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Synthesis and mesomorphic properties on the series of 2-(4-alkylphenyl)-6-methylquinolines and 2-(4-alkoxyphenyl)-6-methylquinolines

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Two homologous series of quinoline-containing liquid crystalline compounds were synthesised. Preparation of these compounds was completed in a short two-step reaction. Fair to good two-step overall yields of 63%–68% and 50%–60% were obtained respectively for the liquid crystalline compounds of 2-(4-alkylphenyl)-6-methylquinolines (*n*PQMe, *n* = 4–8) and 2-(4-alkoxyphenyl)-6-methylquinolines (*m*OPQMe, *m* = 3–7). Spectral analyses were in accordance with the expected structures. Polarising optical microscopy showed both series of compounds only display a nematic phase. Their thermotropic behaviours were further confirmed by differential scanning calorimetry.

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

1. Introduction

As the demand increases for more advanced displays in the future, researchers are expanding their investigations of novel nematic liquid crystals and molecular synthesising methodologies. It is clear newly developed synthetic methods have made available a wealth of novel materials. Many have desirable physical parameters for applications, and others have cost-effective processes for production and/or with quantitative yield for research study (*1*, *2*).

Some quinoline-containing liquid crystalline compounds have been synthesised in past years. Some were synthesised by reacting suitable substituted anilines and benzaldehydes with pyruvic acid (*3*), whereas other compounds were prepared by heating aniline with glycerin, or 1,2-glycols or α,β–unsaturated aldehyde through the Skraup procedure or the Doebner-von Miller variation (*4–8*). Another study reported bis-formylation of acetanilides followed by cyclisation with PPA and conversion into chloroquinoline aldehydes, which were used as an intermediate for further synthesis of quinoline-containing liquid crystalline compounds (*9–11*). Although these methods are of great value for constructing important heterocyclic systems, most suffer from the limited scope of the method applied, a large number of synthetic steps and relatively low yields. On the other hand, some recent patents showed that high-speed response of optical switching element was achieved by quinoline-containing liquid crystalline compounds (*12–14*). All these reasons prompted us to seek a new synthetic method for preparing such liquid crystalline compounds.

Previously, we successfully applied regioselective addition of organometallic reagents to 1-acylpyridinium salts for preparing some pyridine-containing liquid crystals (*15*). Recently, we reported the novel synthesis of a homologous series of quinoline-containing liquid crystalline 2-(4-alkylphenyl)-6-methoxyquinolines (*n*PQOMe, *n* = 4–8) compounds (*16*). As a continuation of our research, the present work reports syntheses of two novel homologous series of 2-(4-alkylphenyl)-6-methylquinolines (*n*PQMe, *n* = 4–8) and 2-(4-alkoxyphenyl)-6-methylquinolines (*m*OPQMe, *m* = 3–7), in which *n* varied from butyl to octyl and *m* varied from propyl to heptyl for comparing the structure–property relationships of the mesophases. The structures of the target materials are as follows:

2. Experimental

2.1 Characterisation

The chemical structures of the compounds were analysed by ^{1}H and ^{13}C-NMR spectra using a Bruker AC 300 spectrometer. Infrared spectra were carried out 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 examination of the microscopic texture of samples sandwiched between two glass plates under a polarising optical microscope (POM) (Olympus BH-2) equipped with a Mettler FP90/FP82HT hot stage. Phase transition temperatures and their corresponding transition enthalpies were determined by differential scanning

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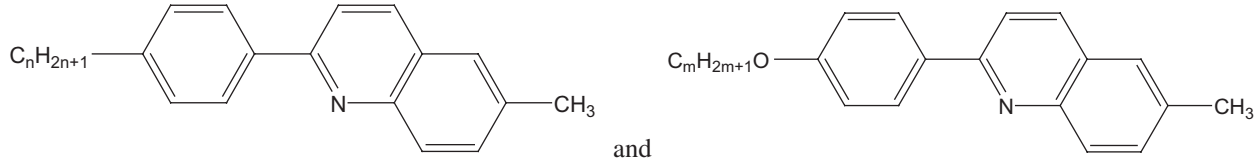


***n*PQMe (*n* = 4–8)** **and** ***m*OPQMe (*m* = 3–7)**

Structure 1.

