Calamitic liquid crystals involving fused ring and their metallomesogens

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In this paper, the authors report two different types of terminally substituted homologous series with an ester–azo central linkage involving fused-ring achiral liquid crystals such as 4-((4-chlorophenyl)diazenyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate (series A) and 4-((4-nitrophenyl)diazenyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate (series B). Their copper (II) metallomesogens were synthesised and characterised by methods such as elemental analysis, Fourier transform infrared, proton (^1H) nuclear magnetic resonance (NMR), carbon-13 (^{13}C) NMR and mass spectroscopic studies. Thermotropic properties were studied by performing polarising optical microscopy and DSC analysis. All liquid crystalline compounds (ligands) display nematic and/or smectic phase/s. Unlike ligands, both types of copper (II) complexes show a solely nematic behaviour. The series B exhibit Sm-form from C_7 derivatives where as series A exhibit Sm-form from C_8 derivatives. The series B is more thermally stable than series A. The series A exhibit monotropic nematic phase for C_4 derivative and monotropic smectic phase for C_{10} derivative. Whereas series B display monotropic nematic phase for C_5 derivative and C_{12} derivative is fully monotropic i.e. both nematic and smectic phase obtained only on cooling cycle.

1. Introduction

Liquid crystals (LCs) are a fascinating phase of matter because of their orientational order with fluidity and optical anisotropy. A number of organic molecules and organic polymers that have delocalised π -electron systems are being extensively studied for applications in the field of non-linear optics.^{1–5}

Azo dye LCs have attracted much attention for their potential uses in optical storage applications because of their easy availability, reasonable photofatigue resistance and the marked transformation of their molecular shape upon E to Z photoisomerisation.^{6–11} They have a reasonable dichroic ratio for reflective LC devices, which are of considerable interest owing to their low power consumption.¹²

Studies of dichroic dyes are attracting much attention due to the development of reflection-type guest–host LC displays. Azo dyes have been proposed as positive dichroic dyes for use in displays.^{13–15} The improvement in the solubility and dichroism of dyes is a challenging subject.

The structure/mesomorphic property relationship is the most attractive area of study for chemists in LC research, and a number

of papers and monographs regarding this subject have been reported in the literature.^{16,17} Nevertheless, the vast range of synthetic possibilities in organic chemistry means that a variety of structures remain relatively unstudied. Within the classic calamitic structure, some functional groups have proven to be very useful in promoting mesomorphic properties. Generally, the ester group or azo group or ester–azo groups have been most commonly used as central bridging units and have been incorporated in many low-temperature systems. In addition, the introduction of aromatic groups such as biphenyl or naphthyl has been widely studied because they give rise to a very stable mesophase and allow the introduction of substituents into different positions, leading to modification of the LC properties.^{18,19}

Metallomesogens have attracted increasing attention due to the possibility of combining the physico-chemical properties contributed by the metal with those of organic framework.^{20–22} However, the understanding and control of phase behaviour are functions of molecular chain length, the nature of the substituents on the ligands, the spacer groups and metal ions. Among the first-row transition metals, metallomesogens with copper (II), exhibiting various smectic, nematic as columnar LC phases, have been prepared and studied.^{23,24}

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Due to the paramagnetism induced by the copper (Cu) (II) centre, these metallomesogens show interesting chemical and physical properties that can lead to potential applications.^{25–30}

In order to evaluate the practical advantages of incorporating the fused-ring naphthalene system in the structure of liquid crystalline materials, the authors report in this paper two homologous series and a study of the mesomorphic properties of the 2,6-naphthyl benzoate terminal core. With this purpose in mind, this study was focused on two series of 2,6-naphthyl benzoate with an ester–azo linking group and chloro and nitro terminal groups and their copper (II) metallomesogens.

