, J$_1$ = 2.1 Hz, J$_2$ = 0.3 Hz, pyridine), 7.99 (d, 2H, J = 9.0 Hz, phenylene), 7.92 (dd, 1H, J$_1$ = 8.1 Hz, J$_2$ = 2.4 Hz, pyridine), 7.74 (dd, 1H, J$_1$ = 8.4 Hz, J$_2$ = 0.6 Hz, pyridine), 7.63 (d, 2H, J = 6.9 Hz, phenyl), 7.50 (t, 2H, J = 7.2 Hz, phenyl), 7.41 (t, 1H, J = 7.2 Hz, phenyl), 7.01 (d, 2H, J = 8.7 Hz, phenylene), 4.00 (t, 2H, J = 6.6 Hz, –CH$_2$), 1.84 (ses, 2H, J = 7.2 Hz, –CH$_2$), 1.07 (t, 3H, J = 7.5 Hz, –CH$_3$).

Scheme 1. **IV** (R=*n*O–, *n* = 3–7; Ar = 1,4-phenylene), **V** (R=*m*O–, *m* = 3–7; Ar = 2,6-naphthalene).

Table 1. Yields of 2-(4-alkoxyphenyl)-5-phenylpyridines (*n*O-PPyP, *n* = 3–7) and 2-(6-alkoxy-naphthalen-2-yl)-5-phenylpyridines (*m*O-NpPyP, *m* = 3–7).

*n*O-PPyP (*n*)	Alkyl group	Yield[a] (%)	*m*O-NpPyP (*m*)	Alkyl group	Yield[a] (%)
3	Propyl	71	3	Propyl	38
4	Butyl	74	4	Butyl	40
5	Pentyl	80	5	Pentyl	36
6	Hexyl	74	6	Hexyl	36
7	Heptyl	78	7	Heptyl	38

[a]Isolated yields by column chromatography (methylene chloride/hexane) on silica gel.

^{13}C-NMR (CDCl$_3$): ppm 160.60, 155.36, 146.99, 137.34, 135.99, 134.53, 130.27, 129.25, 128.41, 128.25, 126.99, 120.08, 115.00, 69.75, 22.67, 10.60. IR (KBr): cm^{-1} 3057 (aromatic C–H stretch), 2980 (aliphatic C–H asymmetric stretch), 2872 (aliphatic C–H symmetric stretch), 1590 (ring stretch), 1514 (ring stretch), 1246 (asymmetric C–O–C stretch), 1074 (symmetric C–O–C stretch), 830 (out-of-plane C–H bend), 775 (out-of-plane C–H bend). Anal. calcd for C$_{20}$H$_{19}$NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.90; H, 6.61; N, 4.78.

2-(4-butoxyphenyl)-5-phenylpyridine (4O-PPyP). ^{1}H-NMR (CDCl$_3$): δ 8.91 (dd, 1H, J_1 = 2.4 Hz, J_2 = 0.6 Hz, pyridine), 8.00 (d, 2H, J = 8.7 Hz, phenylene), 7.91 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.4 Hz, pyridine), 7.73 (dd, 1H, J_1 = 8.4 Hz, J_2 = 0.6 Hz, pyridine), 7.63 (d, 2H, J = 6.9 Hz, phenyl), 7.49 (t, 2H, J = 6.9 Hz, phenyl), 7.41 (t, 1H, J = 7.2 Hz, phenyl), 7.02 (d, 2H, J = 9.0 Hz, phenylene), 4.04 (t, 2H, J = 6.6 Hz, –CH$_2$), 1.77–1.86 (m, 2H, –CH$_2$), 1.53 (ses, 2H, J = 7.2 Hz, –CH$_2$), 1.01 (t, 3H, J = 7.5 Hz, –CH$_3$). ^{13}C-NMR (CDCl$_3$): ppm 160.41, 155.67, 147.47, 137.59, 135.51, 134.34, 130.84, 129.19, 128.27, 128.10, 126.97, 119.84, 114.90, 67.90, 31.39, 19.33, 13.94. IR (KBr): cm^{-1} 3057 (aromatic C–H stretch), 2960 (aliphatic C–H asymmetric stretch), 2866 (aliphatic C–H symmetric stretch), 1592 (ring stretch), 1514 (ring stretch), 1250 (asymmetric C–O–C stretch), 1022 (symmetric C–O–C stretch), 826 (out-of-plane C–H bend), 775 (out-of-plane C–H bend). Anal. calcd for C$_{21}$H$_{21}$NO: C, 83.13; H 6.96; N 4.62. Found: C, 82.76; H, 6.95; N, 4.54.

