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Synthesis, Characterization and Mesomorphic Properties of New Rod-like Thiophene Based Liquid Crystals

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*Two new mesogenic homologous series of Schiff base esters, 2-[4-(4′-n-Alkoxy benzoyloxy) benzylidenamino] 3-cyno thiophine **(Series-A)** and Schiff base cinnamates, 2-[4-(4′-n-alkoxy cinnamoyloxy) benzylidenamino] 3-cyano thiophene **(Series-B)**, comprising a thiophene moiety were synthesized. Structural elucidation was carried out using elemental analysis and spectroscopic techniques such as FT-IR, ^{1}H-NMR and ^{13}C-NMR, and mass spectrometry. The mesomorphic properties and thermal stabilities of the title compounds were studied by using differential scanning calorimetry and optical polarizing microscopy. All the derivatives are mesomorphic in nature showing the nematic phase, and the higher members of Series-A show a smectic C phase whereas Series-B exhibits only the nematic mesophase. The mesomorphic properties of the present series are compared with other structurally related compounds.*

Keywords 3-cyno thiophene; cinnamates; ester; nematic; schiff base; smectic C

1. Introduction

The field of liquid crystals (LCs) has incorporated numerous different organic systems in both low and high molecular weight materials [1–3]. Although classical thermotropic liquid crystals are commonly composed of rod-like molecules, many other types of low molecular mass compounds with unconventional molecular structures have been shown to exhibit liquid crystalline properties [4].

Many series of liquid crystalline compounds containing heterocyclic groups have been synthesized due to their potentially wide range of applications, such as in the optical, electrical, biological, and medical fields [5–9]. During the last decades a large number of mesomorphic compounds containing heterocyclic units were synthesized and evaluated [10,11]. Interest in these compounds arises because the inclusion of heteroatoms can cause

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large changes in the type of mesophase present and/or in the physical properties of the materials.

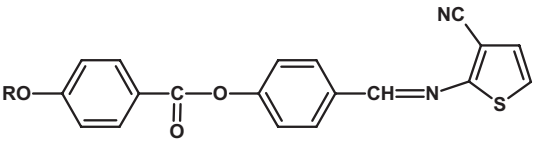
Heterocycles are of great importance as core units in thermotropic liquid crystals due to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape. These materials hold great potential for use in spatial light modulation [12], all-optical signal processing, optical information storage [13], organic thin-film transistors [14,15], fast switching ferroelectric materials [16], fluorescent probes for the detection and analysis of biomolecules etc. [17]. Thiophene in particular has emerged as a core unit that is receiving increasing attention. Sulfur-based heterocycles are also being used to elucidate the structures of complex mesophases. Thiophenes played a major role in the synthesis of systems displaying supramolecular chirality when dissolved in solvents where dissolution is not strongly favored [18]. Five-membered heterocycles have potential for flexoelectric applications such as found in bistable nematic displays. A number of thiophenes [19] have already been evaluated for such applications, and other bent heterocycles may have equal promise.

There are relatively less examples of LC materials incorporating the thiophene ring. This is despite the fact that thiophene-based LC materials (a) have lower melting points than the 1,4-phenylene analogues, (b) promote negative dielectric anisotropy, and (c) have a tendency to generate a range of different liquid crystalline phases [20–26]. Five-membered rings provide materials of low melting point and viscosity, large optical anisotropy, and fast switching times [27].

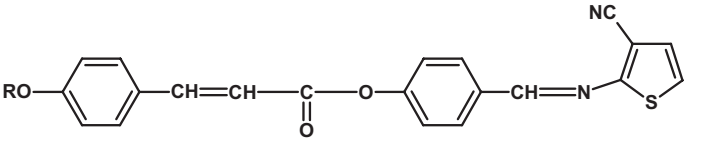
There has been a continuing interest in the study of heterocyclic-based liquid crystal compounds owing to the great variety of their structures. Thiophene-based calamitic liquid crystals are currently the subject of intensive study [28–34]. Their applications as ferroelectric materials as well as potential materials for molecular electronic devices, such as organic field effect transistors, are of special interest. Heterocyclic compounds such as five-membered thiadiazole or thiophene rings can be incorporated into the principal structure of calamitic mesogens [35–39]. Sulfur containing heterocycles are important synthetic intermediates and have found a variety of applications in medicinal, agricultural, and materials chemistry [40–41]. LCs containing heterocyclic cores, such as thiophene, are of particular interest due to their slightly bent structure, which leads to features including a reduced packing ability, a medium to strong lateral dipole and high anisotropy of the polarizability.

The mesomorphic properties of aromatic Schiff base esters arising from substituents varying in their polarities have been reported by Ha et al. [42]. Many mesogenic homologous series contain two central linkages, one of which may be ester and the other azomethine [43,44]. Vora and Rajput [45] reported binary mixtures of cinnamate ester exhibit wide rang of smectic and nematic mesophase. Previously we have reported two mesogenic homologous series of cinnamate-azomethine [46] containing thiophene and furan heterocycles. The ethylene linking group is very useful structural unit connecting one part of a rigid core with another in calamitic mesogene molecules. This fully conjugative group enhances the longitudinal polarizability and extends the molecular length maintaining linearity of the molecule. Recently, there has been a continuing interest in study the effect of an ethylene linking group and thiophene moiety on the mesomorphic properties of such molecules.