2. Experimental

2.1 Materials

For the synthesis of compounds of the homologous series (ligands) and their copper (II) complexes, the following materials were used. Alkyl bromide (Lancaster, England), 4-chloroaniline, 4-nitroaniline, resorcinol, 6-hydroxy-2-naphthoic acid was

obtained from H.L. Chemical & Engineer Pvt. Ltd, Maroli (Surat); *N,N'*-dimethylaminopyridine was purchased from Merck (Germany); and copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and dicyclohexylcarbodiimide were acquired from Fluka Chemie (Switzerland). Anhydrous potassium carbonate, acetone, ethanol, methanol, acetic acid, ethyl acetate, dichloromethane, pyridine, petroleum ether, diethyl ether, dimethylformamide, phosphoryl chloride (POCl_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), ammonia and so on were used as received. Column chromatography was performed on an Acme silica gel (100–200 mesh). The solvents were dried and distilled prior to use.

2.2 Synthesis

The synthetic route for the preparation of series A, B, MC and MD compounds is illustrated in the following section.

2.2.1 Synthesis of 6-alkoxy-2-naphthoic acid

6-Hydroxy-2-naphthoic acid (2.5 g, 13 mmol) and potassium hydroxide (KOH) (1.46 g, 26 mmol) were dissolved in ethanol/

Figure 1. FT-IR spectra of compounds (a) A_8 , (b) A_{16} , (c) B_8 and (d) B_{16}

water (100 ml, 9:1), and the solution was stirred for 20 min. *n*-Alkyl bromide (32.5 mmol) was then added, and the mixture was heated under reflux for 24 h. When the reaction was completed, potassium hydroxide (0.73 g, 13 mmol) was added, and the mixture was heated under reflux for an additional 4 h. The ethanol was evaporated, and the mixture was poured into water and acidified to approximately pH = 2–3 with acetic acid. The precipitate was filtered and washed with water and ether and then recrystallised twice from glacial acetic acid to yield 71–80%

concentrations. The synthetic route has also been described in the literature.^{31,32}

2.2.2 Synthesis of 4-chloro-2',4'-dihydroxy azobenzene and 4-nitro-2',4'-dihydroxy azobenzene

A well-stirred mixture of 4-chloroaniline (1.28 g, 0.01 mol) and 40 ml of 1:1 concentrated hydrochloric acid was cooled below 5°C and a solution of sodium nitrite (NaNO₂) (0.76 g, 0.011 mol) in water (20 ml) was added dropwise in such a way that the

Figure 2. Proton NMR spectra of compounds (a) A₈, (b) A₁₆, (c) B₈ and (d) B₁₆ (continued on next page)

Figure 2. Continued

temperature of the mixture was in the range of 0–5°C. The cold, dark yellow solution was added dropwise to a cold mixture of resorcinol (1.1 g, 0.01 mol), sodium hydroxide (NaOH) (5 g, 10%) and water (50 ml), during which the temperature of the mixture was maintained below 8°C. After the diazotising the solution, the material was stirred for about 30 min and then acidification with aqueous hydrochloric acid provided the crude product, which was collected by filtration, dried in air and crystallised several times from alcohol to yield 65%

concentration. A similar procedure was utilised to synthesise 4-nitro-2',4'-dihydroxy azobenzene (68% concentration).

2.2.3 Synthesis of 4-((4-chlorophenyl)diazenyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate (series A) and 4-((4-nitrophenyl)diazenyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate (series B)

6-*n*-Alkoxy-2-naphthoic acids were heated under reflux with thionyl chloride to produce the corresponding acid chloride.

Monoesters of series I and II were prepared by condensing equimolar quantities of the respective 4-*n*-alkoxybenzoyl chlorides with 4-chloro-2,4-dihydroxy azobenzene in dry pyridine through the Schotten–Baumann reaction following the method reported earlier.³³

The monoesters of series I and II were prepared by condensing equimolar quantities of the respective 4-*n*-alkoxybenzoyl chlorides with 4-nitro-2,4-dihydroxy azobenzene in dry pyridine

through the Schotten–Baumann reaction following the method reported earlier.

