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# Synthesis of two naphthyl-containing homologous series of mesogenic ligands and the related metallomesogens containing Cu(II)†

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Two new naphthyl-containing homologous series of mesogenic ligands, the 4-*n*-alkoxy-2-hydroxybenzylidene-2′-naphthylamines (series I) and 4(4′-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene-2″-naphthylamines (series II), as well as the related metallomesogens of higher homologues containing a Cu(II) atom, have been synthesized. All the ligands and complexes were characterized by a combination of elemental analysis and standard spectroscopic methods. In series **I**, *n*-heptyloxy and *n*-octyloxy derivatives are non-mesogenic whereas the remaining higher members synthesized exhibit a monotropic nematic mesophase. In series II, all the members synthesized exhibit an enantiotropic nematic mesophase. All the metallomesogens of series I synthesized exhibit a monotropic smectic A mesophase, except for the *n*-octyloxy derivative, which is non-mesogenic, whereas metallomesogens of series II exhibit enantiotropic nematic mesophases up to the *n*-tetradecyloxy derivatives; the *n*-tetradecyloxy and *n*-hexadecyloxy derivatives also exhibit smectic C mesophases. All the members of series II and their metallomesogens exhibit mesophases with wide temperature ranges and greater thermal stability as compared to series I and their metallomesogens, respectively. The mesomorphic properties of both the present series and their metallomesogens are compared with each other and with other structurally related series to evaluate the effect of the naphthalene moiety on mesomorphism.

## 1. Introduction

A vast number of mesogenic naphthalene derivatives are reported in the literature [1, 2], as naphthalene derivatives exhibit rich mesomorphism if properly designed. Wiegand [3] reported several mesogenic Schiff bases of 2,6-, 1,5- and 1,4-diaminonaphthalenes. Gray and Jones [4] investigated liquid crystalline properties of different alkoxynaphthoic acids. Coates and Gray [5] synthesized 4-*n*-alkyl/alkoxy phenyl esters of 6-*n*-alkyl/alkoxy-naphthalene-2-carboxylic acids. Dave and others studied a variety of liquid crystalline naphthalene derivatives such as alkoxybenzoates of 1,5- and 1,4-dihydroxynaphthalene [6], esters of cholesterol [7] and alkoxynaphthyliedene Schiff bases [8–10], exhibiting smectic, nematic and cholesteric mesomorphism. Malthete *et al.* [11] synthesized tetraacylated 1, 4, 5, 8-teterahydroxynaphthalene derivatives, which may be looked upon as 'conjoined twin' mesogens. In the last decade, a significant number of research papers on naphthalene LC cores appeared in the literature [12–22]. The synthesis and mesomorphic properties of banana-shaped compounds derived from 2, 7-dihydroxynaphthalene have also been reported [23].

We have previously reported mesogenic homologous series of Schiff base esters containing the naphthalene moiety and studied the effect of lateral thiol [24] and methoxy [25] substituents on mesomorphism. We have also reported the synthesis of mesogenic homologous series of azomesogens without lateral substituent [26], with lateral methyl [27] and chloro [28] groups, and evaluated the effect of lateral methyl as well as chloro groups on mesomorphism. Recently, we reported a mesogenic homologous series of azoesters containing two naphthalene nuclei [29] and studied the effect of the naphthalene moiety on mesomorphism. We have also reported a mesogenic homologous series of Schiff base cinnamates [30] comprising a naphthalene moiety, and investigated the effect of an ethylene linking group (cinnamoyl linkage) and naphthalene moiety on the mesomorphic properties of such compounds.

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The purpose of this study is to continue the search for new mesogenic compounds containing a naphthalene moiety. The salicylaldimine fragment is well recognized as a good mesogen in liquid crystalline materials because the azomethine linkage is stabilized by intramolecular hydrogen bonding, and it has the ability to coordinate metals [31, 32]. The incorporation of transition metals into liquid crystals has led to the study of interesting magnetic, electronic and optical properties in mesomorphic materials [33]. A literature survey reveals that several metallomesogens containing copper atom have been prepared [34]. Thus in the present study we have synthesized two new mesogenic homologous series of salicylaldimines with the naphthalene moiety, viz. the 4-*n*-alkoxy-2-hydroxybenzylidene-2′-naphthylamines (series I) and 4(4′-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene-2″-naphthylamines (series II), as well as metallomesogens of both series of ligands containing the Cu(II) atom, and have examined the phase transition behaviour of these compounds.