2-(4-pentoxyphenyl)-5-phenylpyridine (5O-PPyP). ^{1}H-NMR (CDCl$_3$): δ 8.90 (dd, 1H, J_1 = 2.1 Hz, J_2 = 0.6 Hz, pyridine), 8.00 (d, 2H, J = 8.7 Hz, phenylene), 7.91 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.4 Hz, pyridine), 7.74 (dd, 1H, J_1 = 8.4 Hz, J_2 = 0.6 Hz, pyridine), 7.63 (d, 2H, J = 7.2 Hz, phenyl), 7.50 (t, 2H, J = 6.9 Hz, phenyl), 7.41 (t, 1H, J = 7.2 Hz, phenyl), 7.01 (d, 2H, J = 9.0 Hz, phenylene), 4.03 (t, 2H, J = 6.6 Hz, –CH$_2$), 1.83 (quin, 2H, J = 6.9 Hz, –CH$_2$), 1.37–1.51 (m, 4H, –CH$_2$), 0.96 (t, 3H, J = 7.2 Hz, –CH$_3$). ^{13}C-NMR (CDCl$_3$): ppm 160.59, 155.21, 146.80, 137.21, 135.99, 134.47,

130.07, 129.19, 128.37, 128.21, 126.91, 120.06, 114.95, 68.21, 28.98, 28.24, 22.50, 14.05. IR (KBr): cm^{-1} 3056 (aromatic C–H stretch), 2956 (aliphatic C–H asymmetric stretch), 2870 (aliphatic C–H symmetric stretch), 1590 (ring stretch), 1510 (ring stretch), 1252 (asymmetric C–O–C stretch), 1012 (symmetric C–O–C stretch), 825 (out-of-plane C–H bend), 775 (out-of-plane C–H bend). Anal. calcd for C$_{22}$H$_{23}$NO: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.07; H, 7.29; N, 4.38.

2-(4-hexyloxyphenyl)-5-phenylpyridine (6O-PPyP). ^{1}H-NMR (CDCl$_3$): δ 8.90 (d, 1H, J = 2.1 Hz, pyridine), 8.00 (d, 2H, J = 8.7 Hz, phenylene), 7.91 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz, pyridine), 7.74 (dd, 1H, J_1 = 8.4 Hz, J_2 = 0.6 Hz, pyridine), 7.64 (d, 2H, J = 7.2 Hz, phenyl), 7.49 (t, 2H, J = 6.9 Hz, phenyl), 7.41 (t, 1H, J = 7.2 Hz, phenyl), 7.01 (d, 2H, J = 9.0 Hz, phenylene), 4.03 (t, 2H, J = 6.6 Hz, –CH$_2$), 1.82 (quin, 2H, J = 6.9 Hz, –CH$_2$), 1.34–1.54 (m, 6H, –CH$_2$), 0.93 (t, 3H, J = 6.9 Hz, –CH$_3$). ^{13}C-NMR (CDCl$_3$): ppm 160.99, 154.62, 145.85, 136.95, 136.72, 134.86, 129.32, 128.93, 128.66, 128.53, 126.96, 120.59, 115.15, 68.33, 31.66, 29.27, 25.78, 22.67, 14.91. IR (KBr): cm^{-1} 3054 (aromatic C–H stretch), 2954 (aliphatic C–H asymmetric stretch), 2862 (aliphatic C–H symmetric stretch), 1590 (ring stretch), 1512 (ring stretch), 1252 (asymmetric C–O–C stretch), 1022 (symmetric C–O–C stretch), 826 (out-of-plane C–H bend), 774 (out-of-plane C–H bend). Anal. calcd for C$_{23}$H$_{25}$NO: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.26; H, 7.60; N, 4.20.

2-(4-heptyloxyphenyl)-5-phenylpyridine (7O-PPyP). ^{1}H-NMR (CDCl$_3$): δ 8.90 (dd, 1H, J_1 = 2.4 Hz, J_2 = 0.9 Hz, pyridine), 8.00 (d, 2H, J = 9.0 Hz, phenylene), 7.91 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.4 Hz, pyridine), 7.74 (dd, 1H, J_1 = 8.4 Hz, J_2 = 0.6 Hz, pyridine), 7.63 (d, 2H, J = 6.9 Hz, phenyl), 7.49 (t, 2H, J = 7.2 Hz, phenyl), 7.40 (t, 1H, J = 7.2 Hz, phenyl), 7.01 (d, 2H, J = 9.0 Hz, phenylene), 4.03 (t, 2H, J = 6.6 Hz, –CH$_2$), 1.82 (quin, 2H, J = 6.9 Hz, –CH$_2$), 1.30–1.51 (m, 8H, –CH$_2$), 0.91 (t, 3H, J = 6.9 Hz, –CH$_3$). ^{13}C-NMR