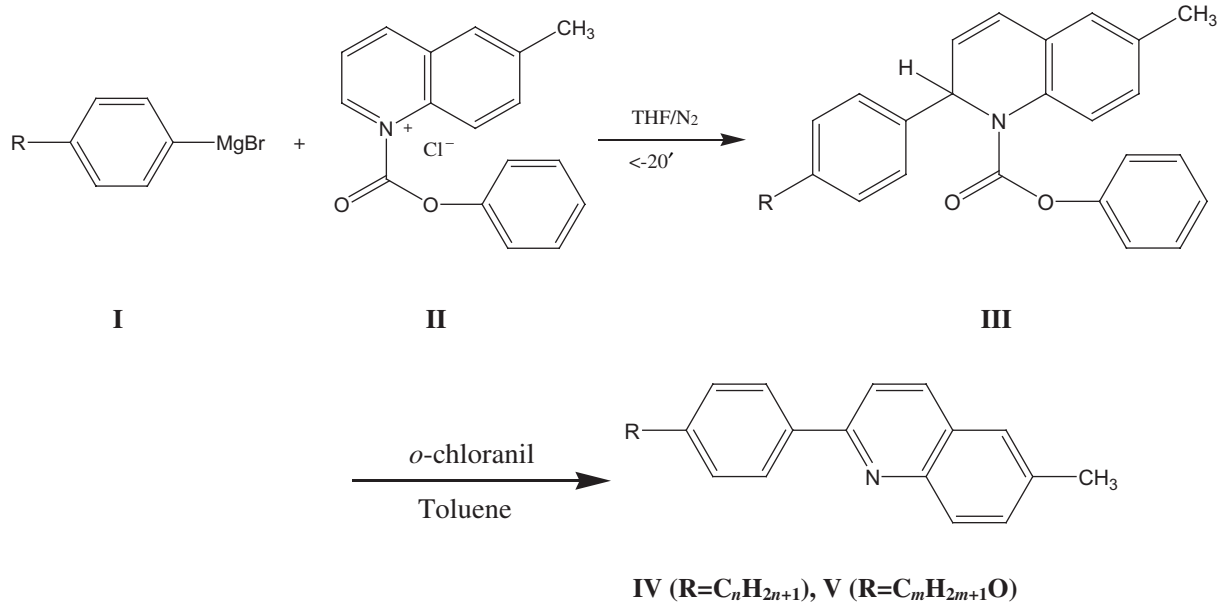
calorimetry (DSC) using a Perkin-Elmer DSC7 calorimeter at a scan rate of 5°C min^{-1}.

2.2 Synthesis

The starting material compounds, 4-alkyl-bromobezene and 4-bromophenol, were purchased from Aldrich Chemical Co. and distilled under reduced pressure before use. Silica gel (MN Kieselgel 60, 70–230 mesh) was used for column chromatography. 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-alkylphenyl)-6-methylquinolines (nPQMe, n = 4–8)

The 2-(4-alkylphenyl)-6-methylquinolines were synthesised according to Scheme 1. The entire synthetic procedures were completed in a short two-step process. Good yields (63%–68%) of 2-(4-alkylphenyl)-6-methylquinolines (*n*PQMe, *n* = 4–8) (Table 1) were obtained. For 4PQMe in **III**: To a (Grignard) solution of 1-bromo-4-butylbenzene (10 mmol) in THF (20 ml) was added freshly dried magnesium granules (11 mmol) under an inert atmosphere. The Grignard solution **I** was then slowly added by syringe into a preformed solution of 6-methylquinolinium chloride **II**, which was prepared from phenyl chloroformate (10 mmol), 6-methylquinoline (10 mmol) in dry THF (20 ml) under –20°C for 30 min. The resulting solution was heated slowly to room temperature and stirred for another 8 h. After evaporating the THF, the residue was extracted with Et_2O. The organic layer was further washed once with 20% NH_4Cl solution and twice with distilled water and brine and dried with magnesium sulfate. For 4PQMe in **IV**: To a solution of dry toluene (20 ml) and compound **III** was added about 1.5eq. *o*-chloranil. The reaction mixture was heated to reflux for about 3 h under inert atmosphere and then quenched by adding 1N NaOH (25 ml) and Et_2O (25 ml) and filtered through Celite. Normal aqueous work-up and isolation with column chromatography (hexane: methylene chloride = 2:1) affords good yield of 2-(4-butylphenyl)-6-methylquinoline (4PQMe) (68%).



Scheme 1.

Table 1. Yields of 2-(4-alkylphenyl)-6-methylquinolines (*n*PQMe, *n* = 4–8) and 2-(4-alkoxyphenyl)-6-methylquinolines (*m*OPQMe, *m* = 3–7).

Entry (*n*)	Alkyl group	Yield[a](%)	Entry (m)	Alkyl group	Yield[a](%)
4	Butyl	68.0	3	Propyl	55
5	Pentyl	65.0	4	Butyl	60
6	Hexyl	63.2	5	Pentyl	58
7	Heptyl	65.4	6	Hexyl	55
8	Octyl	63.0	7	Heptyl	50

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

The crude product 4PQMe was further purified by re-crystallisation several times from ethyl acetate. All compounds gave satisfactory data from ^{1}H-NMR, ^{13}C-NMR, IR and elemental analysis as illustrated below.