## 2. Experimental

### 2.1. *Characterization*

Microanalysis of the compounds was performed on a Coleman carbon–hydrogen analyser; the values obtained are in close agreement with those calculated. IR spectra were determined via 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 an internal reference standard. The chemical shifts are quoted as $\delta$ (parts per million) downfield from the reference. $CDCl_3$ was used as a solvent for all the compounds. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with a heating stage. The enthalpies of transitions reported as $J\,g^{-1}$, were determined from thermograms obtained on a Mettler TA-4000 system, adopting a scanning rate $5°C\,min^{-1}$. The calorimeter was calibrated using pure indium as standard.

### 2.2. *Synthesis*

The synthetic route for series I compounds and their metallomesogens are illustrated in scheme 1. 4-*n*-Alkoxy-2-hydroxybenzaldehydes (**3**) were prepared by the method of Gray and Jones [35]. The six Schiff bases of series I [$\mathbf{L_1}$] were synthesized by condensing equimolar quantities of 4-*n*-alkoxy-2-hydroxybenzaldehydes and 2-aminonaphthalene in boiling ethanol. All the Schiff bases of series I were crystallized from ethanol until constant transition temperatures were obtained. The metallomesogens [$\mathbf{Cu(L_1)_2}$] of series I were synthesized by boiling double moles of series I compounds with copper acetate in ethanol. All the metallomesogens of series I were crystallized from ethanol until the constant transition temperatures were obtained. The melting points and transition temperatures of series I and their metallomesogens are recorded in table 1.

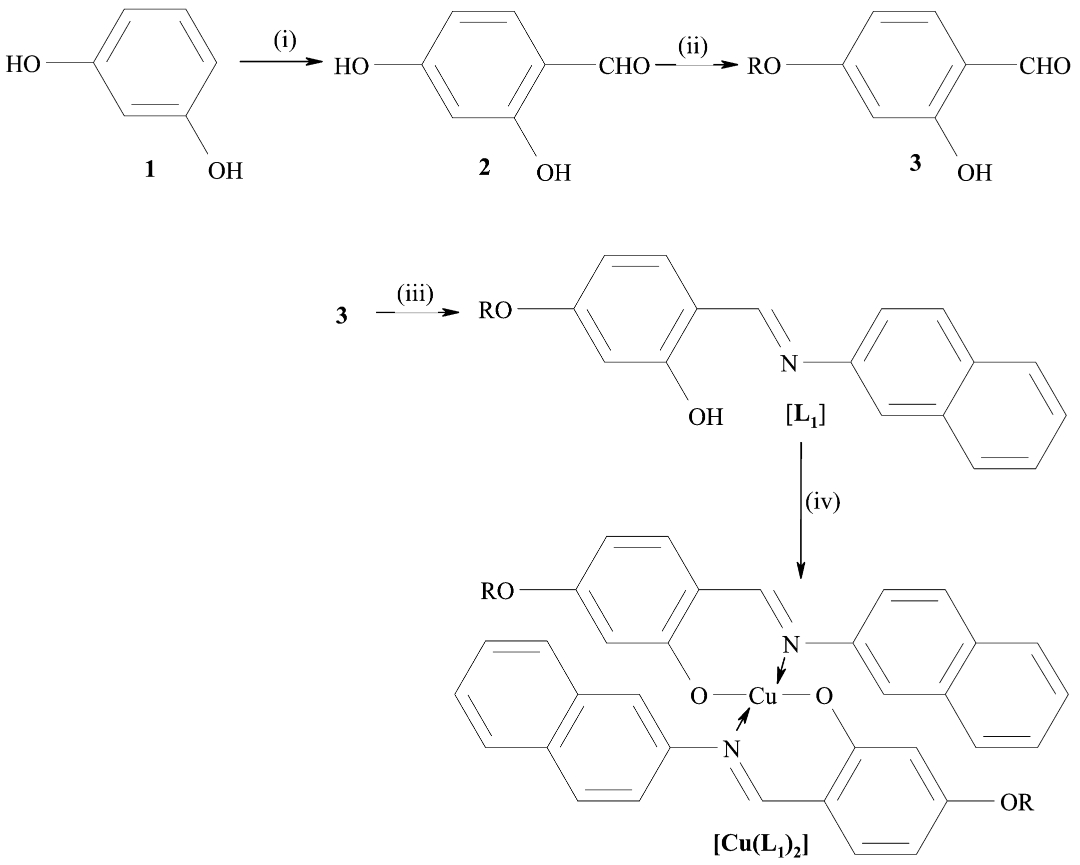
The elemental analyses of all the compounds were found to be satisfactory. The spectral data of a representative member, the *n*-tetradecyloxy derivative, of series I and its metallomesogen are given below.