2.2.4 Synthesis of bis(2-((4-chlorophenyl)diazenyl)-5-(6-alkoxy-2-naphthoyloxy)phenoxy) copper (II) (series MC) and bis(2-((4-nitrophenyl)diazenyl)-5-(6-alkoxy-2-naphthoyloxy)phenoxy) copper (II) (series MD)

Copper (II) chloride dihydrate (0.170 g, 1 mmol) was dissolved in methanol (10 ml), and ammonia was added to it until the colour of

Figure 3. Proton NMR spectra of compounds (a) MC₁₈ and (b) MD₁₈

the solution became blue. Two millimoles of the appropriate ligand (series A or series B) was dissolved in methanol (20 ml). The ligand solution was added to a metal solution, and the reaction mixture was refluxed for 3–4 h. A brown-black precipitate was formed. The precipitate was filtered off and washed with methanol twice or thrice.

2.3 Data: compound A₈ (4-((4-chlorophenyl)diazenyl)-3-hydroxyphenyl 6-octyloxy-2-naphthoate (series A))

Molecular formula: C₃₁H₃₁ClO₄N₂; yield: 80%; clearing point: 209°C; ultraviolet (UV) (chloroform (CHCl₃)) λ_{max}: 258 nm; elemental analysis data: found: carbon (C): 70.38%, hydrogen

(H): 5.68%, nitrogen (N): 5.00%; calculated: carbon: 70.11%, hydrogen: 5.88%, nitrogen: 5.28%; Fourier transform infrared (FT-IR) (potassium bromide (KBr)): ν_{max}: cm⁻¹: 3351 (O–H stretching of –OH group attached to aromatic ring), 3042 (C–H stretching aromatic), 2931, 2855 (C–H stretching aliphatic), 1732 (C=O stretching of ester linkage), 1606 (N=N Schiff base), 1542 (C=C stretching of aromatic), 1219 (C–O–C asymmetric stretching), 1057 (C–O–C symmetric stretching); proton (¹H) nuclear magnetic resonance (NMR) (400 MHz, deuterated chloroform (CDCl₃)): 0.86–0.89 parts per million (ppm) (t, CH₃ of aliphatic chain), 1.26–1.84 ppm (m, CH₂ of aliphatic chain),

Figure 4. Carbon-13 NMR spectra of compounds (a) A₈, (b) A₁₆, (c) B₈ and (d) B₁₆ (continued on next page)

Figure 4. Continued

4.05–4.08 ppm (t, OCH_2 attached with naphthalene ring), 7.10–8.72 ppm (m, phenyl multiplet), 11.25 ppm (s, OH proton of phenyl); *carbon-13* (^{13}C) NMR (deuterated chloroform): 14.13 ppm (CH_3 of aliphatic chain), 22.63–33.85 ppm (CH_2 of aliphatic chain), 68.23 ppm (OCH_2 carbon of alkoxy attached with naphthalene ring), 165.34 ppm (C=O of ester linkage); *mass (gas chromatography–mass spectrometry (GC-MS))*: MS positive electrospray (ES+) m/z (relative intensity %): 531.04 ($\text{M} + 2$) $^+$ m/z .

2.4 Data: compound B₁₆ (3-hydroxy-4-((4-nitrophenyl) diazenyl)phenyl 6-hexadecyloxy-2-naphthoate (series B))

Molecular formula: $\text{C}_{39}\text{H}_{47}\text{O}_3\text{N}_3$; *yield*: 78%; *clearing point*: 212°C; *UV* (chloroform) λ_{max} : 254 nm; *elemental analysis data*: found: carbon: 71.91%, hydrogen: 7.08%, nitrogen: 6.15%; calculated: carbon: 71.64%, hydrogen: 7.25%, nitrogen: 6.43%; *FT-IR* (potassium bromide): ν_{max} : cm^{-1} : 3327 (O–H stretching of –OH

