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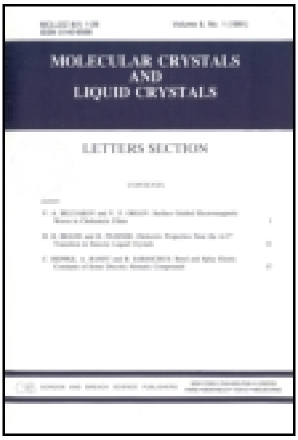

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Synthesis and Mesomorphic Properties of Uncoordinated Liquid Crystal Dimers Bis[4-[(4′-Decyloxyphenyl)Carboxylate]Salicylideneimi Alkanes and Their Copper(II) Complexes

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Synthesis and Mesomorphic Properties of Uncoordinated Liquid Crystal Dimers Bis[4-[(4′-Decyloxyphenyl)Carboxylate]Salicylideneimino] Alkanes and Their Copper(II) Complexes

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Series of symmetrical liquid crystal dimers wherein the spacer connected to two mesogenic units of salicylideneimines consists of the aliphatic chain $-(CH_2)_n-$ *where n adopts even parity numbers from 2 to 10 have been synthesized and characterized. These dimers function as tetradentate ligands which possess strong affinity toward the Cu(II) ion leading to the formation of four-coordinated complexes with Cu—N and Cu—O modes. The uncoordinated dimers exhibit enantiotropic nematic as well as smectic C phases. However, the Cu(II) complexes behave predominantly as nematogens. Correlation study between the effect of variable spacer length and the mesomophic behaviors of these dimers along with their related Cu(II) complexes are reported. The Cu(II) complexes in which the ligands possess shorter spacers were seemed to exhibit higher thermal stability.*

Keywords Cu(II) complexes; nematic; smectic C; symmetrical dimers; tetradentate ligands

1. Introduction

It has well been documented in the last few decades that the symmetrical dimers or "twins" refer to a wide array of liquid crystalline compounds in which a flexible chain formed a bridge between the two mesogenic units [1–3]. The dimers such as α,ω-bis(4-alkylanilinebenzylidine-4′-oxy)alkanes showed a rich smectic polymorphism and the formation of various smectic phases could be influenced by different flexible chain [4]. Earlier study showed that if the flexible chain is shorter, the dimer will be more rigid owing to the coupling of the two mesogenic units. However, both mesogenic units become nearly independent with the increase of the spacer length.

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It has also been established that the parity of carbon numbers in the flexible chain induced the odd–even effect [5,6]. This effect could lead to alternations in clearing temperature and associated enthalpies for the ligand as well as the metal-ligand complexes or metallomesogens. This phenomenon is interesting because the combination of the properties of metals (polarizability, color and magnetism) will result in enhanced mesomorphic behaviors which are essential for the design of new electro-optical devises [7,8].

On the other hand, various studies have established a relationship between these metal ions and their applications in different fields including the nuclear chemistry, metal ion separation, pollution control, industrial processes, hydrometallurgy, and polymer drug graft (antitumor and antibiotic agents) [9].

The Schiff bases or imines possessing *ortho*-hydroxyl (OH) group are essential for the formation of metallomesogens. The chelating abilities and analytical applications are the key factors attracting the interests of researchers in recent years [9]. Previous work has shown that the complexes containing the tetradentate ligands exhibited prominent magnetic and photochemical properties [10–13].

In the present work, a series of dimers bis[4-[(4′-decyloxyphenyl)-carboxylate] salicylideneimino]alkanes (where the alkanes are $-(CH_2)_n-$ with $n = 2, 4, 6, 8$, and 10) was designed and synthesized. A comparative study among these imines and the effect of Cu(II) ion upon the mesomorphic properties of Cu(II) complexes containing these imines has also been carried out.

The synthetic routes toward the formation of the dimers and their Cu(II) complexes are shown in Schemes 1 and 2.