2-(4-Butylphenyl)-6-methylquinoline (4PQMe)
^{1}H-NMR ($CDCl_3$): δ 8.01–8.12 (m, 4H, phenlene and quinoline), 7.81 (d, 1H, J = 8.4 Hz, quinoline), 7.54–7.59 (m, 2H, quinoline), 7.34 (d, 2H, J = 8.1 Hz, phenlene), 2.70 (t, 2H, J = 7.5 Hz, -CH_2), 2.54 (s, 3H, -CH_3), 1.61–1.71 (m, 2H, -CH_2), 1.34–1.46 (m, 2H, -CH_2), 0.96 (t, 3H, J = 7.5 Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 156.6, 146.7, 144.4, 137.0, 136.2, 136.1, 132.0, 129.2, 129.0, 127.5, 127.2, 126.4, 119.0, 35.5, 33.6, 22.4, 21.6, 14.0. IR (KBr): cm^{-1} 3059 (aryl C-H stretch), 2929 (alkyl C-H asymmetric stretch), 2855 (alkyl C-H symmetric stretch), 1601 (ring stretch), 1491 (ring stretch), 835 (C-H out-of-plane bend). Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.15; H, 7.70; N, 5.04.

2-(4-Pentylphenyl)-6-methylquinoline (5PQMe)
^{1}H-NMR ($CDCl_3$): δ 8.05–8.16 (m, 4H, phenlene and quinoline), 7.83 (d, 1H, J = 8.7 Hz), 7.53–7.61 (m, 2H, quinoline), 7.34 (d, 2H, J = 8.4 Hz, phenlene), 2.69 (t, 2H, J = 7.5 Hz, -CH_2), 2.55 (s, 3H, -CH_3), 1.61–1.74 (m, 2H, -CH_2), 1.30–1.41 (m, 4H, -CH_2), 0.91 (t, 3H, J = 6.9 Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 156.5, 146.4, 144.5, 136.7, 136.5, 136.2, 132.1, 129.0, 127.6, 127.2, 126.4, 119.0, 35.8, 31.5, 31.1, 22.6, 21.6, 14.1. IR (KBr): cm^{-1} 3060 (aryl C-H stretch), 2929 (alkyl C-H asymmetric stretch), 2855 (alkyl C-H symmetric stretch), 1601 (ring stretch), 1486 (ring stretch), 835 (C-H out-of-plane bend). Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H 8.01; N 4.84. Found: C, 86.98; H, 8.03; N, 4.79.

2-(4-Hexylphenyl)-6-methylquinoline (6PQMe)
^{1}H-NMR ($CDCl_3$): δ 8.05–8.14 (m, 4H, phenlene and quinoline), 7.83 (d, 1H, J = 8.4 Hz), 7.53–7.60 (m, 2H, quinoline), 7.34 (d, 2H, J = 8.1 Hz, phenlene), 2.70 (t, 2H, J = 7.2 Hz, -CH_2), 2.56 (s, 3H, -CH_3), 1.61–1.74 (m, 2H, -CH_2), 1.27–1.43 (m, 6H, -CH_2), 0.91 (t, 3H, J = 6.9 Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 156.7, 146.9, 144.3, 137.3, 136.1, 136.0, 131.9, 129.4, 129.0, 127.4, 127.2, 126.4, 119.0, 35.8, 31.8, 31.4, 29.0, 22.7, 21.6, 14.2. IR (KBr): cm^{-1} 3060 (aryl C-H stretch), 2929 (alkyl C-H asymmetric stretch), 2855 (alkyl C-H symmetric stretch), 1601 (ring stretch), 1491 (ring stretch), 837 (C-H out-of-plane bend). Anal. Calcd for $C_{22}H_{25}N$: C, 87.08; H, 8.30; N, 4.62. Found: C, 86.72; H, 8.26; N, 4.53.