(CDCl$_3$): ppm 160.72, 155.07, 146.56, 137.10, 136.27, 134.60, 129.77, 129.24, 128.46, 128.32, 126.94, 120.22, 115.02, 68.27, 31.85, 29.31, 29.13, 26.07, 22.67, 14.13. IR (KBr): cm^{-1} 3052 (aromatic C–H stretch), 2982 (aliphatic C–H asymmetric stretch), 2858 (aliphatic C–H symmetric stretch), 1588 (ring stretch), 1512 (ring stretch), 1252 (asymmetric C–O–C stretch), 1012 (symmetric C–O–C stretch), 826 (out-of-plane C–H bend), 774 (out-of-plane C–H bend). Anal. calcd for C$_{24}$H$_{27}$NO: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.28; H, 7.86; N, 4.00.

2.2.2   2-(6-alkoxynaphthalen-2-yl)-5-phenylpyridines (mO-NpPyP, m = 3–7)

A similar synthetic procedure to that used for *n*O-PPyP, *n* = 3–7, was used to obtain *m*O-NpPyP, *m* = 3–7, using the appropriate starting materials. Fair yields (36–40%) of 2-(6-alkoxynaphthalen-2-yl)-5-phenylpyridines (*m*O-NpPyP, *m* = 3–7) were obtained (Table 1). Highly pure products were also collected by re-crystallisation several times from ethyl acetate.

2-(6-propoxy-2-naphthyl)-5-phenylpyridine (3O-NpPyP). ^{1}H-NMR (CDCl$_3$): δ 8.97 (d, 1H, *J* = 1.5 Hz, pyridine), 8.47 (s, 1H, naphthalene), 8.15 (dd, 1H, *J*$_2$ = 8.7 Hz, *J*$_2$ = 1.8 Hz, naphthalene), 7.98 (dd, 1H, *J*$_1$ = 8.4 Hz, *J*$_2$ = 2.4 Hz, pyridine), 7.92 (d, 1H, *J* = 8.1 Hz, pyridine), 7.80–7.88 (m, 2H, naphthalene), 7.66 (d, 2H, *J* = 7.2 Hz, phenyl), 7.51 (t, 2H, *J* = 7.2 Hz, phenyl), 7.42 (t, 1H, *J* = 7.2 Hz, phenyl), 7.22–7.18 (m, 2H, naphthalene), 4.07 (t, 2H, *J* = 6.6 Hz, –CH$_2$), 1.90 (ses, 2H, *J* = 7.5 Hz, –CH$_2$), 1.10 (t, 3H, *J* = 7.5 Hz, –CH$_3$). ^{13}C-NMR (CDCl$_3$): ppm 157.9, 156.3, 148.2, 137.9, 135.2, 135.2, 134.7, 134.1, 130.3, 129.2, 129.1, 128.1, 127.4, 127.1, 126.2, 125.0, 120.3, 119.6, 106.6, 69.7, 22.7, 10.7. IR (KBr): cm^{-1} 3053 (aromatic C–H stretch), 2962 (aliphatic C–H asymmetric stretch), 2876 (aliphatic C–H symmetric stretch), 1598 (ring stretch), 1482 (ring stretch), 1252 (asymmetric C–O–C stretch), 1067 (symmetric C–O–C stretch), 845 (out-of-plane C–H bend), 771 (out-of-plane C–H bend). Anal. calcd for C$_{24}$H$_{21}$NO: C, 84.92; H, 6.24; N, 4.13. Found: C, 84.87; H, 6.22; N, 4.08.

2-(6-butoxy-2-naphthyl)-5-phenylpyridine (4O-NpPyP). ^{1}H-NMR (CDCl$_3$): δ 8.97 (d, 1H, *J* = 1.8 Hz, pyridine), 8.47 (d, 1H, *J* = 1.2 Hz, naphthalene), 8.15 (dd, 1H, *J*$_1$ = 8.7 Hz, *J*$_2$ = 1.8 Hz, naphthalene), 7.98 (dd, 1H, *J*$_1$ = 8.1 Hz, *J*$_2$ = 2.4 Hz, pyridine), 7.91 (d, 1H, *J* = 8.4 Hz, pyridine), 7.80–7.89 (m, 2H, naphthalene), 7.66 (d, 2H, *J* = 7.2 Hz, phenyl), 7.51 (t, 2H, *J* = 7.2 Hz, phenyl), 7.42 (t, 1H, *J* = 7.2 Hz, phenyl), 7.21–7.17 (m, 2H, naphthalene), 4.11 (t, 2H, *J* = 6.6 Hz, –CH$_2$), 1.86 (quin, 2H, *J* = 6.9 Hz, –CH$_2$), 1.56 (ses, 2H, *J* = 7.5 Hz, –CH$_2$), 1.02 (t, 3H, *J* = 7.5 Hz, –CH$_3$). ^{13}C-NMR