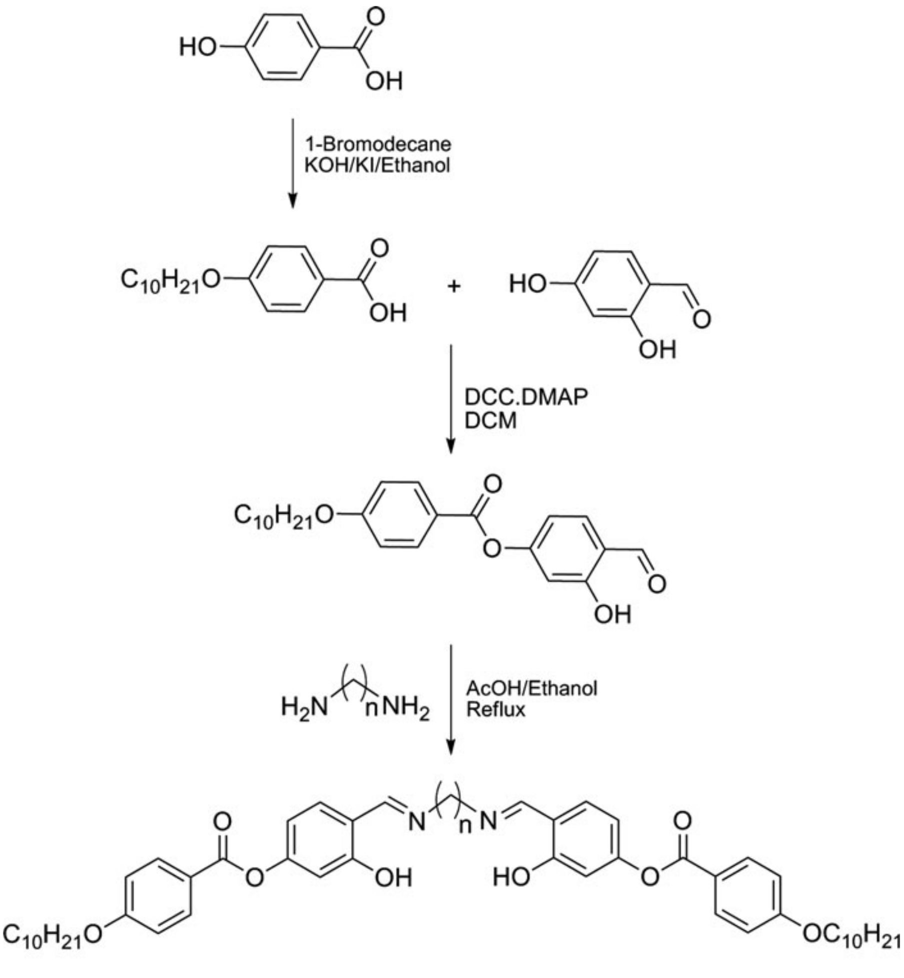
2. Experimental

2.1 Characterization

Elemental analysis was carried out with a Perkin–Elmer 240 microanalyzer. Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrometer. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded on a Bruker AM-400 spectrometer with tetramethylsilane as internal standard. Differential scanning calorimetry (DSC) was conducted on a Perkin–Elmer model DSC Pyris 1 system calibrated with indium and zinc standards. Polarizing microscopy was performed with a Euromex polarizing microscope equipped with a Linkam HFS 91 heating stage and a TP-93 temperature programmer. Small quantity of sample was sandwiched between two thin glass covers. The heating and cooling rates of $\pm 5\ ^\circ\mathrm{C\ min}^{-1}$ were applied on free imines and Cu(II) complexes.

2.2 Synthesis

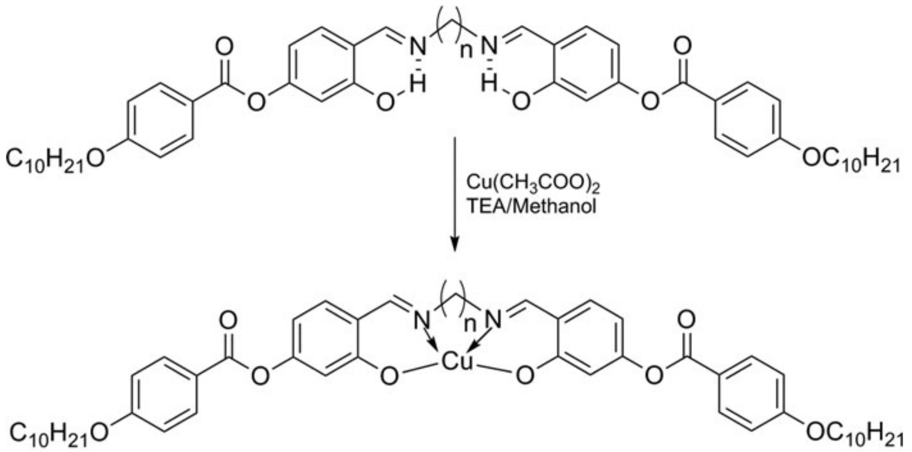
All solvents were purified and dried by standard procedures [14]. The reagents 1-decanol, α, ω-diamine, 2, 4-dihydroxybenzaldehyde, DCC, and DMAP were used as purchased from Aldrich. Other reagents (1-bromodecane, KOH and *p*-hydroxybenzoic acid) were purchased from SRL and used without purification. 1-Bromodecane was reacted with *p*-hydroxybenzoic acid to form 4, 4′-decyloxybenzoic acid by Williamson method. The acids thus obtained were reacted with 2, 4-dihydroxybenzaldehyde in the presence of DCC and DMAP to afford the desired aldehyde. The corresponding aldehyde was subsequently reacted with α, ω-diamine ($NH_2C_nH_{2n}NH_2$; $n = 2, 4, 6, 8$, and 10) leading to the formation of dimers.



