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Mesogenic quinazolone derivatives: synthesis and characterisation

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Two new mesogenic homologous series of quinazolone derivatives have been synthesised by condensation of 4-*n*-alkoxybenzoyloxy benzaldehyde (for series **I**) / 4-*n*-alkoxy-3-methoxybenzoyloxy benzaldehyde (for series **II**) with 3-amino-2-methyl quinazolone in alcohol. The synthesised compounds are characterised by a combination of elemental analysis and standard spectroscopic methods. In series **I**, all the synthesised members exhibit the nematic mesophase. An enantiotropic smectic A phase is observed from the *n*-decyloxy derivative onward to the last homologue synthesised. Methoxy to *n*-propyloxy derivatives of series **II** are non-mesogenic, whereas the rest of the members exhibit a monotropic nematic mesophase. The mesomorphic properties of the present series **I** and **II** are compared with each other and with the other structurally related mesogenic homologous series to evaluate the effect of lateral methoxy substituent and quinazolone moiety on mesomorphism.

Keywords: quinazolone derivatives; Schiff's base ester; smectic A; nematic

1. Introduction

Many mesogenic compounds containing heterocyclic rings such as pyridine, pyrimidine, furyl, thiazole, thiadiazole and oxadiazole have been reported in the literature [1–7]. Significant interest in mesomorphic heterocyclic compounds [2] has dramatically increased due to their more diversified structural figures and distinct mesomorphic properties. Numerous unsaturated structures forming a variety of molecular shapes have been generated and found to exhibit interesting mesomorphic properties. Usually, five- or six-membered heterocycles are involved and they form part of the core in rod-shaped, bent-shaped or disc-shaped molecules. Many series of liquid crystalline compounds containing heterocyclic groups have been synthesised due to their potential wide range of application, such as in optical, electrical and biomedical fields [8, 9]. Heterocyclic compounds such as five-membered thiadiazole or thiophene rings can be incorporated into the principal structure of calamitic mesogens [10–13]. Barbera *et al.* [14] have synthesised 2-pyrazoline derivatives and studied their optical and mesogenic properties. Fused-ring heterocyclic derivatives, which are two condensed rings, are practically planar and rigid molecules. Liquid crystals containing fused heterocyclic ring systems, such as quinoline, flavon, benzo-2, 1, 3-thiadiazole, have also been reported in the literature [15–17]. Pavluchenko *et al.* [18] reported mesogens containing benzothiazole and benzoxazole with different central linkages and different lateral substitution at different positions, and evaluated the effect of structural changes on mesomorphic properties. Dvolaitsky *et al.* [19] reported free radical liquid crystalline properties of quinoxaline derivatives having smectic E, smectic C and smectic A phases. The 2-(4-alkyl and alkoxybiphenyl) quinoxalines [20] present smectic A phases over a large temperature range. The member of the series with the longest known chain (*p*-decyloxy) possesses smectic E and smectic A phases. Hexaalkoxytricycloquinazoline discotic liquid crystals were synthesised by Kumar *et al.* [21] to establish the correlation between liquid crystal molecular core width and its effect on mesomorphism.

Earlier we reported some mesogenic homologous series based on 2-aminonaphthalene moiety and evaluated the effect of naphthalene moiety, various lateral substituents such as $-CH_3$, –Cl, $-OCH_3$, –SH and central linkages such as –CH=N–, –N=N–, –COO–CH=CH–COO– etc. on mesomorphism [22–28]. In this paper, we report the synthesis and characterisation of two homologous series of Schiff's base ester having quinazolone moiety, and compare their mesomorphic properties with each other and with the mesogenic homologous series containing the naphthalene moiety in the molecular core, in order to evaluate the effect of lateral methoxy substituent and quinazolone heterocyclic moiety on mesomorphism. All the mesogenic compounds exhibited either a monotropic or enantiotropic nematic mesophase, thus they might be used as nematic hosts. Moreover, the lower members exhibit the nematic mesophase at high temperature and can be used as stationary phase in gas chromatography.

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2. Experimental details

2.1 Materials

The requisite starting materials such as 4-hydroxybenzoic acid, 2-aminobenzoic acid, acetic anhydride, hydrazine hydrate (99%), 4-hydroxybenzaldehyde, 4-hydroxy-3-methoxy benzaldehyde, 1-bromoalkane, potassium hydroxide, thionyl chloride, pyridine etc. were procured from Aldrich Company and used without any further purification.

2.2 Characterisation

Microanalysis of the compounds was performed on a Coleman carbon–hydrogen analyser, and the values obtained are in close agreement with those calculated. FTIR spectra were determined for KBr pellets using a Shimadzu IR-408 spectrophotometer. ^{1}H NMR spectra were obtained with a Perkin–Elmer R-32 spectrometer using tetramethylsilane (TMS) as internal reference standard. The chemical shifts are quoted in parts per million downfield from the reference; $CDCl_3$ was used as solvent for all the compounds. UV absorption spectra were obtained with Shimadzu-2450 spectrophotometer. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope (POM) equipped with a heating stage. The enthalpies of transitions, reported in J g^{-1}, were measured using differential scanning calorimetry (DSC) via a Mettler Toledo star^e SW 7.01 system at a scanning rate of 5°C min^{-1}. The calorimeter was calibrated using pure indium as standard.