Figure 5. Mass spectra of compounds (a) A₈, (b) A₁₆, (c) B₈ and (d) B₁₆

group attached to aromatic ring), 3034 (C–H stretching aromatic), 2921, 2850 (C–H stretching aliphatic), 1678 (C=O stretching of ester linkage), 1608 (N=N Schiff base), 1626 (C=C stretching of aromatic), 1255 (C–O–C asymmetric stretching), 1045 (C–O–C symmetric stretching); *proton NMR* (400 MHz, deuterated chloroform): 0.85–0.89 ppm (t, CH₃ of aliphatic chain), 1.29–1.81 ppm (m, CH₂ of aliphatic chain), 4.01–4.03 ppm (t, OCH₂ attached with naphthalene ring), 7.20–8.79 ppm (m, phenyl multiplet), 11.39 ppm (s, OH proton of phenyl); *carbon-13 NMR* (deuterated chloroform): 14.13 ppm (CH₃ of aliphatic chain), 22.70–33.85 ppm (CH₂ of aliphatic chain), 68.24 ppm (OCH₂ carbon of alkoxy attached with naphthalene ring), 163.29 ppm (C=O of ester linkage); *mass (GC-MS)*: MS ES+ *m/z* (relative intensity %): 653.8 (M + 3)⁺ *m/z*.

2.5 Data: compound MC₁₈ (bis(2-((4-chlorophenyl) diazenyl)-5-(6-octadecyloxy-2-naphthoyloxy) phenoxy) copper (II) (series MC))

Molecular formula: C₈₂H₁₀₀Cl₂O₈N₄Cu; *yield*: 70%; *heating up to*: 205°C; *UV* (chloroform) λ_{max}: 254, 300 nm; *elemental analysis data*: found: carbon: 70.38%, hydrogen: 7.42%, nitrogen: 3.76%, copper: 4.30%; calculated: carbon: 70.14%, hydrogen: 7.18%, nitrogen:

3.99%, copper: 4.53%; *FT-IR* (potassium bromide): ν_{max}: cm⁻¹: 3078 (C–H stretching aromatic), 2925, 2865 (C–H stretching aliphatic), 1738 (C=O stretching of ester linkage), 1624 (N=N Schiff base), 1582 (C=C stretching of aromatic), 1211 (C–O–C asymmetric stretching), 1042 (C–O–C symmetric stretching); *proton NMR* (400 MHz, deuterated chloroform): 0.85–0.89 ppm (t, CH₃ of aliphatic chain), 1.25–1.89 ppm (m, CH₂ of aliphatic chain), 4.09–4.11 ppm (t, OCH₂ attached with naphthalene ring), 7.10–8.70 ppm (m, phenyl multiplet); *carbon-13 NMR* (deuterated chloroform): 14.25 ppm (CH₃ of aliphatic chain), 22.79–33.89 ppm (CH₂ of aliphatic chain), 68.46 ppm (OCH₂ carbon of alkoxy attached with naphthalene ring), 166.43 ppm (C=O of ester linkage); *mass (GC-MS)*: MS ES+ *m/z* (relative intensity %): 1404.14 (M + 3)⁺ *m/z*.

2.6 Data: compound MD₁₈ (bis-{4-[(5-hydroxy-3-methyl-1-*p*-tolyl-4,5-dihydro-1*H*-pyrazolyl) methyleneamino]phenyl(3-(4-*n*-heptyloxyphenyl) acrylate)copper (II) (series MD))

Molecular formula: C₈₂H₁₀₀O₁₂N₆Cu; *yield*: 66%; *heating up to*: 203°C; *UV* (chloroform) λ_{max}: 252, 304 nm; *elemental analysis*

Scheme 2. Synthetic route for the compounds MC and MD

Table 1. Transition temperature data of series A: °C

Code	R = C _n H _{2n+1} n =	Transition temperature: °C						
		Cr		Sm		N		I
A ₂	2	•	—	•	191	•	225	•
A ₃	3	•	—	•	188	•	222	•
A ₄	4	•	—	•	(185) ^a	•	220	•
A ₅	5	•	—	•	183	•	218	•
A ₆	6	•	—	•	180	•	213	•
A ₇	7	•	—	•	179	•	211	•
A ₈	8	•	93	•	177	•	209	•
A ₁₀	10	•	(91) ^a	•	164	•	195	•
A ₁₂	12	•	88	•	152	•	189	•
A ₁₄	14	•	87	•	142	•	184	•
A ₁₆	16	•	86	•	133	•	176	•
A ₁₈	18	•	80	•	118	•	173	•