Dimer	Chain length (n)
1	2
2	4
3	6
4	8
5	10

Scheme 1. Synthetic route for dimers **1–5**.

2.2.1 Synthesis of 4-decyloxybenzoic acid. 4-Hydroxybenzoic acid (6.4 g, 46 mmol) and anhydrous K_2CO_3 (19 g, 138 mmol) were dissolved in dry acetone (70 mL) and stirred for 1 h at room temperature. 1-Bromodecane (10.1 g, 46 mmol) was added dropwise to this solution followed by the addition of potassium iodide. The solution was heated to 100°C for 24 h with constant stirring. The resulting mixture was filtered and washed with acetone (3 × 20 mL). Filtrate and washing were collected and concentrated by vacuum distillation.



Complex	Chain length (n)
6	2
7	4
8	6
9	8
10	10

Scheme 2. Synthetic route for complexes **6–10**.

The mixture was poured into water (500 mL) and neutralized with 10% HCl solution. The precipitate thus obtained was filtered and recrystallized from ethanol to form desired product.

Yield 65%. M.p. 138°C. $C_{17}H_{26}O_3$: Calc. C, 73.34; H, 9.41; found C, 73.62; H, 9.29. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 2918 (C—H), 2546 (—OH of COOH), 1685 (C=O), 1256(C—O). ^{1}H-NMR ($CDCl_3$), δ/ppm: 11.02 (s, 1H, —COOH), 8.12(d, 2H, Ar—H), 6.96(d, 2H, Ar—H), 4.01(t, 2H, —OCH_2), 1.81(q, 1H, —CH_2), 1.24–1.39 (m, 14h, —CH_2), 0.93(t, 3H, —CH_3). ^{13}C-NMR ($CDCl_3$) δ/ppm: 172.2, 163.7, 132.3, 121.4, 114.18, 68.2, 31.6, 29.0, 25.8 and 22.5.

2.2.2 Synthesis of 4-formyl-3-hydroxyphenyl-4-decyloxybenzoate. A mixture of 4-decyloxybenzoic acid (5 g, 18 mmol), 2, 4-dihydroxybenzaldehyde (2.5 g, 18 mmol), DCC (2.4 g, 20 mmol) and DMAP (0.1 g, 1 mmol) were dissolved in 100 mL of dry CH_2Cl_2 and stirred at room temperature for overnight. The precipitated urea was removed by filtration and the solution was washed with 5% acetic acid followed by saturated brine solution and water. Organic layer was dried over anhydrous sodium sulphate and the solvent was removed under vacuum distillation. The residue thus obtained was purified by column chromatography using 5% methanol in chloroform as eluent.

Yield 70%. $C_{24}H_{30}O_5$: Calc. C, 72.34; H, 7.59; found C, 72.72; H, 7.44. FTIR (KBr pellet) υ_{max}/cm^{-1}: 3198 (aromatic —OH), 2938–2818 (aliphatic —CH—), 1696 (—CHO), 1727 cm^{-1} (ester —CO) and 886 (aromatic —CH). ^{1}H-NMR ($CDCl_3$), δ/ppm: 0.87 (t, 3H, —CH_3); 1.24 (m, 16H, —CH_2); 4.03 (t, 2H, —CH_2O); 6.78(s, 1H, Ar); 6.91 (d, 2H, Ar), 6.95 (d, 2H, Ar) 7.59(d, 1H, Ar); 8.11 (d, 2H, Ar); 9.87 (s,1H, —CHO); 11.53 (s, 1H, —OH) ppm. ^{13}C-NMR ($CDCl_3$) δ/ppm: 194,2, 165.6, 164.5, 163.4, 158.0, 131.9, 130.6, 121.5, 118.2, 114.2, 114.0, 112.6, 68.6, 31.1, 29.4,22.6, 14.1.