$\mathbf{L_1}$: IR ($\nu_{max}$/cm$^{-1}$): 3200–3400(–OH), 3075, 2921, 2853, 2372, 1622(–C=N–), 1472, 1436, 1319, 1249, 1180, 854, 745. $^1$H NMR (300 MHz): 0.88(t, $J$=6.5 Hz, 3H, $-CH_3$), 1.27–1.56 (m, 22H, 11x–$CH_2$–), 1.76–1.85(m, 2H, Ar–O–C–$CH_2$–), 4.01(t, $J$=6.6 Hz, 2H, Ar–O–$CH_2$–), 6.48–6.52(m, 3H, ArH), 7.45–7.52(m, 3H, ArH), 7.66(s, 1H, ArH), 7.83–7.89(m, 3H, ArH), 8.66(s, 1H, –CH=N–), 13.86(s, 1H, Ar–OH). [$\mathbf{Cu(L_1)_2}$]: IR ($\nu_{max}$/cm$^{-1}$): 3058, 2937, 2858, 2370, 1614(–C=N), 1283, 1190, 855, 748, 504 (Cu–O).

The synthetic route for series II compounds and their metallomesogens are illustrated in scheme 2. 4-*n*-Alkoxybenzoic acids (**4**) and 4-*n*-alkoxybenzoyl chlorides (**5**) were synthesized by the modified method of Dave and Vora [36]. 4-*n*-Alkoxybenzoyloxy-2-hydroxy-4′-benzaldehydes (**6**) were synthesized by the method of Dave and Kurian [37]. The twelve Schiff base esters of series II [$\mathbf{L_2}$] were prepared by condensing equimolar quantities of 4-*n*-alkoxybenzoloxy-2-hydroxy-4′-benzaldehyde with 2-aminonaphthalene in boiling ethanol. All the Schiff base esters of series II were crystallized from ethanol until constant transition temperatures were obtained. The metallomesogens [$\mathbf{Cu(L_2)_2}$] of series II were synthesized by boiling double moles of series II compounds with copper acetate in ethanol. All the metallomesogens of series II were crystallized from dimethylformamide until the constant transition temperatures were obtained. The melting points and transition temperatures of series II and their metallomesogens are recorded in table 2.

The elemental analyses of all the compounds were found to be satisfactory. The spectral data of a representative member, the *n*-tetradecyloxy derivative, of series II and its metallomesogen are given below.

$\mathbf{L_2}$: IR ($\nu_{max}$/cm$^{-1}$): 3200–3400 (–OH), 3049, 2928, 2861, 2345, 1717 (–COO–), 1623 (–C=N–), 1510, 1465, 1203, 1072, 1018, 848, 759. $^1$H NMR (300 MHz): 0.88(t, $J$=6.9 Hz, 3H, $-CH_3$), 1.27–1.56(m, 22H, 11x–$CH_2$–), 1.79–1.82(m, 2H, Ar–O–C–$CH_2$–), 4.05(t, $J$=6.5 Hz, 2H, Ar–O–$CH_2$–), 6.83–7.0(m, 4H, ArH), 7.46–7.52(m, 4H, ArH), 7.71(s, 1H, ArH), 7.85–7.93(m, 3H, ArH), 8.15(d, $J$=8.8 Hz, 2H, ArH), 8.78(s, 1H, –CH=N–),



For **[L$_1$]**: R= -$C_nH_{2n+1}$; n=7, 8, 10, 12, 14 and 16; For **[Cu(L$_1$)$_2$]:** R= -$C_nH_{2n+1}$; n=8, 10, 12, 14 and 16