2-(4-Heptylphenyl)-6-methylquinoline (7PQMe)
^{1}H-NMR ($CDCl_3$): δ 8.05–8.13 (m, 4H, phenlene and quinoline), 7.81 (d, 1H, J = 8.7 Hz), 7.53–7.58 (m, 2H, quinoline), 7.34 (d, 2H, J = 8.1 Hz, phenlene), 2.69 (t, 2H, J = 7.5 Hz, -CH_2), 2.54 (s, 3H, -CH_3), 1.62–1.73 (m, 2H, -CH_2), 1.29–1.41 (m, 8H, -CH_2), 0.91 (t, 3H, J = 6.9 Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 156.6, 146.7, 144.5, 137.0, 136.3, 136.1, 132.1, 129.2, 129.0, 127.5, 127.2, 126.4, 119.0, 35.9, 31.8, 31.4, 29.6, 29.4, 22.7, 21.6, 14.2. IR (KBr): cm^{-1} 3062(aryl C-H stretch), 2929 (alkyl C-H asymmetric stretch), 2855 (alkyl C-H symmetric stretch), 1601 (ring stretch), 1489 (ring stretch), 835 (C-H out-of-plane bend). Anal. Calcd for $C_{23}H_{27}N$: C, 87.02; H, 8.57; N, 4.41. Found: C, 86.82; H, 8.58; N, 4.36.

2-(4-Octylphenyl)-6-methylquinoline (8PQMe)
^{1}H-NMR ($CDCl_3$): δ 8.05–8.13 (m, 4H, phenlene and quinoline), 7.82 (d, 1H, J = 8.7 Hz), 7.53–7.59 (m, 2H, quinoline), 7.34 (d, 2H, J = 8.1 Hz, phenlene), 2.69 (t, 2H, J = 7.5 Hz, -CH_2), 2.55 (s, 3H, -CH_3), 1.62–1.72 (m, 2H, -CH_2), 1.25–1.40 (m, 10H, -CH_2), 0.90 (t, 3H, J = 6.9Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 156.7, 146.8, 144.4, 137.2, 136.2, 136.1, 132.0, 129.3, 129.0, 127.5, 127.2, 126.4, 119.0, 35.9, 32.0, 31.5, 29.6, 29.4, 22.8, 21.6, 14.2. IR (KBr): cm^{-1} 3061 (aryl C-H stretch), 2929 (alkyl C-H asymmetric stretch), 2855 (alkyl C-H symmetric stretch), 1601 (ring stretch), 1489 (ring stretch), 835 (C-H out-of-plane bend). Anal. Calcd for $C_{24}H_{29}N$: C, 86.96; H, 8.82; N, 4.23. Found: C, 86.91; H, 8.83; N, 4.14.

2.2.2. *2-(4-Alkoxyphenyl)-6-methylquinolines (mOPQMe, m = 3–7)*

A similar synthetic procedure to that used for *n*PQMe, *n* = 4–8 was used to obtain *m*OPQMe, *m* = 3–7 using the appropriate starting materials. Fairly good yields (50%–60%) of 2-(4-alkoxyphenyl)-6-methylquinolines (*m*OPQMe, *m* = 3–7) were obtained. Highly pure products were also collected by re-crystallisation several times from ethyl acetate.

2-(4-Propoxyphenyl)-6-methylquinoline (3OPQMe)
^{1}H-NMR ($CDCl_3$): δ 8.03–8.13 (m, 4H, phenlene and quinoline), 7.77 (d, 1H, J = 8.7 Hz, quinoline),

7.52–7.55 (m, 2H, quinoline), 7.03 (d, 2H, J = 9 Hz, phenlene), 4.00 (t, 2H, J = 6.6 Hz, -OCH_2), 2.53 (s, 3H, -CH_3), 1.80–1.91 (m, 2H, -CH_2), 1.07 (t, 3H, J = 7.2Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 160.4, 156.2, 147.0, 136.0, 135.7, 132.3, 131.9, 129.3, 128.8, 127.0, 126.4, 118.6, 114.9, 69.7, 22.7, 21.6, 10.6. IR (KBr): cm^{-1} 3058 (aryl C-H stretch), 2934 (alkyl C-H asymmetric stretch), 2878 (alkyl C-H symmetric stretch), 1599 (ring stretch), 1493 (ring stretch), 1250 (asymmetric C-O-C stretch), 1069 (symmetric C-O-C stretch), 826 (C-H out-of-plane bend). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.30; H, 6.93; N, 5.09.

2-(4-Butoxy-phenyl)-6-methylquinoline (4OPQMe) ^{1}H-NMR ($CDCl_3$): δ 8.03–8.14 (m, 4H, phenlene and quinoline), 7.76 (d, 1H, J = 8.4 Hz, quinoline), 7.52–7.55 (m, 2H, quinoline), 7.03 (d, 2H, J = 9 Hz, phenlene), 4.032 (t, 2H, J = 6.45 Hz, -OCH_2), 2.53 (s, 3H, -CH_3), 1.77–1.86 (m, 2H, -CH_2), 1.47–1.59 (m, 2H, -CH_2), 1.01 (t, 3H, J = 7.2 Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 160.3, 156.2, 147.0, 136.0, 135.7, 132.3, 131.9, 129.3, 128.8, 127.0, 126.4, 118.6, 114.9, 67.9, 31.4, 21.6, 19.3, 13.9. IR (KBr): cm^{-1} 3058 (aryl C-H stretch), 2934 (alkyl C-H asymmetric stretch), 2875 (alkyl C-H symmetric stretch), 1599 (ring stretch), 1495 (ring stretch), 1252 (asymmetric C-O-C stretch), 1010 (symmetric C-O-C stretch), 826 (C-H out-of-plane bend). Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.35; H, 7.30; N, 4.75.