2.3 Synthesis

The synthetic route to the series **I** and **II** compounds is illustrated in Scheme 1.

4-*n*-Alkoxybenzoic acid **(A)** and 4-*n*-alkoxybenzoyl chloride **(B)** were synthesised by a modification of the method of Dave and Vora [29]. 4-*n*-Alkoxybenzoyloxy benzaldehyde / 4-*n*-alkoxy-3-methoxybenzoyloxy benzaldehyde **(C)** was synthesised by the method of Dave and Kurian [30]. 2-Methyl-3, 1-benzoxazine **(D)** and 3-amino-2-methyl quinazolone **(E)** were synthesised following the procedure reported elsewhere [31].

*2.3.1 General method for preparation of series **I** and **II** compounds*

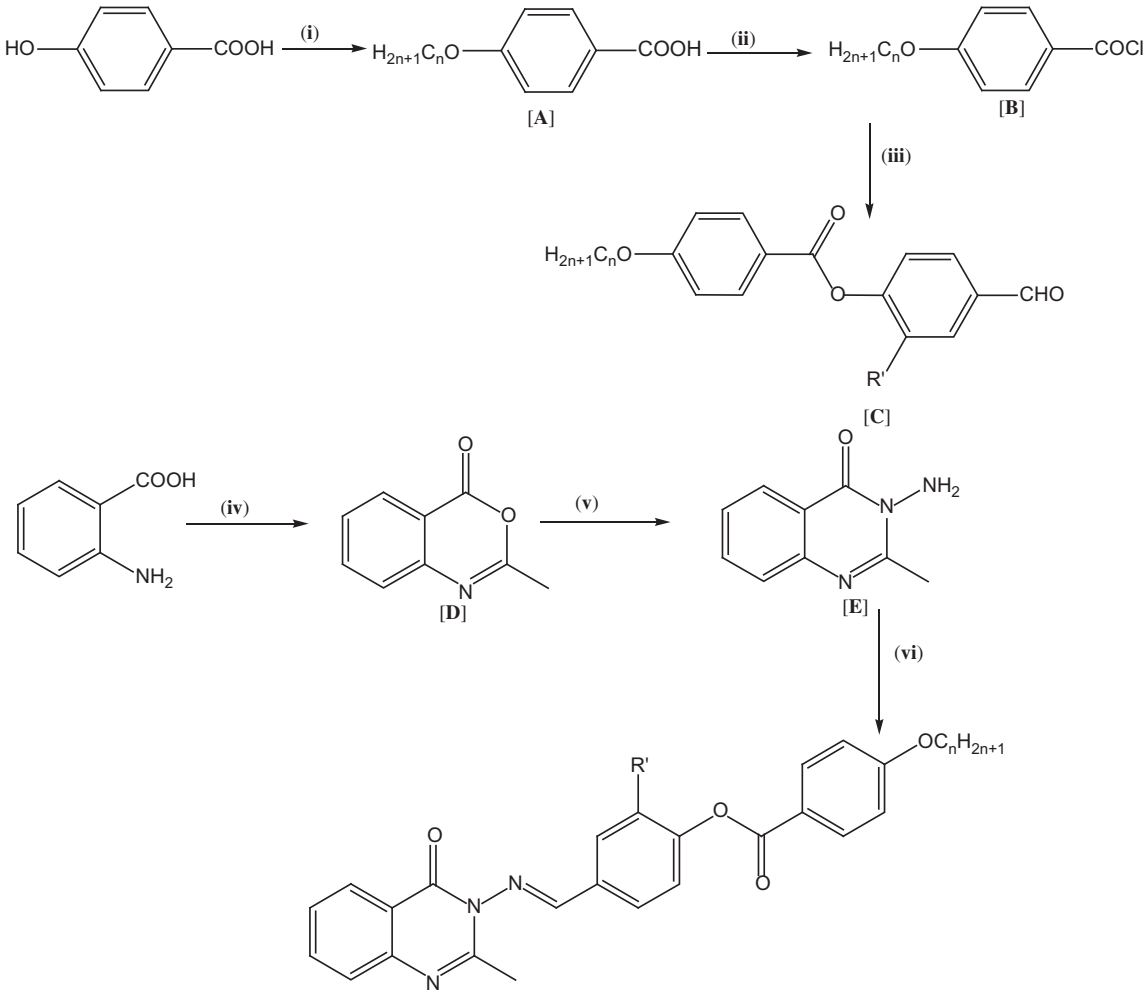
The Schiff's base esters of series **I** and **II** were synthesised by condensing equimolar quantities of 4-*n*-alkoxybenzoyloxy benzaldehyde (for series **I**) / 4-*n*-alkoxy-3-methoxy benzoyloxy benzaldehyde (for series **II**) **(C)** with 3-amino-2-methyl quinazolone **(E)** in boiling ethanol. Excess of ethanol was distilled off under reduced pressure. All the Schiff's bases of the series were crystallised from ethanol until constant transition temperatures were obtained.