^a Monotropic phase

Cr, crystalline; Sm, smectic; N, nematic; I, isotropic

• indicates the state or particular phase

Table 2. Transition temperature data of series B: °C

Code	R = C _n H _{2n+1} n =	Transition temperature: °C			
		Cr	Sm	N	I
B ₂	2	•	—	•	•
B ₃	3	•	—	•	•
B ₄	4	•	—	•	•
B ₅	5	•	—	•	•
B ₆	6	•	—	•	•
B ₇	7	•	109	•	•
B ₈	8	•	106	•	•
B ₁₀	10	•	104	•	•
B ₁₂	12	•	(103) ^a	•	•
B ₁₄	14	•	101	•	•
B ₁₆	16	•	100	•	•
B ₁₈	18	•	95	•	•

^a Monotropic phase

• indicates the state or particular phase

data: found: carbon: 69.35%, hydrogen: 7.21%, nitrogen: 5.54%, copper: 4.30%; calculated: carbon: 69.10%, hydrogen: 7.07%, nitrogen: 5.90%, copper: 4.46%; FT-IR (potassium bromide): $\nu_{\max}$: cm⁻¹: 3080 (C–H stretching aromatic), 2918, 2825 (C–H stretching aliphatic), 1753 (C=O stretching of ester linkage), 1626 (N=N Schiff base), 1584 (C=C stretching of aromatic), 1202 (C–O–C asymmetric stretching), 1038 (C–O–C symmetric stretching); proton NMR (400 MHz, deuterated chloroform): 0.85–0.88 ppm (t, CH₃ of aliphatic chain), 1.25–1.87 ppm (m, CH₂ of aliphatic chain), 4.10–4.12 ppm (t, OCH₂ attached

with naphthalene ring), 7.12–8.72 ppm (m, phenyl multiplet); carbon-13 NMR (deuterated chloroform): 14.19 ppm (CH₃ of aliphatic chain), 22.94–33.97 ppm (CH₂ of aliphatic chain), 68.45 ppm (OCH₂ carbon of alkoxy attached with naphthalene ring), 168.02 ppm (C=O of ester linkage); mass (GC-MS): MS ES+ m/z (relative intensity %): 1425.25 (M + 3)⁺ m/z .

The FT-IR, proton NMR, carbon-13 NMR and mass spectra of compounds A₈, A₁₆, B₈, B₁₆, MC₁₈ and MD₁₈ are shown in Figures 1–6.

Figure 7. (a) Transition temperature plotted against number of carbon atoms in alkoxy chain of series A; (b) transition temperature plotted against number of carbon atoms in alkoxy chain of series B