2-(4-Pentyloxy-phenyl)-6-methylquinoline (5OPQMe) ^{1}H-NMR ($CDCl_3$): δ 8.01–8.13 (m, 4H, phenlene and quinoline), 7.75 (d, 1H, J = 8.4 Hz, quinoline), 7.52–7.55 (m, 2H, quinoline), 7.03 (d, 2H, J = 8.7 Hz, phenlene), 4.02 (t, 2H, J = 6.6 Hz, -OCH_2), 2.53 (s, 3H, -CH_3), 1.78–1.88 (m, 2H, -CH_2), 1.36–1.53 (m, 4H, -CH_2), 0.99 (t, 3H, J = 7.2 Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 160.3, 156.1, 146.9, 135.9, 136.6, 132.2, 129.2, 128.7, 126.9, 126.3, 118.5, 114.8, 68.1, 29, 28.2, 22.5, 21.5, 14. IR (KBr): cm^{-1} 3060 (aryl C-H stretch), 2929 (alkyl C-H asymmetric stretch), 2857 (alkyl C-H symmetric stretch), 1599 (ring stretch), 1495 (ring stretch), 1256 (asymmetric C-O-C stretch), 1018 (symmetric C-O-C stretch), 826 (C-H out-of-plane bend). Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.41; H, 7.56; N, 4.57.

2-(4-Hexyloxy-phenyl)-6-methylquinoline (6OPQMe) ^{1}H-NMR ($CDCl_3$): δ 8.01–8.13 (m, 4H, phenlene and quinoline), 7.79 (d, 1H, J = 8.4 Hz, quinoline), 7.52–7.55 (m, 2H, quinoline), 7.03 (d, 2H, J = 8.7 Hz, phenlene), 4.03 (t, 2H, J = 6.6 Hz, -OCH_2), 2.54 (s, 3H, -CH_3), 1.77–1.87 (m, 2H, -CH_2), 1.42–1.54 (m, 2H, -CH_2), 1.33–1.41 (m, 4H, -CH_2), 0.93 (t, 3H, J = 7.2 Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 160.4, 156.3, 147.0, 136.0, 135.7, 132.3, 131.9, 129.3, 128.8, 127.0, 126.4, 118.6, 114.9, 68.3, 31.7, 29.3, 25.8, 22.7, 21.6, 14.1. IR (KBr): cm^{-1} 3058 (aryl C-H stretch), 2936 (alkyl C-H asymmetric stretch), 2863 (alkyl C-H symmetric stretch), 1599 (ring stretch), 1495 (ring stretch), 1252 (asymmetric C-O-C stretch), 1026 (symmetric C-O-C stretch), 826 (C-H out-of-plane bend). Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.75; H, 7.88; N, 4.35.

2-(4-Heptyloxy-phenyl)-6-methylquinoline (7OPQMe) ^{1}H-NMR ($CDCl_3$): δ 8.05–8.12 (m, 4H, phenlene and quinoline), 7.77 (d, 1H, J = 8.7 Hz, quinoline), 7.53–7.55 (m, 2H, quinoline), 7.03 (d, 2H, J = 8.7 Hz, phenlene), 4.02(t, 2H, J = 6.6 Hz, -OCH_2), 2.53 (s, 3H, -CH_3), 1.77–1.87 (m, 2H, -CH_2), 1.33–1.51 (m, 8H, -CH_2), 0.92 (t, 3H, J = 6.6 Hz, -CH_3). ^{13}C-NMR ($CDCl_3$): ppm 160.4, 156.1, 146.7, 136.2, 135.8, 132.0, 129.1, 128.8, 126.9, 126.4, 118.6, 114.8, 68.2, 31.9, 29.3, 29.2, 26.1, 22.7, 21.6, 14.2. IR (KBr): cm^{-1} 3060 (aryl C-H stretch), 2925 (alkyl C-H asymmetric stretch), 2861 (alkyl C-H symmetric stretch), 1599 (ring stretch), 1495 (ring stretch), 1254 (asymmetric C-O-C stretch), 1015 (symmetric C-O-C stretch), 826 (C-H out-of-plane bend). Anal. Calcd for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.84; H, 8.16; N, 4.15.