*2.2.3 Synthesis of N,N′-bis{4′-(4″-decyloxybenzoyloxy)-2′-hydroxybenzylidine}ethane-1,2-diamine (**1**).* To a hot solution of the 4-formyl-3-hydroxyphenyl-4-decyloxybenzoate (0.5 g, 1.3 mmol) in 15 mL absolute ethanol was added dropwise with a solution of 1,2-diaminoethane (0.03 g, 0.51 mmol) in 2 mL absolute ethanol. The reaction mixture was refluxed under nitrogen atmosphere for 1 h. Upon cooling, the crystalline product was separated by filtration and purified several times by recrystallization using acetone/THF (10:1) mixture. The product crystallized in yellow solids. The above synthetic procedure was applied to the other homologues and all the analytical data are summarized as follows:

1: Yields 85%. $C_{50}H_{64}N_2O_8$: Calc. C, 73.14; H, 7.86; N, 3.41; found C, 73.73; H, 7.32; N, 3.52. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2918 cm^{-1} (aromatic —OH), 2921, 2820 (aliphatic —CH), 1718 (ester —C=O), 1634 (imine C=N), and 881 (aromatic —CH). ^{1}H-NMR ($CDCl_3$), δ/ppm: 11.24 (s, 2H, —OH), 8.35 (s, 2H, —CH=N), 8.09 (d, 4H, ArH), 7.61(d, 2H, ArH), 7.21 (d, 2H, ArH), 6.95 (d, 4H, ArH), 6.78(d, 2H, ArH), 4.03 (t, 4H, —CH_2O), 3.54 (t, 4H,=NCH_2), 1.24–1.80 (m, 32H, —CH_2), 0.85(t, 6H, —CH_3). ^{13}C-NMR ($CDCl_3$) δ/ppm: 165.3, 164.0, 160.9, 157.1, 154.8, 129.6, 121.7, 114.1, 110.5, 68.8, 60.4, 55.9, 31.0, 29.7, 26.0, 22.7, 14.2.

2: Yield 79%; $C_{52}H_{68}N_2O_8$: Calc. C, 73.55; H, 8.07; N, 3.30; found C, 73.58; H, 8.01; N, 3.29. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2918 (aromatic —OH), 2921, 2820 (aliphatic —CH), 1724 (ester —C=O), 1634 (imine C=N), and 881 (aromatic —CH). ^{1}H-NMR ($CDCl_3$), δ/ppm: 11.24 (s, 2H, —OH), 8.35 (s, 2H, —CH=N), 8.07 (d, 4H, ArH), 7.61 (d, 2H, ArH), 7.22 (d, 2H, ArH), 6.94 (d, 4H, ArH), 6.79(d, 2H, ArH), 4.03 (t, 4H, —CH_2O), 3.54 (t, 4H,=NCH_2), 1.24–1.99 (m, 36H, —CH_2), 0.85 (t, 6H, —CH_3). ^{13}C-NMR ($CDCl_3$) δ/ppm: 165.3, 164.1, 160.8, 157.0, 154.8, 129.4, 121.7, 114.1, 110.8, 68.8, 60.4, 55.9, 31.0, 29.7, 26.0, 22.7, 14.2.

3: Yield 76%; $C_{54}H_{72}N_2O_8$: Calc. C, 73.94; H, 8.27; N, 3.19; found C, 73.67; H, 8.54; N, 3.11. ^{1}H-NMR ($CDCl_3$), δ/ppm: 2919 (aromatic —;OH), 2920, 2818 (aliphatic —CH), 1719 (ester —C=O), 1632 (imine C=N), and 881 (aromatic —CH). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 11.24 (s, 2H, —OH), 8.33 (s, 2H, —CH=N), 8.04 (d, 4H, ArH), 7.61 (d, 2H, ArH), 7.22 (d, 2H, ArH), 6.96 (d, 4H, ArH), 6.77(d, 2H, ArH), 4.03 (t, 4H, —CH_2O), 3.54 (t, 4H,=NCH_2), 1.24–1.99(m, 40H, —CH_2), 0.85 (t, 6H, —CH_3). ^{13}C-NMR ($CDCl_3$) δ/ppm: 165.2, 164.4, 160.6, 157.0, 154.5, 129.6, 121.7, 114.1, 110.8, 68.8, 60.4, 55.9, 31.0, 29.7, 26.0, 22.7, 14.2.