(CDCl$_3$): ppm 157.9, 156.3, 148.2, 137.8, 135.2, 135.2, 134.7, 134.1, 130.3, 129.2, 129.1, 128.1, 127.4, 127.1, 126.1, 125.0, 120.3, 119.6, 106.5, 67.9, 31.4, 19.4, 14.0. IR (KBr): cm^{-1} 3053 (aromatic C–H stretch), 2962 (aliphatic C–H asymmetric stretch), 2871 (aliphatic C–H symmetric stretch), 1598 (ring stretch), 1482 (ring stretch), 1252 (asymmetric C–O–C stretch), 1067 (symmetric C–O–C stretch), 847 (out-of-plane C–H bend), 771 (out-of-plane C–H bend). Anal. calcd for C$_{25}$H$_{23}$NO: C, 84.95; H, 6.56; N, 3.96. Found: C, 84.92; H, 6.59; N, 3.94.

2-(6-pentyloxy-2-naphthyl)-5-phenylpyridine (5O-NpPyP). ^{1}H-NMR (CDCl$_3$): δ 8.97 (d, 1H, *J* = 1.8 Hz, pyridine), 8.47 (d, 1H, *J* = 1.2 Hz, naphthalene), 8.15 (dd, 1H, *J*$_1$ = 8.4 Hz, *J*$_2$ = 1.8 Hz, naphthalene), 7.97 (dd, 1H, *J*$_1$ = 8.4 Hz, *J*$_2$ = 2.4 Hz, pyridine), 7.91 (d, 1H, *J* = 8.4 Hz, pyridine), 7.80–7.88 (m, 2H, naphthalene), 7.66 (d, 2H, *J* = 6.9 Hz, phenyl), 7.51 (t, 2H, *J* = 6.9 Hz, phenyl), 7.42 (t, 1H, *J* = 7.2 Hz, phenyl), 7.21–7.17 (m, 2H, naphthalene), 4.10 (t, 2H, *J* = 6.6 Hz, –CH$_2$), 1.88 (quin, 2H, *J* = 6.9 Hz, –CH$_2$), 1.56–1.37 (m, 4H, –CH$_2$), 0.97 (t, 3H, *J* = 6.9Hz, –CH$_3$). ^{13}C-NMR (CDCl$_3$): ppm 157.9, 156.3, 148.2, 137.9, 135.2, 135.2, 134.7, 134.1, 130.3, 129.2, 129.1, 128.1, 127.4, 127.1, 126.1, 125.0, 120.3, 119.6, 106.6, 68.2, 29.1, 28.4, 22.6, 14.1. IR (KBr): cm^{-1} 3048 (aromatic C–H stretch), 2957 (aliphatic C–H asymmetric stretch), 2856 (aliphatic C–H symmetric stretch), 1598 (ring stretch), 1482 (ring stretch), 1252 (asymmetric C–O–C stretch), 1047 (symmetric C–O–C stretch), 847 (out-of-plane C–H bend), 771 (out-of-plane C–H bend). Anal. calcd for C$_{26}$H$_{25}$NO: C, 84.98; H, 6.86; N, 3.81. Found: C, 84.88; H, 6.84; N, 3.86.