3. Results and discussion

The mesophases of 2-(4-alkylphenyl)-6-methylquinolines (*n*PQMe, n = 4–8) and 2-(4-alkoxyphenyl)-6-methylquinolines (*m*OPQMe, m = 3–7) were identified by observing optical texture under a POM. In the series of *n*PQMe, monotropic nematic phases of n = 5 and 7 were observed in relatively wide mesophase ranges of 10°C and 7°C, respectively. On the contrary, 4PQMe and 6PQMe do not show any mesophases under POM, while the nematic phase of 8PQMe appears monotropically in a short temperature range within 1°C. 5PQMe provides the widest mesomorphic range. We also find the nematic phase range decreases, while the $T_{I\text{-}N}$ values increase, as the alkyl chain length increases. This series of compounds supports the contention the odd carbon atom alkyl chain has a terminal methyl group, extending the long molecular axis and tending to be mesomorphic in nature, whereas an even number of carbon chains in the terminal methyl group tending to lie off axis, do not (*17*).

The nematic phase was also found to be the only mesophase present in the series of *m*OPQMe, in which mesophase was not found when m = 3, monotropic when m = 4, 5 and enantiotropic when m = 6, 7. The mesomorphic temperature ranges for *m*OPQMe,

m = 4, 5, 6, 7 on cooling were 12.4°C, 11.5°C, 19.1°C, 19.3°C respectively and 3.3°C and 2°C when m = 6, 7 on heating. Compared with the series of *n*PQMe, the series of *m*OPQMe has a tendency of the nematic phase range to increase, while the $T_{I\text{-}N}$ values generally decrease, as the alkyl chain length increases. With the nematic sample of 5OPQMe between two crossed polarisers, the formation of schlieren texture with the presence of four-brush and two-brush singularities can be clearly noted (see Figure 1).

It is known that for series of nematogens, a regular alternation of nematic-to-isotropic transition temperatures occurs and when these are plotted against the number of carbons in the terminal alkyl chain the points lies on two curves (*17*). When the alkyl group is directly attached to a ring, the upper curve is for the odd members and the lower curve for the even members. When the terminal group is an n-alkoxy-group, the reverse situation occurs because the oxygen is geometrically equivalent to a CH_2 group. The odd–even effect of the $T_{I\text{-}N}$ values is clearly identified in the *m*OPQMe series, in which m = 4, 5, 6, 7 are 113.7°C, 102.5°C, 108.7°C, 104.6°C, respectively (see Table 2).

The variation of the $T_{I\text{-}N}$ values is large initially in a temperature range of 11.2°C and decreasing as the alkyl chain length increases. Damping of the alternation of the $T_{I\text{-}N}$ values has been explained in terms of the statistical increase in the number of non-extended conformations possible for the longer alkyl chains giving a progressive decrease in the differences in the anisotropies of molecular polarisability between odd and even members (*17*). On the contrary, the odd–even effect of the $T_{I\text{-}N}$ values in *n*PQMe series can barely be identified, in which n = 5, 7, 8 are 62.5°C, 67°C, 67.8°C, respectively. The variation of the $T_{I\text{-}N}$ values was small in the *n*PQMe series and the $T_{I\text{-}N}$ values increases as the alkyl chain length increases. The sensitivity of the $T_{I\text{-}N}$ values in *m*OPQMe series toward the odd-even effect is clear.

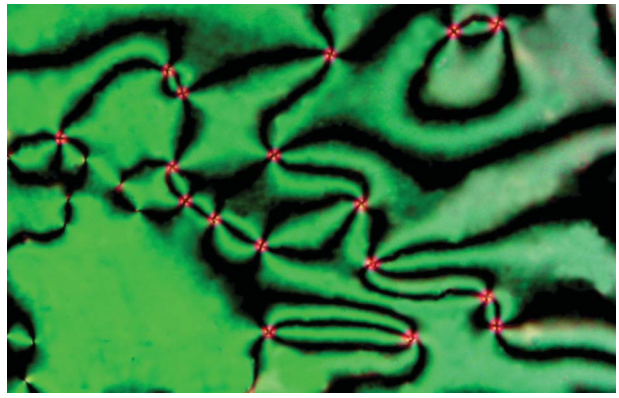


Figure 1. Polarised optical micrograph of nematic schlieren texture of 2-(4-pentoxyphenyl)-6-methylquinoline 5OPQMe arises from isotropic phase on cooling to 102°C with magnification of ×100.