4: Yield 71%; $C_{56}H_{76}N_2O_8$: Calc. C, 74.30; H, 8.46; N, 3.09; found C, 74.56; H, 8.65; N, 3.21. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2918 (aromatic —OH), 2922, 2818 (aliphatic —CH), 1726 (ester —C=O), 1638 (imine C=N) and 882 (aromatic —CH). ^{1}H-NMR ($CDCl_3$), δ/ppm: 11.24 (s, 2H, —OH), 8.35 (s, 2H, —CH=N), 8.08 (d, 4H, ArH), 7.62(d, 2H, ArH), 7.26 (d, 2H, ArH), 6.96 (d, 4H, ArH), 6.77(d, 2H, ArH), 4.03 (t, 4H, —CH_2O), 3.54 (t, 4H,=NCH_2), 1.24–1.99 (m, 44H, —CH_2), 0.85 (t, 6H, —CH_3). ^{13}C-NMR ($CDCl_3$) δ/ppm: 165.5, 164.2, 160.6, 157.0, 154.0, 129.4, 121.6, 114.1, 110.8, 68.8, 60.4, 55.9, 31.0, 29.7, 26.0, 22.7, 14.2.

5: Yield 79; $C_{58}H_{80}N_2O_8$: Calc. C, 74.64; H, 8.64; N, 3.00; found C, 74.62; H, 8.55; N, 3.81. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2918 (aromatic —OH), 2921, 2819 (aliphatic —CH), 1728 (ester —C=O), 1636 (imine C=N), and 881 (aromatic —CH). ^{1}H-NMR ($CDCl_3$), δ/ppm: 11.24 (s, 2H, —OH), 8.34 (s, 2H, —CH=N), 8.09 (d, 4H, ArH), 7.61 (d, 2H, ArH), 7.22 (d, 2H, ArH), 6.95 (d, 4H, ArH), 6.76 (d, 2H, ArH), 4.07 (t, 4H, —CH_2O), 3.54 (t,

Table 1. Phase transition temperatures (°C) and associated enthalpies [kJ.mol^{-1}] for dimers upon cooling

Dimer	Cr_1		Cr_2		SmC		N		Iso
1	●	98.6 [16.8]	●	128.3 [9.2]	●	148.0 [2.7]			●
2	●	92.4 [20.5]	●	118.1 [13.8]	●	163.0 [5.8]			●
3	●	149.2 [34.5]			●	177.8 [14.4]			●
4	●	65.3 [20.4]	●	116.7 [13.0]	●	149.0 [1.4]	●	154.5 [5.2]	●
5	●	73.2 [25.8]					●	142.2 [17.3]	●

Dimers **3** and **4** were compared with those reported by Maja Sepelj et al (2006).
Cr, Crystal; SmC, smectic C; N, nematic; Iso, isotropic.

4H, =NCH_2), 1.24–1.80 (m, 48H, —CH_2), 0.85 (t, 6H, —CH_3). ^{13}C-NMR ($CDCl_3$) δ/ppm: 165.1, 164.5, 160.7, 157.5, 154.8, 129.6, 121.5, 114.1, 110.5, 68.8, 60.4, 55.9, 31.0, 29.7, 26.0, 22.7, 14.2.

*2.2.4 Synthesis of N,N′-bis{4′-(4-decyloxybenzoyloxy)-2′-hydroxybenzylidine}ethane-1,2-diamine) copper(II) (**6**).* The Cu(II) complexes were synthesized through the reported procedure [15]. Copper acetate monohydrate (0.04 g, 0.2 mmol) was added to a hot solution of compound **1** (0.30 g, 0.2 mmol) in 30 mL ethanol. The reaction mixture was refluxed for 5 h and then cooled to room temperature. The solid, collected by filtration, was washed with water, ethanol, and recrystallized from CH_2Cl_2/MeOH to give a green microcrystalline solid. The same synthetic procedure was adopted for all homologues and their analytical data are summarized below.