Elemental analysis, FTIR and ^{1}H NMR spectral data of few representative members of series **I** and **II** are given below.

2.3.1.1 2-Methyl-3-[4'-(4''-n-butyloxybenzoyloxy) benzylidine]quinazolone **(4)**. Yield: 69%. ^{1}H NMR spectrum (400 MHz): δ 0.91 (t, J=6.4Hz, 3H, $-CH_3$), 1.38–1.42 (m, 2H, $-CH_2-$), 1.68 (quint., 2H, Ar–O–C–CH_2-), 2.49 (s, 3H, Ar–CH_3), 4.07 (t, J=6.5 Hz, 2H, Ar–O–CH_2-), 7.10 (d, J=9.0 Hz, 2H, Ar–H at C-3'' and C-5''), 7.50 (d, J=8.9 Hz, 2H, Ar–H at C-3' and C-5'), 7.64 (d, J=9.0 Hz, 1H, Ar–H at C-8), 7.80–7.95 (m, 4H, Ar–H at C-2', C-6', C-6 and C-7), 8.09 (d, J=8.8 Hz, 2H, Ar–H at C-2'' and C-6''), 8.16 (d, J=8.9 Hz, 1H, Ar–H at C-5), 9.01 (s, 1H of –CH=N–). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 2925 (ν_{C-H} aromatic), 2850 (ν_{C-H} aliphatic), 1740 (–COO–), 1700 (–C=O– of quinazolone), 1600 (–C=N–), 1510 (–C=N– of quinazolone), 1310, 1250, 1180 (aryl ether), 825, 790. Elemental analysis: Calculated for $C_{27}H_{25}N_3O_4$: C, 71.20; H, 5.49; N, 9.23%. Found: C, 71.01; H, 5.32; N, 9.15%.

2.3.1.2 2-Methyl-3-[4'-(4''-n-hexyloxybenzoyloxy) benzylidine]quinazolone **(6)**. Yield: 65%. ^{1}H NMR spectrum (400 MHz): δ 0.88 (t, J=6.4 Hz, 3H, $-CH_3$), 1.26–1.40 (m, 6H, 3 X $-CH_2-$), 1.75 (quint., 2H, Ar–O–C–CH_2-), 2.49 (s, 3H, Ar–CH_3), 4.07 (t, J=6.5 Hz, 2H, Ar–O–CH_2-), 7.11 (d, J=9.0 Hz, 2H, Ar–H at C-3'' and C-5''), 7.52 (d, J=8.9 Hz, 2H, Ar–H at C-3' and C-5'), 7.65 (d, J=8.8 Hz, 1H, Ar–H at C-8), 7.83–7.94 (m, 4H, Ar–H at C-2', C-6', C-6 and C-7), 8.10 (d, J=9.0 Hz, 2H, Ar–H at C-2'' and C-6''), 8.17 (d, J=8.9 Hz, 1H, Ar–H at C-5), 9.05 (s, 1H of –CH=N–). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 2960 (ν_{C-H} aromatic), 2855 (ν_{C-H} aliphatic), 1740 (–COO–), 1695 (–C=O– of quinazolone), 1610 (–C=N–), 1515 (–C=N– of quinazolone), 1305, 1250, 1180 (aryl ether), 825, 790. Elemental analysis: Calculated for $C_{29}H_{29}N_3O_4$: C, 72.04; H, 6.01; N, 8.69%. Found: C, 71.86; H, 5.95; N, 8.45%.

2.3.1.3 2-Methyl-3-[4'-(4''-n-octyloxybenzoyloxy) benzylidine]quinazolone **(8)**. Yield: 70%. ^{1}H NMR spectrum (400 MHz): δ 0.91 (t, J=6.4 Hz, 3H, $-CH_3$), 1.20–1.36 (m, 10H, 5 X $-CH_2-$), 1.73 (quint., 2H, Ar–O–C–CH_2-), 2.59 (s, 3H, Ar–CH_3), 4.07 (t, J=6.5 Hz, 2H, Ar–O–CH_2-), 7.11 (d, J=9.0 Hz, 2H, Ar–H at C-3'' and C-5''), 7.53 (d, J=8.9 Hz, 2H, Ar–H at C-3' and C-5'), 7.63 (d, J=8.8 Hz, 1H, Ar–H at C-8), 7.81–7.97 (m, 4H, Ar–H at C-2', C-6', C-6 and



Scheme 1. Synthetic route to series **I** and **II** compounds, where n = 1-8, 12, 14 and 16. R' = -H (series **I**) and $-OCH_3$ (series **II**). Reagents and conditions: **(i)** C_nH_{2n+1}–Br, alcoholic KOH, reflux; **(ii)** $SOCl_2$ excess, reflux; **(iii)** 4-hydroxybenzaldehyde or 4-hydroxy-3-methoxybenzaldehyde in pyridine, cold aqueous (1:1) HCl; **(iv)** acetic anhydride, reflux; (**v**) hydrazine hydrate, ethanol, reflux; (**vi**) C in ethanol, reflux.