2.7 Technique

Elemental analysis (carbon, hydrogen, nitrogen) was performed using a Thermo Scientific Flash 2000 analyser (Thermo Fisher Scientific Inc., Waltham, MA, USA) at Gujarat Narmada Valley Fertilizer Company Ltd (Bharuch, India). Infrared spectra were recorded with a Thermo Scientific Nicolet iS10 FT-IR spectrophotometer (Thermo Fisher Scientific Inc.) at the Department of Chemistry, Veer Narmad South Gujarat University, in the frequency range of 4000–400 cm⁻¹ with the samples embedded in potassium bromide discs. The proton NMR and carbon-13 NMR spectra of the compounds were recorded with a Bruker Avance II 400 NMR spectrometer using deuterated chloroform as a solvent and tetramethylsilane as an internal reference at the Sophisticated Analytical Instrument Facilities (Saif), Chandigarh. The electron ionisation mass spectra of the compound were recorded with a Finnigan Mat-8230 mass spectrometer (Bremen, Germany) also at Saif, Chandigarh. A Merck 60 F524 thin-layer plate (Merck (India) Pvt. Ltd., Mumbai, India) was used for thin-layer chromatography (TLC) and examined under short-wave UV light. The UV–visible spectra of a 10⁻⁵ M solution of the samples using chloroform as the solvent were recorded with a Thermo Scientific Evolution 300 UV–visible spectrometer (Thermo Fisher Scientific Inc.) in the range of 200–800 nm. Thermal analyses and differential scanning calorimetry (DSC) of the LC compounds were carried out at Mettler Toledo India Pvt. Ltd., Powai, Mumbai. DSC analysis was performed using a Mettler Toledo DSC-1 instrument (Geneva, Switzerland) at a heating rate of 10°C/min in a nitrogen (N₂) atmosphere. Some of the DSC samples were analysed at the Sophisticated Instrumentation Centre for Applied Research and Testing, Vallabh Vidyanagar, on a PerkinElmer DSC analyser (PerkinElmer (India) Pvt. Ltd., Thane (West), India). Optical microscopy studies were carried out with a Nikon Eclipse 50i Pol microscope (Japan) equipped with a Linkam Analysa-LTS 420 hot stage (London, UK) at the Department of Chemistry, Veer Narmad South Gujarat University. The textures of the compounds were observed using polarised light with crossed polariser with the sample in a thin film sandwiched between a glass slide and a coverslip.

3. Results and discussion

In the present study, 12 homologues from each of the two (ligand) series 4-((4-chlorophenyl)diazanyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate (series A) and 3-hydroxy-4-((4-nitrophenyl)diazanyl)

phenyl 6-hexadecyloxy-2-naphthoate (series B) were synthesised as per the synthetic route given in Scheme 1. The authors also synthesised seven metallomesogens from each of the two complex series bis(2-((4-chlorophenyl)diazanyl)-5-(6-alkoxy-2-naphthoyloxy)phenoxy) copper (II) (series MC) and bis(2-((4-nitrophenyl)diazanyl)-5-(6-alkoxy-2-naphthoyloxy)phenoxy) copper (II) (series MD) as per the synthetic route given in Scheme 2.

These compounds were subjected to elemental analysis. The elemental analysis data agreed with the composition of the expected structure. The metal, copper, was estimated gravimetrically as copper (II) oxide (CuO). Each compound was subjected to TLC (Merck Kiesel gel 60 F254 pre-coated plates). It shows one spot, indicating a single compound. All the compounds were purified by column chromatography on silica gel (80–120 mesh) using a mixture of ethyl acetate/petroleum ether (7:3) followed by repeated recrystallisation from ethanol.

3.1 Thermal and phase behaviour

The melting points and transition temperatures of the LC compounds of series A and series B are given in Tables 1 and 2. Optical microscopy revealed that series A compounds exhibit the enantiometric nematic phase (C₂, C₃, C₅–C₈, C₁₀, C₁₂, C₁₄, C₁₆ and C₁₈) homologues except for the C₄ compound. The C₄ homologue (C₄H₉) exhibits a monotropic nature. The smectic A phase starts from compound C₈ and persists up to the last member of the series. Compound C₁₀ exhibits a monotropic smectic A phase. The plot of transition temperature against the number of carbon atoms in the alkoxy chain (Figure 7(a)) exhibits no odd–even effect for any transition temperature. The transition temperature of smectic A phase decreased as the series was ascended. This was due to the increase in the number of –CH₂– groups in the alkoxy straight chain – that is, the dilution effect.³⁴ Similarly, the Cr–N and Sm–A–N transition temperatures also show a decreasing tendency as the series ascends.