6: Yield 69%. $C_{50}H_{62}CuN_2O_8$: Calc. C, 68.04; H, 7.08; N, 3.17; found C, 68.17; H, 7.13; N, 3.24. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2851 (aliphatic —CH), 1734 (ester —C=O), 1615 (imine C=N), and 547 (CuO)

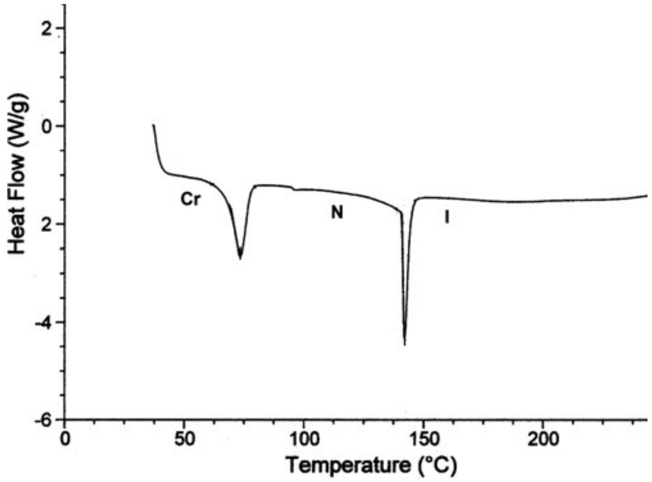


Figure 1. Representative DSC traces for dimer **5**.

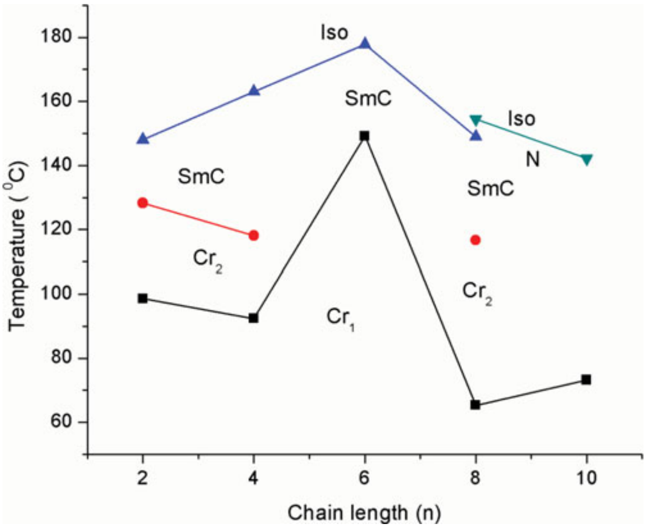


Figure 2. Correlation between transition temperature and methylene chain length for dimers **1–5**.

7: Yield 78%. $C_{52}H_{66}CuN_2O_8$: Calc. C, 68.58; H, 7.31; N, 3.08; found C, 68.46; H, 7.44; N, 3.25. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2851 (aliphatic —CH), 1732 (ester —C=O), 1616 (imine C=N), and 540 (CuO)

8: Yield 77%. $C_{54}H_{70}CuN_2O_8$: Calc. C, 69.09; H, 7.52; N, 2.98; found C, 69.12; H, 7.76; N, 2.45. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2852 (aliphatic —CH), 1734 (ester —C=O), 1616 (imine C=N), and 525 (CuO)

9: Yield 81%; $C_{56}H_{74}CuN_2O_8$; C, 69.57; H, 7.72; N, 2.90; found C, 69.88; H, 7.49; N, 2.75. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2830 (aliphatic —CH), 1727 (ester —C=O), 1616 (imine C=N), and 550 (CuO)

10: Yield 74%; $C_{58}H_{78}CuN_2O_8$: Calc. C, 70.03; H, 7.90; N, 2.82; found C, 70.15; H, 7.67; N, 2.99. FTIR (KBr pellet) υ_{max}/cm^{-1}: 2838 (aliphatic —CH), 1726 (ester —C=O), 1615 (imine C=N), and 540 (CuO).

Table 2. Phase transition temperatures (°C) and associated enthalpies (kJ.mol^{-1}) for complexes upon heating

Complex	Cr		N		Iso
6	•	106.4 [30.0]	•	197.4 [16.8]	•
7	•	152.0 [30.5]	•	254.1 [20.7]	•
8	•	145.2 [33.6]	•	190.2 [23.2]	•
9	•	139.8 [29.7]	•	179.1 [20.8]	•
10	•	123.2 [28.2]	•	166.4 [11.4]	•

Cr, Crystal; N, nematic; Iso, isotropic.