C-7), 8.11 (d, J=9.0 Hz, 2H, Ar–H at C-2" and C-6"), 8.17 (d, J=8.9 Hz, 1H, Ar–H at C-5), 9.04 (s, 1H of –CH=N–). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 2950 (ν_{C-H} aromatic), 2840 (ν_{C-H} aliphatic), 1750 (–COO–), 1690 (–C=O– of quinazolone), 1610 (–C=N–), 1510 (–C=N– of quinazolone), 1305, 1250, 1180 (aryl ether), 825, 790. Elemental analysis: Calculated for $C_{31}H_{33}N_3O_4$: C, 72.79; H, 6.45; N, 8.21%. Found: C, 72.57; H, 6.37; N, 8.08%.

2.3.1.4 2-Methyl-3-[4'-(4"-n-dodcyloxybenzoyloxy) benzylidine]quinazolone **(10)**. Yield: 72%. ^{1}H NMR spectrum (400 MHz): δ 0.82 (t, J=6.4 Hz, 3H, $-CH_3$), 1.24–1.42 (m, 18H, 9 X $-CH_2-$), 1.70 (quint., 2H, Ar–O–C–CH_2-), 2.49 (s, 3H, Ar–CH_3), 4.01 (t, J=6.6 Hz, 2H, Ar–O–CH_2-), 7.11 (d, J=9.0 Hz, 2H, Ar–H at C-3" and C-5"), 7.52 (d, J=8.9 Hz, 2H, Ar–H at C-3' and C-5'), 7.65 (d, J=9.0 Hz, 1H, Ar–H at C-8), 7.85–7.94 (m, 4H, Ar–H at C-2', C-6', C-6 and C-7), 8.15 (d, J=9.0 Hz, 2H, Ar–H at C-2" and C-6"), 8.17 (d, J=8.9 Hz, 1H, Ar–H at C-5), 9.02 (s, 1H of –CH=N–). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 2950 (ν_{C-H} aromatic), 2850 (ν_{C-H} aliphatic), 1745 (–COO–), 1700 (–C=O– of quinazolone), 1610 (–C=N–), 1515 (–C=N– of quinazolone), 1305, 1250, 1175 (aryl ether), 825, 790. Elemental analysis: Calculated for $C_{35}H_{41}N_3O_4$: C, 74.07; H, 7.23; N, 7.40%. Found: C, 73.85; H, 7.19; N, 7.39%.

2.3.1.5 2-Methyl-3-[4'-(4"-n-pentyloxybenzoyloxy) -3'-methoxybenzylidine]quinazolone **(16)**. Yield: 60%. ^{1}H NMR spectrum (300 MHz): δ 0.94 (t, J=6.5 Hz, 3H, $-CH_3$), 1.39–1.49 (m, 4H, 2 X $-CH_2-$), 1.81 (quint., 2H, Ar–O–C–CH_2-), 2.64 (s, 3H, Ar–CH_3), 3.90 (s, 3H,

Ar–OCH_3), 4.07 (t, *J*=6.7 Hz, 2H, Ar–O–CH_2–), 6.96 (d, *J*=9.0 Hz, 2H, Ar–H at C-3" and C-5"), 7.26 (d, *J*=8.9 Hz, 1H, Ar–H at C-5'), 7.42–7.47 (m, 2H, Ar–H at C-6 and C-7), 7.64–7.75 (m, 3H, Ar–H at C-2', C-6' and C-8), 8.14 (d, *J*=8.9 Hz, Ar–H at C-2" and C-6"), 8.17 (d, *J*=9.0 Hz, 1H, Ar–H at C-5), 9.00 (s, 1H of –CH=N–). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 2950 (ν_{C-H} aromatic), 2850 (ν_{C-H} aliphatic), 1740 (–COO–), 1695 (–C=O– of quinazolone), 1610 (–C=N–), 1515 (–C=N– of quinazolone), 1305, 1250, 1180 (aryl ether), 825, 790. Elemental analysis: Calculated for $C_{29}H_{29}N_3O_5$: C, 69.73; H, 5.81; N, 8.41%. Found: C, 69.69; H, 5.77; N, 8.35%.