2-(6-hexyloxy-2-naphthyl)-5-phenylpyridine (6O-NpPyP). ^{1}H-NMR (CDCl$_3$): δ 8.97 (d, 1H, *J* = 1.5 Hz, pyridine), 8.47 (s, 1H, naphthalene), 8.15 (dd, 1H, *J*$_1$ = 8.7 Hz, *J*$_2$ = 1.8 Hz, naphthalene), 7.98 (dd, 1H, *J*$_1$ = 8.4 Hz, *J*$_2$ = 2.4 Hz, pyridine), 7.92 (d, 1H, *J* = 8.1 Hz, pyridine), 7.81–7.88 (m, 2H, naphthalene), 7.66 (d, 2H, *J* = 6.9 Hz, phenyl), 7.51 (t, 2H, *J* = 7.2 Hz, phenyl), 7.42 (t, 1H, *J* = 7.2 Hz, phenyl), 7.21–7.17 (m, 2H, naphthalene), 4.10 (t, 2H, *J* = 6.6 Hz, –CH$_2$), 1.87 (quin, 2H, *J* = 6.9 Hz, –CH$_2$), 1.53 (quin, 2H, *J* = 6.9 Hz, –CH$_2$), 1.43–1.31 (m, 4H, –CH$_2$), 0.93 (t, 3H, *J* = 6.9 Hz, –CH$_3$). ^{13}C-NMR (CDCl$_3$): ppm 157.9, 156.3, 148.2, 137.8, 135.2, 135.2, 134.7, 134.1, 130.3, 129.2, 129.0, 128.1, 127.3, 127.0, 126.1, 125.0, 120.3, 119.6, 106.6, 68.2, 31.7, 29.3, 25.9, 22.7, 14.1. IR (KBr): cm^{-1} 3053 (aromatic C–H stretch), 2927 (aliphatic C–H asymmetric stretch), 2871 (aliphatic C–H symmetric stretch), 1598 (ring stretch), 1482 (ring stretch), 1252 (asymmetric C–O–C stretch), 1039 (symmetric C–O–C

stretch), 845 (out-of-plane C–H bend), 771 (out-of-plane C–H bend). Anal. calcd for $C_{27}H_{27}NO$: C, 85.00; H, 7.13; N, 3.67. Found: C, 85.02; H, 7.16; N, 3.56.

2-(6-heptyloxy-2-naphthyl)-5-phenylpyridine (7O-NpPyP). ^{1}H-NMR (CDCl$_3$): δ 8.97 (d, 1H, J = 1.5 Hz, pyridine), 8.47 (s, 1H, naphthalene), 8.15 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.5 Hz, naphthalene), 7.97 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz, pyridine), 7.91 (d, 1H, J = 8.4 Hz, pyridine), 7.80–7.88 (m, 2H, naphthalene), 7.66 (d, 2H, J = 7.2 Hz, phenyl), 7.51 (t, 2H, J = 7.2 Hz, phenyl), 7.42 (t, 1H, J = 7.2 Hz, phenyl), 7.21–7.17 (m, 2H, naphthalene), 4.10 (t, 2H, J = 6.6 Hz, –CH$_2$), 1.87 (quin, 2H, J = 6.6 Hz, –CH$_2$), 1.52 (quin, 2H, J = 6.9 Hz, –CH$_2$), 1.42–1.34 (m, 6H, –CH$_2$), 0.92 (t, 3H, J = 6.6 Hz, –CH$_3$). ^{13}C-NMR (CDCl$_3$): ppm 157.9, 156.3, 148.2, 137.8, 135.2, 135.2, 134.7, 134.1, 130.3, 129.2, 129.0, 128.1, 127.3, 127.1, 126.1, 125.0, 120.3, 119.6, 106.5, 68.2, 31.9, 29.4, 29.2, 26.2, 22.7, 14.2. IR (KBr): cm^{-1} 3048 (aromatic C–H stretch), 2922 (aliphatic C–H asymmetric stretch), 2856 (aliphatic C–H symmetric stretch), 1601 (ring stretch), 1472 (ring stretch), 1252 (asymmetric C–O–C stretch), 1037 (symmetric C–O–C stretch), 847 (out-of-plane C–H bend), 771 (out-of-plane C–H bend). Anal. calcd for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.54. Found: C, 84.66; H, 7.32; N, 3.46.

3. Results and discussion

Mesophase transition temperatures and their corresponding transition enthalpies were determined by DSC with heating and cooling rates of 5°C min^{-1},

with the exception of 7O-PPyP (see below). A representative DSC thermogram of 6O-PPyP is shown in Figure 1. In the first cooling process, four exothermic peaks were observed at 143.65, 138.82, 134.65 and 114.84°C, while two endothermic peaks were observed at 140.80 and 144.39°C in the second heating process. This phase transition behaviour was also observed for the second cooling and third heating processes.