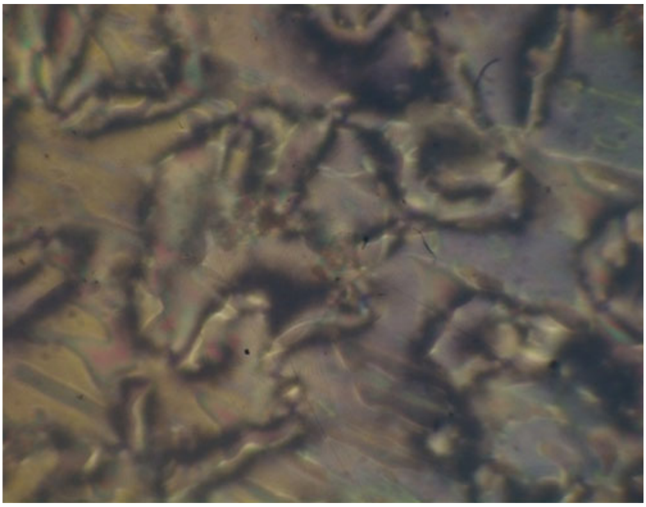


Figure 3. Photomicrograph of complex **6** at 154°C on heating.

3. Results and Discussion

3.1 Mesomorphic Behaviors

3.1.1 Uncoordinated liquid crystal dimers bis[4-[(4′-decyloxyphenyl)-carboxylate]salicylideneimino]alkanes (where the alkanes are $-(CH_2)_n-$ *in which* $n = 2, 4, 6, 8,$ *and 10),* ***1–5****.* The synthesis of symmetrical dimers **1–5** have been carried out by conventional method (Scheme 1). It is well illustrated in Scheme 1 that these dimers consist of four electron donating atoms and hence function as tetradentate ligands.

All of these dimers show various phases when temperature is varied. The measured phase transition temperature and associated enthalpy values for compounds **1–5** upon cooling are shown in Table 1. All of the compounds except compound **5** exhibit SmC

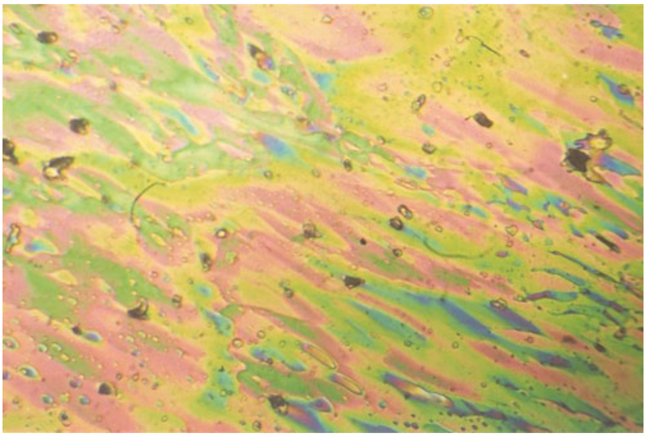


Figure 4. Photomicrograph of complex **8** at 160°C on heating.

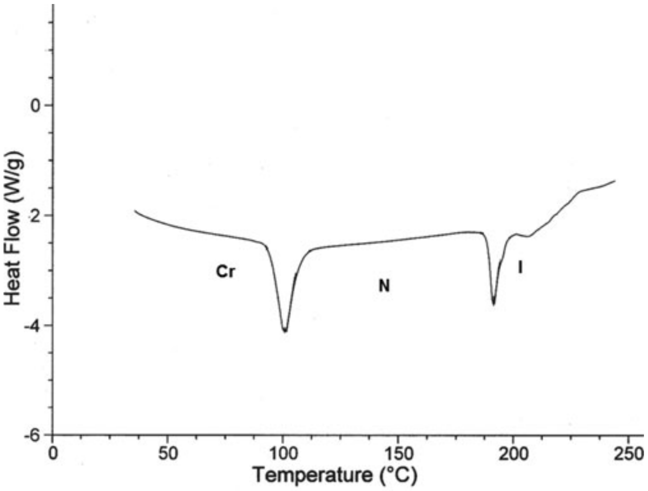


Figure 5. Representative DSC thermogram of complex **6**.

phase. It is apparent that cooling upon the homologues **1–3** from isotropic liquid led to Iso-SmC transitions at 148.0°C, 163.0°C, and 177.8°C, respectively. However, when the spacer length within this series increases from C6 to C8 as that in compound **4**, the Iso-N transition was initially observed at 154.5°C prior to the N-SmC transition at 149.5°C. The formation of the nematic phase in compound **4** can be substantiated on the basis of high mobility of threads inside the droplet with the flashes when subjected to mechanical stress. From the same cooling process, ligand **5** experiences the Iso-N transition only before crystallization at 73.2°C. A representative DSC thermogram related to compound **5** is shown in Fig. 1. The correlation between the transition temperatures and methylene chain lengths in dimers **1**–**5** is shown in Fig. 2. It can also be seen in Fig. 2 that the smectogenic properties vanished when the spacer length increased from C8 to C10 in respective compounds **4** and **5**. The $\mathrm{Cr_1}$-SmC transition temperature reaches the maximum at 149.0°C in compound **3** leading to the highest temperature of Iso-SmC transition in comparison to analogues **1** and **2**.