In the case of series B, the C₂–C₁₈ (ethoxy to *n*-octadecyloxy) derivatives exhibit an enantiotropic nematic mesophase as in series A except that the C₅ and C₁₂ derivatives display a monotropic nematic phase. The smectic A mesophase starts from the C₇ derivative and persists up to the last member of the homologous series except that the C₁₂ derivative exhibits a

Table 3. Transition temperature data of series MC: °C

Code	R = C _n H _{2n+1} n =	Transition temperature: °C				
		Cr		N		I
MC ₇	7	•	—	•	230	•
MC ₈	8	•	—	•	227	•
MC ₁₀	10	•	—	•	220	•
MC ₁₂	12	•	129	•	217	•
MC ₁₄	14	•	—	•	214	•
MC ₁₆	16	•	138	•	209	•
MC ₁₈	18	•	142	•	205	•

• indicates the state or particular phase

Table 4. Transition temperature data of series MD: °C

Code	R = C _n H _{2n+1} n =	Transition temperature: °C				
		Cr		N		I
MD ₇	7	•	—	•	238	•
MD ₈	8	•	—	•	234	•
MD ₁₀	10	•	118	•	225	•
MD ₁₂	12	•	—	•	216	•
MD ₁₄	14	•	—	•	207	•
MD ₁₆	16	•	127	•	199	•
MD ₁₈	18	•	132	•	185	•

• indicates the state or particular phase

Figure 8. DSC thermograms of different compounds: (a) A₈, (b) A₁₆, (c) B₈ and (d) B₁₆ (continued on next page)

monotropic smectic A mesophase. It has been observed that the C₁₂ compound of series B was fully monotropic in nature. A similar trend in transition temperatures was observed in 4-*n*-alkylphenyl-2'-chloro-4-(6-*n*-alkyl-2-naphthoyloxy)benzoates by Coates and Gray.³⁵ The plot of transition temperature against the number of carbon atoms in the alkoxy chain (Figure 7(b)) exhibits a decreasing tendency in the Cr–N, N–I, Sm–N and Cr–Sm transition temperatures, and no odd–even effect could be seen in the transition temperature.

Series A and series B differ only in their terminal groups. Series A and B consist of –Cl and –NO₂ terminal groups, respectively,

and the alkoxy chain length of 6-alkoxy-2-naphthoic acid was varied. It has been observed that the transition temperature of series B is higher than that of series A. This may be attributed to the more polar nature of the –NO₂ group, giving series B higher stability and higher temperature than that of the less polar –Cl terminal group.

The transition temperatures of copper metallomesogens of series MC and MD are given in Tables 3 and 4. The brown paramagnetic complexes MC₁₆ and MC₁₈ were shown to have a liquid crystalline structure. The complex MC₁₆ (R = –C₁₆H₃₃) showed a transition to a liquid crystalline phase at temperatures in

Figure 8. Continued

the range of 138–139°C. It exhibits the schlieren texture of the nematic phase. The MC₁₈ (R = –C₁₈H₃₇) analogue showed a parallel behaviour. Similarly, MD₁₆ and MD₁₈ (R = –C₁₆H₃₃ and –C₁₈H₃₇), both paramagnetic complexes, showed transition to a LC phase at 127 and 132°C, respectively, showing the threaded texture of the nematic phase.

The DSC thermograms of series A and series B compounds A₈ and B₈ (R = –C₈H₁₇) and A₁₆ and B₁₆ (R = –C₁₆H₃₃) are shown

in Figures 8(a)–8(d). The thermograms of compounds A₈ and A₁₆ show three phase transition peaks at 93.05, 177.15 and 209.66 and 86.14, 133.46 and 176.33°C, respectively. Similarly, the thermograms of compounds B₈ and B₁₆ also show three phase transition peaks at 106.14, 133.45 and 214.84 and 100.92, 121.41 and 194.75°C, respectively. These temperatures were exactly equivalent to the temperature observed by polarising optical microscopy (POM) corresponding to smectic A, nematic and isotropic transition temperatures.