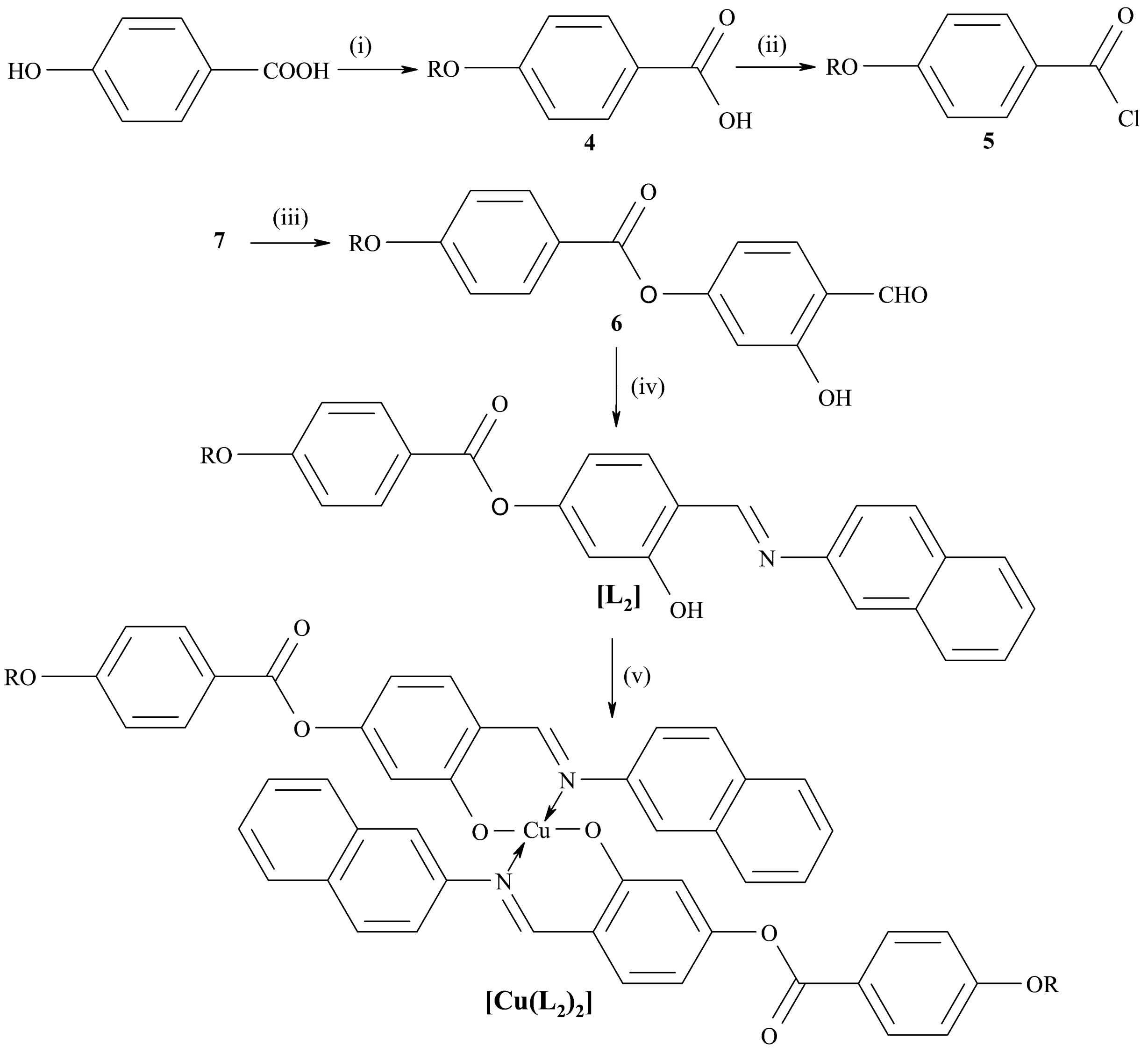
**Reagents and conditions:** (i) DMF, $POCl_3$, aq. 50%$CH_3COONa$; (ii) RBr, KOH, EtOH (iii) 2-amino naphthalene, EtOH, AcOH, reflux; (iv) $(CH_3COO)_2Cu$, EtOH, reflux

Scheme 1. Synthetic route to series I **[L$_1$]** and Cu-complexes **[Cu(L$_1$)$_2$]**.

Table 1. Transition temperatures (°C) of series compounds I and their Cu-complexes.

| Compound No. | $R=-C_nH_{2n+1}$ $n=$ | Cr | | SmA | | N | | I |
|---|---|---|---|---|---|---|---|---|
| *Series I*: **[L$_1$]** | | | | | | | | |
| **1** | 7 | • | 104 | — | — | — | | • |
| **2** | 8 | • | 97 | — | — | — | | • |
| **3** | 10 | • | 82 | — | — | (• | 80)[a] | • |
| **4** | 12 | • | 92 | — | — | (• | 81) | • |
| **5** | 14 | • | 97 | — | — | (• | 82) | • |
| **6** | 16 | • | 82 | — | — | (• | 79) | • |
| *Metallomesogens of series I*: **[Cu(L$_1$)$_2$]** | | | | | | | | |
| **7** | 8 | • | 171 | — | — | — | — | • |
| **8** | 10 | • | 164 | (• | 158)[a] | — | — | • |
| **9** | 12 | • | 167 | (• | 157) | — | — | • |
| **10** | 14 | • | 166 | (• | 153) | — | — | • |
| **11** | 16 | • | 156 | (• | 153) | — | — | • |

[a](): Indicates monotropic value.



For **[L$_2$]**: R= -C$_n$H$_{2n+1}$; n=1-8, 10, 12, 14 and 16; For **[Cu(L$_2$)$_2$]**: R= -C$_n$H$_{2n+1}$; n=8, 10, 12, 14 and 16

**Reagents and conditions:** (i) RBr, KOH, EtOH; (ii) SOCl$_2$, reflux 2h; (iii) **2** in pyridine, room temp., several hours; (iv) 2-aminonaphthalene, EtOH, AcOH, reflux; (v) (CH$_3$COO)$_2$Cu, EtOH, reflux

Scheme 2. Synthetic route to series II [L$_2$] and Cu-complexes [**Cu(L$_2$)$_2$**].