2.3.1.6 2-Methyl-3-[4'-(4"-n-hexyloxybenzoyloxy)-3'-methoxybenzylidine]quinazolone **(17)**. Yield: 58%. ^{1}H NMR spectrum (300 MHz): δ 0.92 (t, *J*=6.5 Hz,3H, –CH_3), 1.32–1.48 (m, 6H, 3 X –CH_2–), 1.80 (quint., 2H, Ar–O–C–CH_2–), 2.67 (s, 3H, Ar–CH_3), 3.89 (s, 3H, Ar–OCH_3), 4.02 (t, *J*=6.7 Hz, 2H, Ar–O–CH_2–), 6.99 (d, *J*=8.8 Hz, 2H, Ar–H at C-3" and C-5"), 7.24 (d, *J*=9.0 Hz, 1H, Ar–H at C-5'), 7.42–7.46 (m, 2H, Ar–H at C-6 and C-7), 7.64–7.74 (m, 3H, Ar–H at C-2', C-6' and C-8), 8.12 (d, *J*=9.0 Hz, 2H, Ar–H at C-2" and C-6"), 8.17 (d, *J*=8.8 Hz, 1H, Ar–H at C-5), 8.96 (s, 1H of –CH=N–). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 2950 (ν_{C-H} aromatic), 2850 (ν_{C-H} aliphatic), 1755 (–COO–), 1700 (–C=O– of quinazolone), 1610 (–C=N–), 1515 (–C=N– of quinazolone), 1305, 1250, 1180 (aryl ether), 825, 790. Elemental analysis: Calculated for $C_{30}H_{31}N_3O_5$: C, 70.17; H, 6.04; N, 8.18%. Found: C, 70.10; H, 6.01; N, 8.11%.

2.3.1.7 2-Methyl-3-[4'-(4"-n-dodecyloxybenzoyloxy)-3'-methoxybenzylidine]quinazolone **(21)**. Yield: 65%. ^{1}H NMR spectrum (300 MHz): δ 0.94 (t, *J*=6.5 Hz, 3H, –CH_3), 1.39–1.49 (m, 18H, 9 X –CH_2–), 1.80 (quint., 2H, Ar–O–C–CH_2–), 2.63 (s, 3H, Ar–CH_3), 3.90 (s, 3H, Ar–OCH_3), 4.01 (t, *J*=6.6 Hz, 2H, Ar–O–CH_2–), 6.98 (d, *J*=9.0 Hz, 2H, Ar–H at C-3" and C-5"), 7.26 (d, *J*=8.8 Hz, 1H, Ar–H at C-5'), 7.43–7.47 (m, 2H, Ar–H at C-6 and C-7), 7.64–7.75 (m, 3H, Ar–H at C-2', C-6' and C-8), 8.15 (d, *J*=8.9 Hz, 2H, Ar–H at C-2" and C-6"), 8.17 (d, *J*=9.0 Hz, 1H, Ar–H at C-5), 8.99 (s, 1H of –CH=N–). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 2950 (ν_{C-H} aromatic), 2850 (ν_{C-H} aliphatic), 1745 (–COO–), 1695 (–C=O– of quinazolone), 1610 (–C=N–), 1515 (–C=N– of quinazolone), 1305, 1250, 1180 (aryl ether), 825, 790. Elemental analysis: Calculated for $C_{36}H_{43}N_3O_5$: C, 72.36; H, 7.20; N, 7.03%. Found: C, 72.27; H, 7.13; N, 6.94%.

2.3.1.8 2-Methyl-3-[4'-(4"-n-hexadecyloxybenzoyloxy)-3'-methoxybenzylidine]quinazolone **(22)**. Yield: 70%. ^{1}H NMR spectrum (300 MHz): δ 0.89 (t, *J*=6.5 Hz, 3H, –CH_3), 1.32–1.50 (m, 26H, 13 X –CH_2–), 1.80 (quint, 2H, Ar–O–C–CH_2–), 2.67 (s, 3H, Ar–CH_3), 3.89 (s, 3H, Ar–OCH_3), 4.04 (t, *J*=6.7 Hz, 2H, Ar–O–CH_2–), 6.96 (d, *J*=9.0 Hz, 2H, Ar–H at C-3" and C-5"), 7.26 (d, *J*=8.8 Hz, 1H, Ar–H at C-5'), 7.42–7.46 (m, 2H, Ar–H at C-6 and C-7), 7.64–7.75 (m, 3H, Ar–H at C-2', C-6' and C-8), 8.14 (d, *J*=9.0 Hz, 2H, Ar–H at C-2" and C-6"), 8.17 (d, *J*=9.0 Hz, 1H, Ar–H at C-5), 8.99 (s, 1H of –CH=N–). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 2950 (ν_{C-H} aromatic), 2850 (ν_{C-H} aliphatic), 1750 (–COO–), 1690 (–C=O– of quinazolone), 1610 (–C=N–), 1515 (–C=N– of quinazolone), 1305, 1250, 1180 (aryl ether), 825, 790. Elemental analysis: Calculated for $C_{40}H_{51}N_3O_5$: C, 73.50; H, 7.81; N, 6.43%. Found: C, 73.43; H, 7.78; N, 6.33%.

3. Results and discussion

3.1 Synthesis

The synthetic route with reaction conditions for the preparation of series **I** and **II** compounds is shown in Scheme 1.

The UV absorption data for the solution of series **I** and **II** compounds in dichloromethane at 5×10^{-6}M concentration at 25°C are listed in Table 1. For compounds of series **I**, three strong absorption bands appeared in the range of λ_{max} 230–232 nm, 265–270 nm and 275–278 nm. For compounds of series **II**, two absorption bands appeared in the range of λ_{max} 225–230 nm and 258–260 nm.

Table 1. UV/Vis electronic absorption data for series **I** and **II** compounds.