Previous reports have established that the presence of smectic phase particularly in symmetrical dimers could be attributed to the terminal chain length which was greater than half of the spacer length. This generalization is applicable to current compounds especially for compounds **1**–**4** and this observation concurs with that suggested by Date et al. [4].

*3.1.2 Cu(II) complexes, **6–10**.* Knowing from the earlier section that all the dimers **1**–**5** can be categorized as tetradentate ligands possessing O and N donor atoms, it gives the dimers an advantage to form the new bonds with electron deficient metal atom or ion [16].

It had been reported that the copper complexes possessing the ligand with longer terminal chain favored the formation of nematic phase but the analogues with shorter terminal chain were inclined to smectogenic behavior [17]. However, all the present complexes exhibit exclusively the phase sequence of Cr—N—Iso (Table 2). The measured phase transition temperature and associated enthalpy values for Cu(II) complexes **6–10** upon heating are shown in Table 2. The photomicrographs for complexes **6** and **8** at 154°C and 160°C are illustrated in respective Figs. 3 and 4.

A representative DSC thermogram of complex **6** is shown in Fig. 5. Comparison between the phase transition temperatures of the ligands (**1**–**5**) and their respective complexes

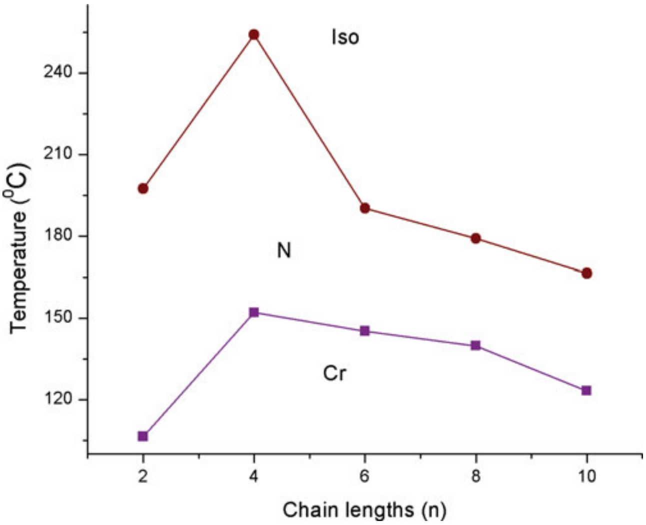


Figure 6. Correlation of transition temperature with respect to the chain length of complexes **6–10**.

(**6–10**) shows that transition temperatures of the earlier increase drastically upon complexation. However, the homologues **6–10** on heating led to Cr—N transitions at 106.4°C, 152.0°C, 145.2°C, 139.8°C, and 123.2°C, respectively.

The correlation between the transition temperatures and respective spacer lengths are summarized in Fig. 6. One of the notable features is that when the spacer length increased from C2 to C4, the mesophase range (ΔN) for complex **6** increased from 91.0°C to 102.1°C in complex **7**. However, further increase of the spacer length from C4 to C6 and C8 would lead to a decline in the thermal stability (45.0°C and 39.3°C for complexes **8** and **9**, respectively). This value was seemed to ascend when it moved from complexes **9** to **10** wherein the ΔN value increased to 43.2°C.

4. Conclusions

All the target dimers **1–5** exhibited enantiotropic mesophase. The homologous dimers **1-3** exhibit exclusively the SmC phase. While dimer **4** exhibits both N and SmC on cooling from the isotropic, the member with longest spacer **5** is predominantly nematogen. These dimers behave as tetradentate ligands coordinating to Cu ion through Cu—N and Cu—O modes. All the Cu(II) complexes containing **1–5** were nematogens. The Cu(II) complexes containing the ligands with shorter spacers (C2 and C4) exhibit higher thermal stability at the mesophase region in comparison to those with C6, C8, and C10 spacers.

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