13.70(s, 1H, Ar–OH). [**Cu(L$_2$)$_2$**]: IR ($\nu_{\max}$/cm$^{-1}$): 3049, 2928, 2861, 2345, 1730 (–COO–), 1608 (–C=N–), 1512, 1472, 1218, 1075, 1014, 845, 761, 505(Cu–O).

## 3. Results and discussion

The liquid crystalline phases were observed under the polarizing microscope. Thin films of samples were obtained by sandwiching them between a glass slide and a cover slip. All the compounds of series I and their metallomesogens exhibit monotropic mesomorphism. On cooling the isotropic liquid of series I compounds, higher members ($n \geqslant 10$) showed small droplets which coalesce to a classical schlieren texture of the nematic phase, whereas their metallomesogens gave focal-conic textures characteristic of the SmA mesophase. In series II, on cooling the isotropic liquid, all the derivatives synthesized exhibited schlieren textures of the nematic

Table 2. Transition temperatures (°C) of series II compounds and their Cu-complexes.

| Compound No. | $R{=}-C_nH_{2n+1}$ $n$= | Cr | | SmC | | N | | I |
|---|---|---|---|---|---|---|---|---|
| *Series II*: $[\mathbf{L_2}]$ | | | | | | | | |
| **12** | 1 | • | 149 | — | — | • | 252 | • |
| **13** | 2 | • | 143 | — | — | • | 249 | • |
| **14** | 3 | • | 139 | — | — | • | 245 | • |
| **15** | 4 | • | 136 | — | — | • | 243 | • |
| **16** | 5 | • | 134 | — | — | • | 237 | • |
| **17** | 6 | • | 125 | — | — | • | 232 | • |
| **18** | 7 | • | 117 | — | — | • | 227 | • |
| **19** | 8 | • | 119 | — | — | • | 221 | • |
| **20** | 10 | • | 116 | — | — | • | 210 | • |
| **21** | 12 | • | 116 | — | — | • | 203 | • |
| **22** | 14 | • | 115 | — | — | • | 196 | • |
| **23** | 16 | • | 114 | — | — | • | 185 | • |
| *Metallomesogens of series II*: $[\mathbf{Cu(L_2)_2}]$ | | | | | | | | |
| **24** | 8 | • | 193 | — | — | • | 247 | • |
| **25** | 10 | • | 192 | — | — | • | 246 | • |
| **26** | 12 | • | 191 | — | — | • | 244 | • |
| **27** | 14 | • | 167 | • | 210 | • | 245 | • |
| **28** | 16 | • | 155 | • | — | — | 246 | • |

phase. On cooling the isotropic liquid of the metallomesogens of series II, the *n*-octyloxy to *n*-tetradecyloxy derivatives exhibit schlieren textures of the nematic phase, and only the *n*-tetradecyloxy derivative on further cooling exhibits the schlieren texture of the SmC mesophase. The highest homologue of the metallomesogens of series II, on cooling the isotropic liquid, showed only a schlieren texture characteristics of the SmC mesophase.

In the present study, the enthalpy changes of several derivatives of series I and II were measured by differential scanning calorimetry; data are recorded in table 3.

### 3.1. *Series I: 4-n-alkoxy-2-hydroxybenzylidene-2′-naphthylamines*

Six compounds were synthesized and their mesogenic properties evaluated. The *n*-heptyloxy and *n*-octyloxy derivatives are non-mesogenic. All the higher members ($n \geqslant 10$) exhibit a monotropic nematic mesophase, whereas the higher homologues of Cu-metallomesogens of series I exhibit a monotropic smectic A mesophase. The transition temperatures of series I and their metallomesogens are shown in table 1. A plot of transition temperature against the number of carbon atoms in the alkyl chain shows a slight increase in N to I

Table 3. DSC data for selected compounds of series I and II.

| Series | Compound No. | Transition | Peak temp./°C | $\Delta H$/J g$^{-1}$ | $\Delta S$/J g$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|
| I | **4** | (Heating Cycle) | | | |
| | | Cr–I | 91.5 | 113.10 | 0.3103 |
| | | (Cooling Cycle) | | | |
| | | I–N | 80.7 | 1.80 | 0.0050 |
| | | N–Cr | 71.6 | 100.30 | 0.2910 |
| | **5** | (Heating Cycle) | | | |
| | | Cr–I | 99.5 | 79.80 | 0.2142 |
| | | (Cooling Cycle) | | | |
| | | I–N | 81.8 | 1.20 | 0.0034 |
| | | N–Cr | 66.4 | 62.00 | 0.1827 |
| II | **20** | Cr–N | 114.3 | 63.97 | 0.1665 |
| | | N–I | 208.0 | 0.99 | 0.0021 |
| | **22** | Cr–N | 114.6 | 62.33 | 0.1608 |
| | | N–I | 196.4 | 0.32 | 0.0007 |

transition temperatures, with a slight decrease for the last homologue of series I (figure 1), whereas in the homologous series of metallomesogens, the SmA to I transition temperatures decreases gradually with increasing chain length (figure 2).