The monotropic nematic mesophase in the homologues of *n*PQMe, n = 4–8 generally appears in a moderate temperature range between 67°C and 53°C, while that in the homologues of *m*OPQMe, m = 3–7, in a moderately high temperature range between 113°C and 85°C. Comparison between *n*PQMe and *m*OPQMe highlights that the latter series not only has a wider mesomorphic range but also has higher $T_{I\text{-}N}$ values of 30 to 40°C than the former. All these results clearly demonstrate the dipoles built-in from the ethereal linkage of alkoxy terminal chain in

Table 2. Phase transition temperatures (°C) and corresponding transition enthalpies (J g^{-1}), in parentheses, for homologous series of *n*PQMe, n = 4–8 and *m*OPQMe, m = 3–7 were determined by the second scans at a heating and cooling rate of 5°C min^{-1} from differential scanning calorimetry.

Compound (*n*PQMe or *m*OPQMe)	Phase transition temperatures (°C) and their corresponding transition enthalpies (J g^{-1})	
	Heating	Cooling
n = 4	Cr 61(41.02) I	I 32(43.94) Cr
n = 5	Cr 72(57.04) I	I 62.5 (1.04) N 53(58.79) Cr
n = 6	Cr 76(53.02) I	I 63 [b] Cr
n = 7	Cr 79(58.29) I	I 67(0.9) N 60(54.63) Cr
n = 8	Cr 77(60.09) I	I 67.8 [c] N 66.7 [c] Cr
m = 3	Cr 126.2(30.6) I	I 111.0(28.9) Cr
m = 4	Cr 120.5(31.7) I	I 113.7(0.61) N 101.3(26.7) Cr
m = 5	Cr 110.1(29.9) I	I 102.5(0.38) N 91.0(25.6) Cr
m = 6	Cr 106.0(24.4) N 109.3(0.39) I	I 108.7(0.40) N 89.6(22.8) Cr
m = 7	Cr 102.9(32.5) N 104.9(0.33) I	I 104.6(0.33) N 85.3(32.4) Cr

[a]Cr = crystalline phase, N = nematic phase, I = isotropic phase.
[b]A shoulder (at 63.7°C) appears on the peak at 62.3°C, and no mesophase can be detected under POM.
[c]The shoulder peak of *n*PQMe, n = 8 at 67.8°C becomes higher than the one in *n*PQMe, n = 6, and nematic phase is observed under a polarising optical microscope.

Table 3. Phase transition temperatures (°C) for the homologous series of *x*PQOMe, *x* = 4–8 were determined by the second scans at a heating and cooling rate of 5°C min^{-1} from DSC.

Entry	$T_{Cr\text{-}N}$[a] [$T_{Cr\text{-}I}$]	$T_{N\text{-}I}$	$T_{I\text{-}N}$	$T_{N\text{-}Cr}$
x = 4	[97.6]		86.9	79.2
x = 5	96.9	100.0	98.4	73.5
x = 6	[92.0]		83.6	67.9
x = 7	94.0	96.2	94.8	79.2
x = 8	[88.5]		85.8	69.0

[a]Cr = crystalline phase, N = nematic phase, I = isotropic phase.

*m*OPQMe, operating at an angle across the quinoline liquid crystalline molecule (*17*), do help to enhance the nematic mesophase thermal stability.

It has been explained (*18*) that in series of higher nematic-to-isotropic transition temperatures, the thermal fluctuations of the alkyl chain will reduce the proportions of those conformers which are especially favourable for nematic thermal stability and so the falling type of N–I curve will be noted. Thus, a progressive decrease in $T_{I\text{-}N}$ values was observed as in the *m*OPQMe, *m* = 3–7. On the contrary, in series of lower nematic-to-isotropic transition temperatures, the carbon chain adopts the more stable, planar, zig-zag conformation and leads to a progressive increase in $T_{I\text{-}N}$ values, as in the *n*PQMe, *n* = 4–8.

Lastly, results of this study can be compared with one of our in-press articles, which describes synthesis and thermotropic behaviours on the homologous series of xPQOMe (*16*). With an ethereal group insertion between quinoline moiety and methyl group in *n*PQMe, compounds in the series of *x*PQOMe, *x* = 4–8, have their nematic phase ranges appearing in the moderately high temperature range between 65°C and 100°C, higher than those of *n*PQMe. In addition, compounds in *x*PQOMe series have not only wider mesomorphic ranges but also higher $T_{I\text{-}N}$ values of 15 to 30°C than those of *n*PQMe (see Table 3). Compared with *m*OPQMe, having its ethereal group buried in the middle of the calamitic molecule, the exposed terminal ethereal group in the series of *x*PQOMe provides not only the early appearance of nematic phase but also somewhat wider mesomorphic ranges (see Figure 2). All this evidence indicates that an ethereal functional group can be used to fine tune the range and stability of the nematic mesomorphic phase.