	λ_{max}	
n	**Series I**	**Series II**
1	232, 268, 278	230, 260
2	232, 268, 278	229, 259
3	232, 268, 278	228, 260
4	232, 268, 278	230, 260
5	232, 268, 278	230, 260
6	230, 270, 275	230, 258
7	232, 268, 278	228, 260
8	232, 268, 275	225, 260
10	232, 268, 278	230, 260
12	232, 268, 278	230, 260
14	232, 265, 275	228, 258
16	232, 265, 278	230, 260

3.2 Phase behaviour

*3.2.1 Series **I**: 2-Methyl-3-[4'-(4"-n-alkoxybenzoyloxy) benzylidine] quinazolone*

Twelve compounds of series **I** were synthesised and their mesogenic properties evaluated. Methoxy and ethoxy derivatives exhibit a monotropic nematic mesophase. *n*-Propyloxy to *n*-hexadecyloxy derivatives exhibit an enantiotropic nematic mesophase. SmA mesophase commences from *n*-decyloxy derivative and persists up to the last homologue synthesised (Table 2). Figure 1 shows the plot of transition temperatures against the number of carbon atoms in the alkoxy chain, from which can be noted a steady fall in the N–Iso transition temperatures and little odd–even effect. The SmA–N transition temperatures rise as the series ascends.

*3.2.2 Series **II**: 2-Methyl-3-[4'-(4"-n-alkoxybenzoyloxy)-3'-methoxy benzylidine] quinazolone*

Twelve compounds of series **II** were synthesised and their mesogenic properties evaluated. Lower members (i.e. $n \leq 3$) are non-mesogenic. *n*-Butyloxy to *n*-hexadecyloxy derivatives exhibit a monotropic nematic mesophase (Table 2). Figure 2 shows the plot of transition temperatures against the number of carbon atoms in the alkoxy chain, from which can be noted that Iso–N transition temperatures tend to fall as the series ascends.

3.3 DSC studies

As representative cases, the phase transition enthalpies were measured for the *n*-octyloxy and *n*-hexadecyloxy derivative of series **I** and *n*-pentyloxy and *n*-octyloxy derivatives of series **II** by DSC. The results are recorded in Table 3.

The mesophase assignments according to POM observation are in good agreement with the corresponding DSC thermograms. All compounds studied exhibit clear-cut transition temperatures in their DSC thermograms.

3.4 Mesogenic properties and molecular constitution

It is well known that thermotropic liquid crystals are highly sensitive to their molecular constitution. It is of prime importance, from the chemist's point of view, to determine the effects of alterations in the molecular core on the mesogenic properties of a

Table 2. Transition temperatures (°C) of the series **I** and **II** compounds.

Compound no.	R= -C_nH_{2n+1} *n*=	Cr		Sm A		N		Iso
Series **I**								
1	1	•	205	–	–	(•	202)	•
2	2	•	227	–	–	(•	200)	•
3	3	•	158	–	–	•	192	•
4	4	•	151	–	–	•	192	•
5	5	•	131	–	–	•	179	•
6	6	•	124	–	–	•	178	•
7	7	•	105	–	–	•	166	•
8	8	•	102	–	–	•	162	•
9	10	•	86	•	105	•	158	•
10	12	•	90	•	110	•	138	•
11	14	•	97	•	118	•	139	•
12	16	•	95	•	132	•	137	•
Series **II**								
13	1	•	178	–	–			•
14	2	•	168	–	–			•
15	3	•	170	–	–			•
16	4	•	162	–	–	(•	106)	•
17	5	•	166	–	–	(•	101)	•
18	6	•	153	–	–	(•	95)	•
19	7	•	152	–	–	(•	94)	•
20	8	•	130	–	–	(•	93)	•
21	10	•	132	–	–	(•	92)	•
22	12	•	134	–	–	(•	90)	•
23	14	•	128	–	–	(•	82)	•
24	16	•	132	–	–	(•	88)	•

Note: Cr: Crystalline; SmA: Smectic A phase; N: Nematic phase; Iso: Isotropic liquid; ( ) monotropic value

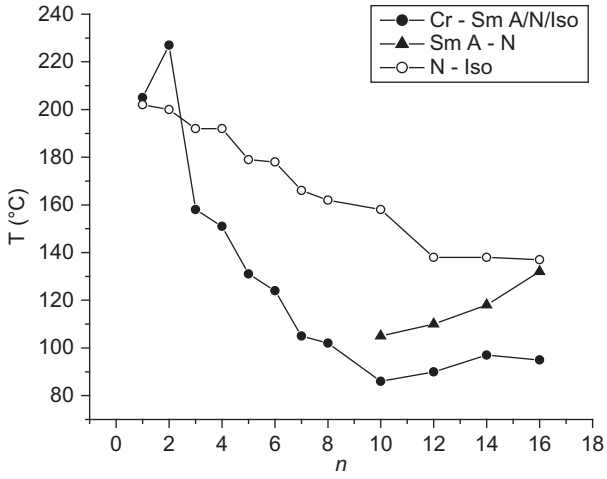


Figure 1. The phase behaviour for series **(I)** compounds.