### 3.2. *Series II: 4-(4′-n-alkoxybenzoyloxy)-2-hydroxybenzylidene-2″-naphthylamines*

All the members synthesized exhibit an enantiotropic nematic mesophase, whereas the metallomesogens of series II exhibit an enantiotropic nematic mesophase up to the *n*-tetradecyloxy derivative, while the *n*-tetradecyloxy and *n*-hexadecyloxy derivatives exhibit an enantiotropic smectic C mesophase. The transition temperatures of series II compounds and their metallomesogens are shown in table 2. The phase behaviour of series II is given in figure 3, which shows a gradual decrease in the N to I transition temperature, whereas in the case of series II metallomesogens, the N to I transition temperatures decrease very little with increasing chain length (figure 4). The SmC to N or I transition temperatures increase gradually.

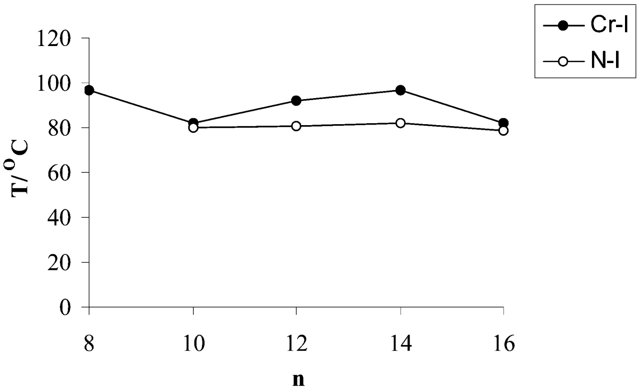


Figure 1. The phase behaviour of series I: [$L_1$].

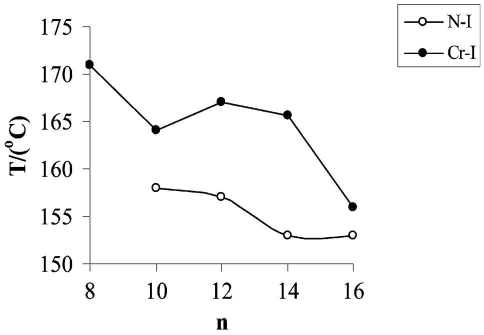


Figure 2. The phase behaviour of metallomesogens of series I: [$Cu(L_1)_2$].

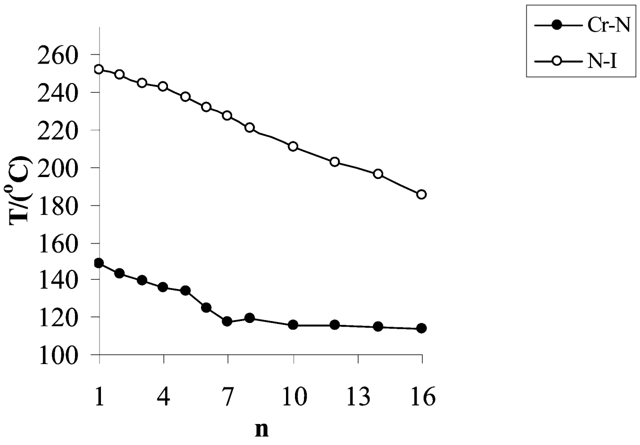


Figure 3. The phase behaviour of series II: [$L_2$].

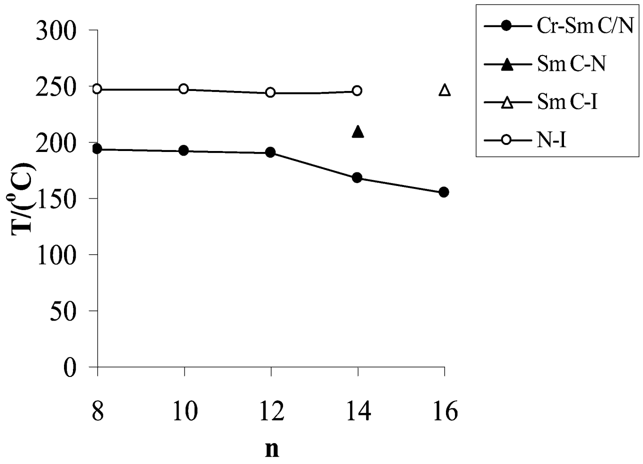
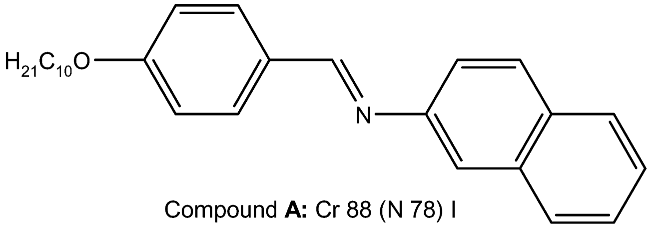