The mesophases of the homologues of 2-(4-alkoxyphenyl)-5-phenylpyridines (*n*O-PPyP, *n* = 3–7) were identified by observing the optical textures under a polarised optical microscope with two crossed polarisers. No mesophase was observed for 3O-PPyP, a monotropic nematic phase was observed for 4O-PPyP and a monotropic nematic and smectic A phase were observed for 5O-PPyP. In the first cooling process of 6O-PPyP, there were schlieren disclinations with the presence of four-brush and two-brush singularities between 143.65 and 138.82°C (Figure 2), a fan texture between 138.82 and 134.65°C (Figure 3) and a broken fan texture between 134.65 and 114.84°C (Figure 4), which were assigned to nematic, smectic A and smectic C phases, respectively [29]. In the second heating process of 6O-PPyP, there was only a fan texture between 140.80 and 144.39°C. 7O-PPyP showed similar thermotropic behaviour to that of 6O-PPyP.

Initially, with a scanning rate of 5°C min^{-1} under the DSC cooling scan, the isotropic-to-nematic transition ($T_{\text{I-N}}$) peak of 7O-PPyP appeared as an unclear shoulder on the nematic-to-smectic A transition ($T_{\text{N-SmA}}$) peak. However, with a scanning rate of 1°C min^{-1}, two eminent peaks with their bases still slightly overlapped could be identified. The range of the nematic phase, evaluated by DSC, in 7O-PPyP is less than 0.7°C. With discretion, we were able to observe the nematic texture within such a
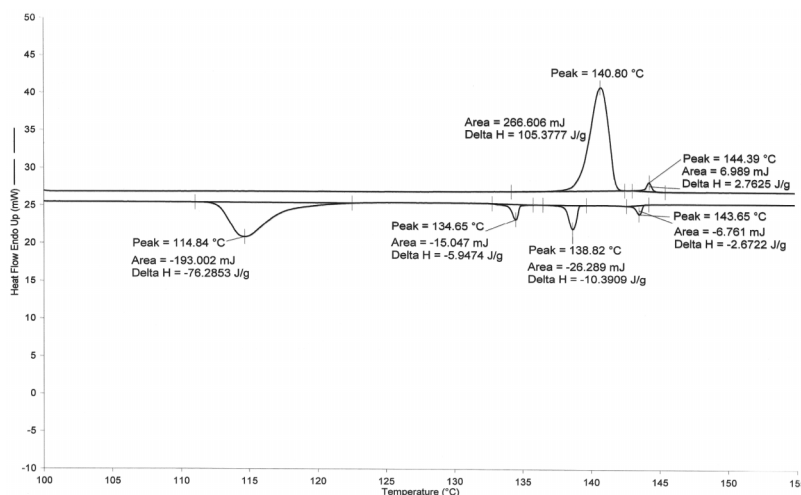

Figure 1. Thermograms of 2-(4-hexyloxyphenyl)-5-phenylpyridine (6O-PPyP) were determined by the second scans at a heating and cooling rate of 5°C min^{-1} from DSC.
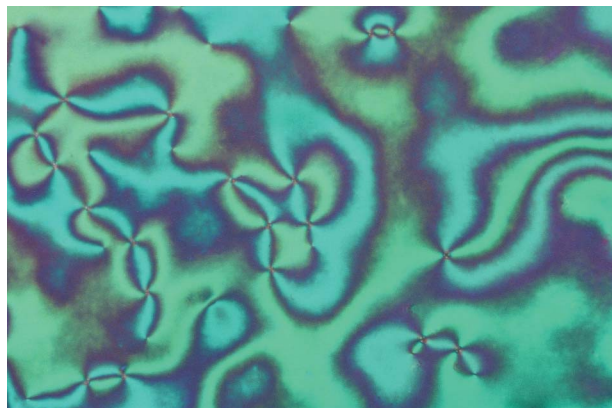
Figure 2. Polarised optical micrograph of the nematic schlieren texture of 2-(4-hexyloxyphenyl)-5-phenylpyridine (6O-PPyP) arises from the isotropic phase on cooling to 143.2°C with a magnification of ×100.