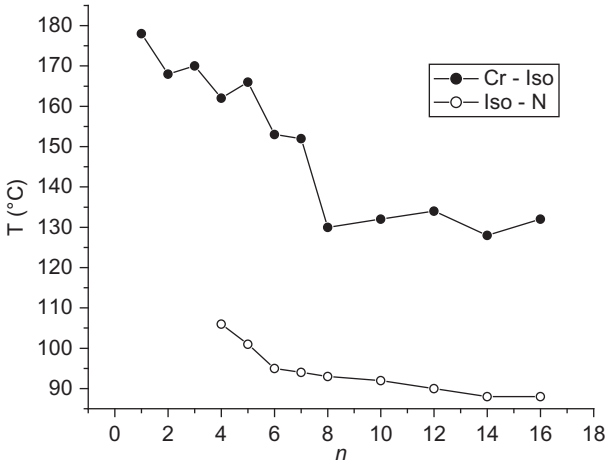


Figure 2. The phase behaviour for series **(II)** compounds.

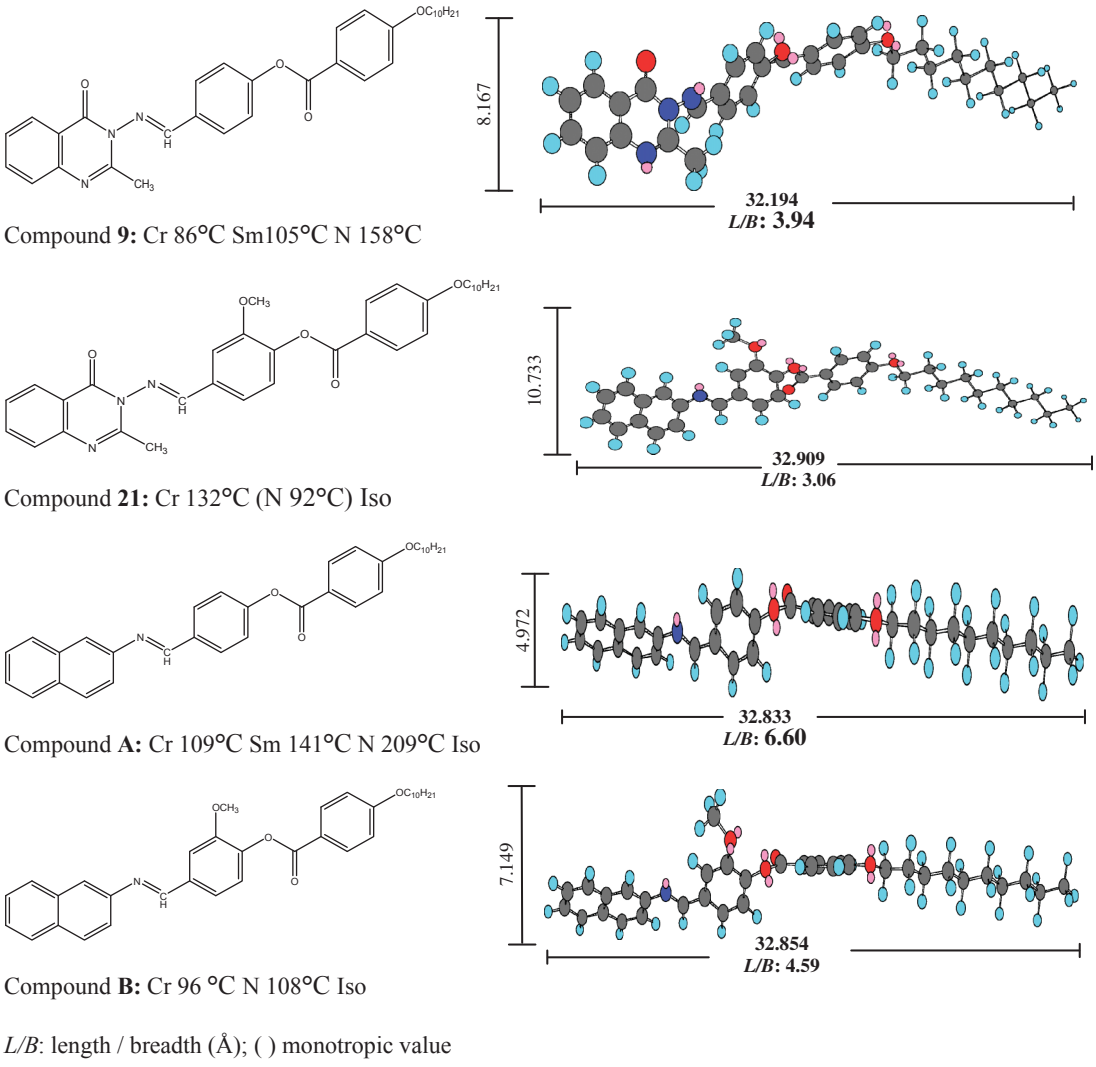
compound. The thermal stability and mesophase length as a measure of mesomorphism can be correlated with the molecular constitution of the compounds. Figure 3 summarises the molecular structure, transition temperatures and energy-minimised ball and stick model (MM2 models derived from CS Chemdraw Ultra 7.0 software) with length and breadth of the *n*-decyloxy derivative of the present series **I** and **II** (compounds **9** and **21**) and structurally related compounds **A** and **B** reported in the literature [22–28].