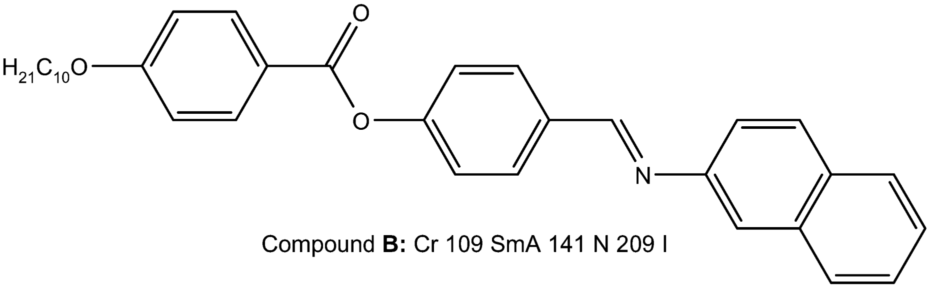
Figure 4. The phase behaviour of metallomesogens of series II: [$Cu(L_2)_2$].

### 3.3. *Compareson with structurally related compounds*

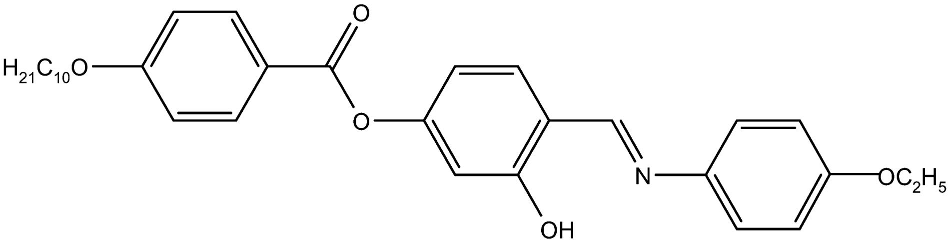
Figure 5 gives a comparison of transition temperatures and molecular structure of the structurally related known compounds **A** [24] **B** [24], **C** [34*a*] and **D** [34*a*]. Compound **3** exhibits a monotropic nematic mesophase, whereas **20** exhibits an enantiotropic nematic mesophase. Tables 1 and 2 show that the nematic mesophase length and nematic thermal stability of compound **20** are higher by 45°C and 130°C, respectively, than for **3**. The molecular structures of compounds **3** and **20** (schemes 1 and 2) show that **20** has an additional third phenyl ring and an ester central linkage. The additional phenyl ring increases the length of the molecule, and is well supported by the central linking group (–COO–), which preserves the linear shape of the molecule. This, central linking group also increases the molecular polarity of compound **20**. All these factors