Table 5. Transition temperatures and DSC data of series A, B, MC and MD

Series	Code	Transition	Peak temp. (microscopic temp.): °C	ΔH : J/g	ΔS : J/(g K)
A	A ₈	Cr–Sm	93.05 (93)	9.62	0.0262
		Sm–N	177.15 (177)	11.46	0.0254
		N–I	209.06 (209)	8.33	0.0172
	A ₁₆	Cr–Sm	86.14 (86)	13.92	0.0367
		Sm–N	133.46 (133)	31.08	0.0764
		N–I	176.33 (176)	11.95	0.0265
B	B ₈	Cr–Sm	106.14 (106)	13.92	0.0367
		Sm–N	133.46 (133)	31.08	0.0764
		N–I	214.84 (215)	4.27	0.0087
	B ₁₆	Cr–Sm	100.92 (101)	3.79	0.0375
		Sm–N	121.41 (122)	11.19	0.0921
		N–I	194.75 (195)	14.31	0.0734
MC	MC ₁₈	Cr–N	141.66 (142)	12.18	0.0859
		N–I	204.57 (205)	3.51	0.0171
MD	MD ₁₈	Cr–N	131.95 (132)	4.08	0.0100
		N–I	185.20 (185)	14.88	0.0324

temp., temperature; ΔH , enthalpy; ΔS , entropy

A comparison of the transition temperatures obtained by POM and DSC thermogram data is given in Table 5. It was observed that the transition temperatures were almost the same.

The DSC thermograms of copper LC complexes MC₁₈ and MD₁₈ (R = –C₁₈H₃₇), given in Figures 9(a) and 9(b), exhibit two phase transition peaks at 141.66 and 204.57 and 131.95 and 185.2°C, respectively. It could be seen that after complex formation, the compound became more rigid and showed two transition peaks. The ligand molecules MC₁₈ and MD₁₈ showed three phase transitions. The authors observed that the isotropic phase, in the

case of a complex compound, was not found, but it forms a glassy product as observed in early studies.³⁶

The MC₁₈ and MD₁₈ (R = –C₁₈H₃₇) copper LC complexes were subjected to electron paramagnetic resonance studies. The electron spin resonance spectra for the 1:1 chloroform + toluene (C₆H₅CH₃) frozen solution gave, respectively, $g_{\parallel} = 2.09$, $g_{\perp} = 2.035$, $A_{\parallel} = 15.4$ (copper-63 (⁶³Cu)) and $A_{\perp} = 4.0$ (copper-63); $|g| = 2.08$; and $|A| = 7.8$ and $g_{\parallel} = 2.098$, $g_{\perp} = 2.035$, $A_{\parallel} = 15.5$ (copper-63) and $A_{\perp} = 4.1$ (copper-63); $|g| = 2.082$; and $|A| = 7.9$ ($A \times 10^{-3}$ C/m).

The magnetic moment (μ_{eff}), determined by the Faraday method, at room temperature of both copper (II) LC complexes was in the range of 1.78–1.82 μ_B , indicating one unpaired electron present in the complexes; no other interaction was present, and the copper (II) LC complexes were mononuclear and non-electrolytic compounds.

The texture of compounds A₈, A₁₆, B₈, B₁₆, MC₁₈ and MD₁₈ obtained from the heating/cooling of the compound in the POM is shown in Figure 10.

4. Conclusion

Two homologous series containing fused rings were synthesised and characterised. The thermal stability of series B, which contains a terminal –NO₂ group, was higher than that of series A, which contains a terminal –Cl group. Both series exhibited liquid crystalline properties. Both showed an enantiometric nematic phase, while higher homologues showed an enantiotropic smectic A phase. The copper complexes of series A and B ligands were also synthesised and showed a liquid crystalline threaded nematic phase. The copper (II) LC compounds were paramagnetic and non-electrolytic in nature.

Figure 9. DSC thermograms of metallomesogens (a) MC₁₈ and (b) MD₁₈

Figure 10. Optical texture obtained from POM on heating/cooling the compound: (a) nematic (schlieren-like) phase observed on cooling at 133°C (A_{16}), (b) smectic A phase obtained on cooling at 93°C (A_8), (c) smectic A (fan-shaped) phase exhibited on cooling at 106°C (B_8), (d) smectic A phase observed on cooling at 100°C (B_{16}), (e) nematic (schlieren-like) phase observed on cooling at 142°C (MC_{18}) and (f) nematic droplets observed on cooling at 131°C (MD_{18})

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