Figure 3. Polarised optical micrograph of the smectic A texture of 2-(4-heptyloxyphenyl)-5-phenylpyridine (7O-PPyP) arises from the isotropic phase on cooling to 139.1°C with a magnification of ×100.
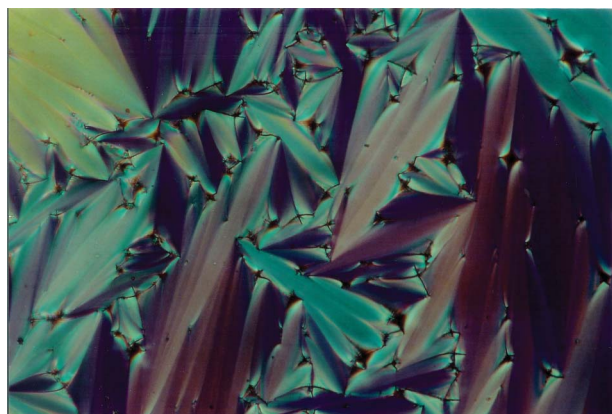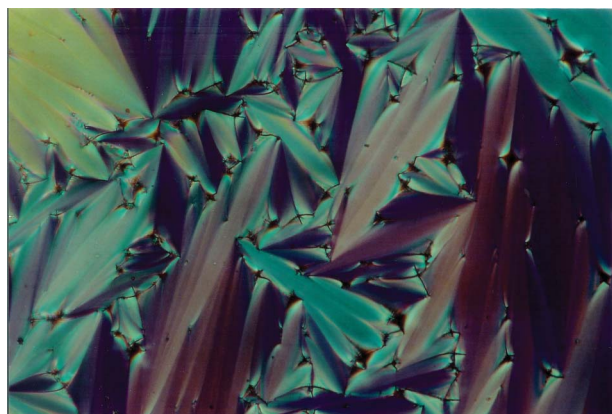

Figure 4. Polarised optical micrograph of the smectic C texture of 2-(4-heptyloxyphenyl)-5-phenylpyridine (7O-PPyP) arises from the isotropic phase on cooling to 134.5°C with a magnification of ×100.

narrow temperature range under the polarised optical microscope. Through Gaussian analysis, these two thermal transitions (T_{I-N} and T_{N-SmA}) and their corresponding enthalpies are evaluated and listed in Table 2.

A gradually increasing trend of polymesomorphism was observed upon increasing the alkyl chain length of the *n*O-PPyP series. In addition, the ranges of the nematic phase decrease and the ranges of the smectic phase increase upon increasing the alkyl chain length of the *n*O-PPyP series. It is known that the purely nematic behaviour giving way to the predominantly or purely smectic behaviour in the higher homologues is quite general [30].

In the series of *m*O-NpPyP, *m* = 3–7, all compounds exhibit an enantiotropic nematic phase with an additional narrow monotropic smectic A phase observed in 8O-NpPyP (Figure 5). The nematic ranges in mO-NpPyP, appear in the moderate–high temperature range between 151 and 211°C during the cooling thermal scan, and are much wider than those in *n*O-PPyP. The result shows that a slightly extended and tilted hard core, such as 2,6-naphthalene, provides a much better nematogen than 1,4-phenylene [31,32].

The T_{I-N} values in *n*O-PPyP remain constant at around 140°C as *n* increases, while those in the *m*O-NpPyP series show a slightly decreasing trend as *m* increases. The odd–even effect of the T_{I-N} values can be identified from *n* = 4 to 7 in the *n*O-PPyP series (140.07, 138.75, 143.65 and 141.07, respectively (see Table 2)) and from *m* = 3 to 7 in the *m*O-NpPyP series (205.2, 210.5, 201.6, 201.3 and 194.4, respectively). It is known that the oxygen is equivalent to a CH_2 group, so that the even carbon atom alkyl chain has a terminal CH_3 group that extends along the long molecular axis, whereas the odd number carbon chain of the terminal CH_3 group tends to lie off axis [33, 34]. Both series show that a higher T_{I-N} value was observed for those compounds with even carbon atom alkyl chains. All nematic-to-isotropic transitions in these non-polar pyridine-containing liquid crystals show a low transition enthalpy of less than 1 kJ mol^{-1}.

In the homologues of 2-(4-n-alkoxyphenyl)-5-(4-methylphenyl)pyridines (abbreviated as *n*O-PPyP-1), which have an extra methyl group at the mesogenic end of *n*O-PPyP, a rich liquid crystalline polymesomorphism appears suddenly at *n* = 4, [17]. Apparently, this characteristic sudden increase of polymesomorphism observed by Yano *et al.* should not be attributed to the central pyridine moiety alone. The extra terminal methyl group, which connects directly to the mesogenic end, also plays a crucial role.

On the other hand, contrary to the series of *n*O-PPyP compounds that show both a nematic phase and a smectic phase, the series of 4-n-alkylterphenyls (abbreviated as *n*-PPP), a structure of a terphenyl with one end having an alkyl chain, show no mesomorphic

Table 2. Phase transition temperatures (°C) and corresponding transition enthalpies (KJ mol⁻¹), in parentheses, for homologous series of *n*O-PPyP, *n* = 3–7, and *m*O-NpPyP, *m* = 3–7, were determined by the second scans at a heating and cooling rate of 5°C min⁻¹ from DSC.