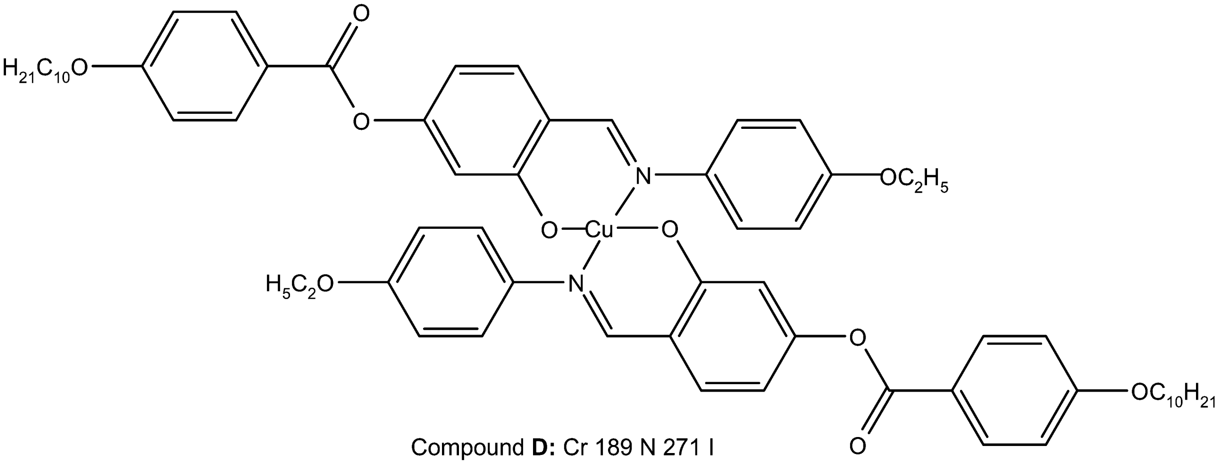
Compound **A**: Cr 88 (N 78) I



Compound **B**: Cr 109 SmA 141 N 209 I



Compound **C**: Cr 107 N 238 I



Compound **D**: Cr 189 N 271 I

Figure 5. Transition temperatures (°C) and molecular structures of compounds **A**, **B**, **C** and **D**.

are responsible for the greater mesophase length and higher thermal stability of **20** in comparison with **3**.

Reference to table 1 and figure 4 indicates that the temperature width of the nematic mesophase and thermal stability of compound **3** is higher by 6°C and 2°C, respectively, as compared with those of **A**. Molecular structure indicates that the compounds **3** and **A** differ only at the *ortho*-position of the azomethine linkage at the aldehyde moiety. Compound **3** has a –OH group at the *ortho*-position to the azomethine linkage, whereas **A** has no substituent attached (i.e. –H). This is confirmed by spectral techniques. An infrared spectrum shows a –OH stretching band at 3200–3400 $cm^{-1}$ and a singlet at

13.86 in the $^1$H NMR spectrum. The effect of replacing the hydrogen by hydroxyl in the ortho-position to azomethine not only promotes intramolecular hydrogen bonding but also enhances the thermal stability of the molecule, Thus the effect induced by the increase in width due to the lateral position has been eliminated to some extent by the intermolecular attractive forces caused by the free –OH group. This is also reflected in a comparison of compounds **20** and **B**. The temperature range of the nematic mesophase and transition temperature of **20** are greater by 26°C and 1°C, respectively, as compared with those of **B**. The structure of **20** differs from that of **B** only in the lateral substituent. Compound **20** has a lateral phenolic –OH substituent *ortho* to the –CH=N–, whereas **B** has no lateral substituent. The compounds of series II may give rise to shielding effects due to intramolecular association and hence the polarizability along the long axis of molecule will be larger in such a compound than in unsubstituted analogues. This will result in slightly higher clearing temperatures and greater mesophase temperature widths than the corresponding compounds with no *ortho* hydroxyl group (i.e. compound **B**).

The data listed in tables 1 and 2 also reveal that series I and II are both purely nematogenic whereas compounds of the analogous series without a lateral phenolic substituent have greater smectogenic tendencies. It appears that the lateral hydroxyl group not only increases the breadth of the molecules of series I and II but also reduces coplanarity in the system due to steric interactions. Both these factors would tend to eliminate the smectogenic tendencies from the series I and II.

Reference to tables 1 and 2 indicates that thermal stability of the Cu-metallomesogens **8** and **25** is much higher than for the respective ligands **3** and **20**. This is understandable as the metal atom is incorporated in the ligand. These tables also indicate that series I is purely nematogenic, whereas the Cu-complexes of the same series exhibit a smectic A mesophase, which may be due to the presence of interdigitated layers of partially melted chains, and a possible coupling of copper atoms in pairs inside the layers [33*b*, 34*i*, 34*g*, 38]. Comparing the phase behaviour for series II and its Cu-complexes, it can be seen that series II is nematogenic while the Cu-complex of the higher homologue ($n \geqslant 14$) exhibits a SmC mesophase; such a change in the phase behaviour salicylaldimine based copper complexes is well reported in the literature [34*a*, 38] and the present work exemplifies the trend.

The temperature width of the nematic mesophase and transition temperature of compound **20** are lower by 37°C and 28°C as compared with compound **C**. The structure of compound **20** differs from **C** only at one terminus. Compound **C** contains an ethoxy group whereas **20** contains a naphthalene moiety, which increases the breadth of the molecule and reduces the temperature width of the nematic mesophase and transition temperature. The same effect is observed in their Cu-complexes, where the nematic mesophase length and transition temperature of compound **25** is lower by 28°C and 25°C as compared with **D**.

## 4. Conclusion

Two new naphthyl mesogenic homologous series of ligands and the related Cu-complexes have been synthesized. Both series of ligands are purely nematogenic, whereas the incorporation of a metal centre into the ligand molecule leads to more ordered Cu-complex mesophases with very high thermal stabilities. The presence of the naphthalene moiety slightly reduce the mesophase thermal stabilities, while a lateral hydroxyl group promotes intramolecular hydrogen bonding and enhances the temperature range of mesophase as well as the thermal stabilities.

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