Mesophase transition temperatures and their corresponding transition enthalpies were determined by DSC with heating and cooling rates of 5°Cmin^{-1} (see Table 2). All nematic-to-isotropic transitions in these non-polar quinoline-containing liquid crystals show a low transition enthalpy less than 1 J g^{-1}. A representative DSC thermogram of 5OPQMe is shown in Figure 3.

4. Conclusion

Two series of new liquid crystalline compounds, *n*PQMe and *m*OPQMe, derived from 6-methylquinoline, have been synthesised. Both series only display nematic mesophase. Their thermotropic behaviours are examined. Compounds in the *m*OPQMe series not only have wider mesomorphic ranges but also higher $T_{I\text{-}N}$ values than those in the *n*PQMe series. Synthesis and mesomorphic studies of other homologous series of quinoline-containing liquid crystalline will be investigated and reported elsewhere.

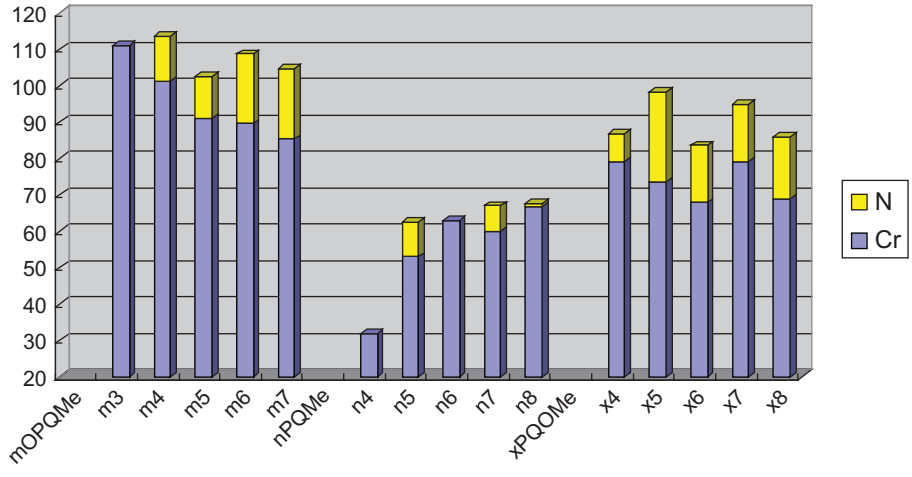


Figure 2. Plot of transition temperatures as a function of terminal alkyl chain length for compounds of *m*OPQMe, *m* = 3–7, *n*PQMe, *n* = 4–8 and *x*PQOMe, *x* = 4–8 during cooling at 5°C min^{-1}.

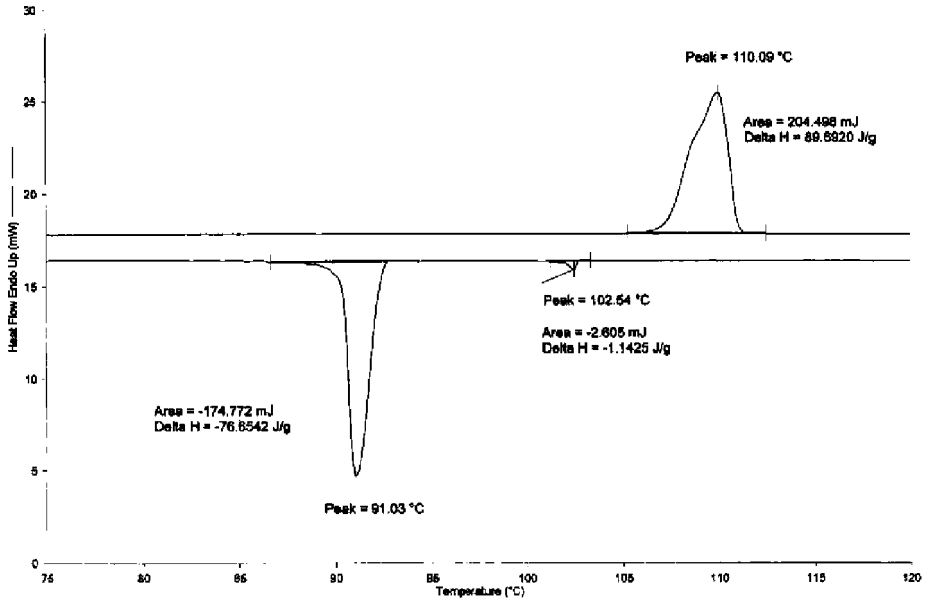


Figure 3. Heating and cooling thermograms of 5OPQMe were determined by the second scans at a rate of 5°C min^{-1} from differential scanning calorimetry.

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