	Phase transition temperatures (°C) and their corresponding transition enthalpies (kJ mol⁻¹)	
Cpd	Heating[a]	Cooling[a]
3O-PPyP	Cr 161.43(35.09) I	I 139.48(35.95) Cr
4O-PPyP	Cr 153.68(28.82) I	I 140.07(0.59) N 136.07(25.75) Cr
5O-PPyP	Cr 146.16(33.90) I	I 138.75(0.53) N 136.84(5.79) SmA 119.92(24.52) Cr
6O-PPyP	Cr 140.80(34.93) SmA 144.39(0.92) I	I 143.65(0.89) N 138.82(3.44) SmA 134.65(1.97) SmC 114.84(25.28) Cr
7O-PPyP	Cr 135.41(28.69) SmA 141.41(5.88) I	I 141.07[b] (0.88) N 140.41[b] (4.70) SmA 135.23(1.62) SmC 114.12(25.4) Cr
3O-NpPyP	Cr 195.2(34.19) N 205.7(0.32) I	I 205.9(0.33) N 172.8(30.42) Cr
4O-NpPyP	Cr 186.5(39.68) N 211.0(0.49) I	I 210.5(0.52) N 158.5(37.82) Cr
5O-NpPyP	Cr 177.4(44.19) N 202.1(0.49) I	I 201.6(0.51) N 155.2(40.89) Cr
6O-NpPyP	Cr 172.2(45.61) N 201.8(0.58) I	I 201.3(0.72) N 151.3(41.69) Cr
7O-NpPyP	Cr 167.3(43.18) N 194.8(0.52) I	I 194.4(0.50) N 156.7(0.22) SmA 145.6(39.21) Cr

[a]Cr = crystalline phase, Sm = smectic phase, N = nematic phase, I = isotropic phase.
[b]A small peak at 141.07°C connects with the peak at 140.41°C, and a nematic Schlieren mesophase can be detected within the range under POM.
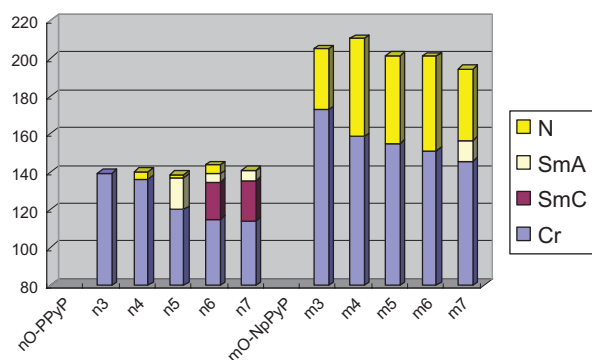

Figure 5. Plot of transition temperatures as a function of the terminal alkyl chain length for compounds of *n*O-PPyP, *n* = 3–7, and *m*O-NpPyP, *m* = 3–7, during cooling at 5°C min⁻¹.

behaviour [35]. This is in accordance with our previous finding [26] that the replacement of the relatively non-polar phenyl core by a polar pyridine moiety enhances not only the early appearance of the smectic phase, but also that of the nematic phase. It is apparent that the pyridine moiety within the mesogen not only aids the appearance of the smectic mesophase, but also reduces the thermal stabilities of the crystal, and simultaneously enhances the intermolecular anisotropic forces causing the early appearance of a nematic phase. Although it was noted [11] that changes, such as replacing a phenyl or *p*-phenylene ring by a pyridyl ring, are not likely to have an obvious effect upon molecular twist, polarisability etc., the change in mesomorphic behaviour from a non-polar *n*-PPP molecule to a polar *n*O-PPyP molecule is evident.

It was indicated that nematic liquid crystals with high birefringence are useful in mixtures designed for twisted nematic and supertwisted nematic displays that require a precise combination of cell thickness and optical anisotropy values; in order to maximise the transmission of light, thinner cells are needed and therefore compounds of higher optical anisotropy have to be used [36, 37]. It was also pointed out that the naphthalene compound always has a higher optical anisotropy than the phenyl compound; therefore, it is suitable for the application of the above-mentioned displays [38].

In conclusion, two homologous series compounds of *n*O-PPyP and *m*O-NpPyP derived from 5-phenyl-pyridine were synthesised, and their thermotropic behaviours were examined. We find that the pyridine moiety within the mesogen not only favours the appearance of smectic behaviour, but also reduces the thermal stabilities of the crystal, and simultaneously introduces an attractive force and causes the appearance of the nematic phase. The experimental results also show that a slightly extended and tilted hard core, such as the 2,6-naphthalene moiety, provides a much better nematogen than 1,4-phenylene.

Acknowledgement

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