Compound **9** exhibits enantiotropic SmA and nematic mesophases, while compound **21** exhibits only monotropic nematic mesophase. The nematic mesophase length and thermal stability (N–Iso transition temperature) of compound **21** is lower by 65°C and 66°C as compared with compound **9**. The molecules of compound **9** and **21** differ only at the central benzene nucleus. Compound **21** has a lateral -OCH_3 group, whereas in compound **9** the central phenyl ring is unsubstituted. The lateral methoxy group increases the breadth of the molecule of compound **21** and also the non-coplanar arrangement of the system due to steric interactions. Moreover the length/breadth (*L*/*B*) ratio of compound **9** (3.94) is greater as compared with compound **21** (3.06). All these factors would be responsible for the elimination of the smectogenic tendencies from compound **21**, as well as lower thermal stability as compared with compound **9**. This factor was also responsible for the monotropic nature of the mesophase observed in compound **21**.

The smectic mesophase length and the thermal stabilities of compound **9** are lower by 13°C and 36°C, respectively, as compared with the structurally related compound **A** [22–28]. Also, the nematic

Table 3. DSC data for series **I** and **II** compounds.

Series	R = -C_nH_{2n+1} *n*=	Transition	Peak temperature (°C)	ΔH (J g^{-1})	ΔS (J (g°K)$^{-1}$)
I	8	Cr–N	104.45	99.10	0.2603
		N–Iso	160.45	1.05	0.0024
		Iso–N	161.08	1.12	0.0025
		N–Cr	61.90	107.76	0.3217
	16	Cr–SmA	92.77	70.15	0.1917
		SmA–N	130.19	1.22	0.0030
		N–Iso	137.59	0.993	0.0024
		Iso–N	135.88	0.775	0.0018
		N–SmA	129.87	1.09	0.0027
		SmA–Cr	72.07	66.95	0.1940
II	5	Cr–Iso	166.04	125.54	0.2859
		Iso–N	100.18	13.28	0.0355
		N–Cr	70.36	109.64	0.3193
	8	Cr–Iso	128.54	113.52	0.2827
		Iso–N	94.64	14.18	0.0393
		N–Cr	55.01	100.61	0.3067



Compound **9:** Cr 86°C Sm105°C N 158°C

Compound **21:** Cr 132°C (N 92°C) Iso

Compound **A:** Cr 109°C Sm 141°C N 209°C Iso

Compound **B:** Cr 96 °C N 108°C Iso

L/B: length / breadth (Å); ( ) monotropic value

Figure 3. Molecular structures, transition temperatures and energy-minimised ball and stick model (MM2 models derived from CS Chemdraw Ultra 7.0 software) with dimensions of compounds **9, 21, A** and **B** (colour version online).

mesophase length and thermal stabilities of compound **9** are lower by 5°C and 51°C, respectively, as compared with compound **A**. Molecules of compound **9** and **A** differ only in their aromatic moiety at one end. Compound **9** has a 2-methylquinazolone heterocyclic moiety, whereas compound **A** has a naphthalene moiety at the same position. Nash and Gray [32] had reported that the hetero-atom in a pyridine or related ring system is known to behave similarly to aromatic nitro-group, which increases overall axial polarisability of the molecule. Thus the presence of the 2-methylquinazolone heterocyclic ring in compound **9** might increase overall polarisability of the molecule; however, the carbonyl group of the quinazolone ring system, as well as the lateral methyl substituent, actually lead to a reduction in the polarisability anisotropy and also increases the overall molecular breadth as compared with unsubstituted naphthyl derivatives; it can be seen from Figure 3 that the *L*/*B* ratio for compound **9** (*L*/*B*: 3.06) is lower as compared with compound **A** (*L*/*B*: 6.60). Gray [33] has explained that increases in molecular breadth reduce both nematic and smectic mesophase thermal stability.

This is also reflected in the comparison of compounds **21** and **B** [22–28]. Enantiotropic nematic behaviour was observed for compound **B**, whereas compound **21** has a monotropic nematic phase with both lower mesophase length and thermal stability by 5°C and 24°C, respectively, as compared with compound **B**, because the *L*/*B* ratio for compound **21** (*L*/*B*: 3.06) is lower as compared with compound **B** (*L*/*B*: 4.59).

4. Conclusion

In this article, we have presented the synthesis and characterisation of two new mesogenic homologous series of quinazolone to evaluate the effect of lateral methoxy substituents and the quinazolone heterocyclic moiety on mesomorphism. The mesomorphic properties exhibited by the present series **I** and **II** show that the members of series **I** exhibit higher mesophase thermal stability as compared with those of series **II** due to increase in the breadth of the molecule of series **II**. The lateral methoxy substituent eliminates the smectic mesophase for the present series **II** due to increase in the breadth of the molecule.

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