The present investigation concerns the synthesis, characterization, and mesomorphic properties of two new liquid crystalline homologous series with a common central linkage (azomethine) with a differing central linkage (cinnamate-ester) with a terminal heterocyclic moiety such as 2-amino-3-cyanothiophene.



2-[4-(4′-n-alkoxy benzoyloxy)benzylidenamino] 3-cyano thiophine (Series-A)



2-[4-(4′- n-alkoxy cinnamoyloxy)benzylidenamino] 3-cyano thiophine (Series-B).

Where, R=C_nH_{2n+1}, n=1 to 8,10,12,14,16,18.

2. Experimental Details

2.1 Materials

4-Hydroxy benzoic acid and 4-hydroxy benzaldehyde were obtained from Merck (Germany). Alkyl bromide (Lancaster, England). 2-amino 3-cyano thiophine and malonic acid were purchased from Fluka Chemie (Switzerland). N,N′-dicyclohexylcarbodiimide (DCC) were purchased from Acros Organics (USA). DMAP (*N,N*-dimethylaminopyridine) was purchased from Merck (Germany). Pyridine, piperidine, anhydrous potassium carbonate, acetone, ethanol, methanol, acetic acid, ethyl acetate, HCl, KOH, NaOH etc. were used as received. Column chromatography was performed using Acme's Silica Gel (100–200 mesh). Solvents were dried and distilled prior to use.

2.2 Measurements

The C, H, and N contents of selected mesogenic samples was estimated by G.N.F.C. (Gujarat Narmda Valley Fertilizer Company Ltd., Bharuch). Infrared spectra were recorded with a THERMO SCIENTIFIC NICOLET iSO-10 spectrophotometer in the frequency range 4000–400 cm^{-1} with samples embedded in KBr discs at our department. High resolution (400 MHz) NMR spectra of the mesogenic compounds were recorded at room temperature as 15%–20% solution in $CDCl_3$ using TMS as internal standard on a BRUKER AVANCE II 400 NMR spectrometer at SAIF (Sophisticated Analytical Instrument Facilities), Panjab University, Chandigarh. Mass spectra (TOF MS ES^+) of the compounds were recorded using Finnegan MAT-8230 Mass Spectrometer at SAIF (Sophisticated Analytical Instrument Facilities), Panjab University, Chandigarh. Thin-layer chromatography (TLC) analyses were performed using aluminium-backed silica-gel plates (Merck60 F524) and examined under shortwave UV light. Thermal (DSC) analyses of the liquid crystalline compounds were carried out from Atul Industries Ltd. P-P site Atul. DSC analyses were performed on METTELER M-3 thermo balance (Switzerland) with microprocessor TA-300 instrument at a heating rate of 10°C/min in N_2 atmosphere. The optical microscopy studies were

determined by using polarizing microscope NICON ECLIPSE 50i POL (Japan) equipped with Linkam Analysa-LTS420 hot stage (London) at our department. The textures of the compounds were observed using polarized light with crossed polarizers with the sample in a thin film sandwiched between a glass slide and cover slip.

2.3 Synthesis of Series-A and Series-B Compounds

2.3.1 4-n-alkoxy benzoic acid. Number of methods is known for alkylation of 4-hydroxy benzoic acid. However, in the present study, the method devloped by Dave and Vora [47] was followed. The clearing point of these compounds was compared with the reported one and they are almost similar to reported values [48,49].

2.3.2 4-(4′-n-alkoxy benzoyloxy) benzaldehydes. The compound has been prepared by etherification of the appropriate 4′-n-alkoxy acid (2.02 mmol) and 4-hydroxy benzaldehydes (0.246 g, 2.02 mmol), dicyclohexylcarbodiimide (0.457 g, 2.22 mmol) and dimethylaminopyridine (0.002 g, 0.2 mmol) in dry CH_2Cl_2 (20 mL) was stirred at room temperature for 24 h. The ensuing white precipitate was isolated by Buchner filtration and discarded, while the filtrate was evaporated to dryness in vacuo. The resultant crude residue was purified by column chromatography on silica gel eluting with dichloromethane, followed by repeated recrystallization from ethanol until constant transition temperatures were achieved [50–52].

2.3.3 2-[4-(4′-n-alkoxy benzoyloxy) benzylidenamino] 3-cyano thiophene. A mixture of 4-(4′-*n*-alkoxy benzoyloxy) benzaldehydes (10 mmol) and 2-amino 3-cyano thiophene (1.241g, 10 mmol) and three drops of acetic acid in absolute ethanol (10 mL) were refluxed for 4 h. The reaction mixture was allowed to cool and was stirred at room temperature overnight. The residue obtained on removal of solvent was chromatographed on silica gel (100–200 mesh) using petroleum ether (60°C–80°C) ethyl acetate mixture (80:20) as eluant. Removal of solvent from the eluant afforded a solid material, which was crystallized repeatedly from ethanol until constant transition temperatures were obtained. The purity of these compounds was checked by thin layer chromatography (Merck silica gel 60 F254 precoated plates).

Data:

A_6: Yield 82%. **Clearing Point (C.P.)** 94°C, **UV-Visible ($CHCl_3$)** λmax: 354 nm, 278 nm, Found C, 70.55; H, 6.16; N, 6.08; Calc. for $C_{29}H_{32}N_2SO_3$ (488 gm/mole); C, 70.43; H, 6.08; N, 6.08;%. **IR (KBr)** υmax cm^{-1} 3079 (C−H Str. aromatic), 2932, 2858 (C−H Str. aliphatic), 1731 (C=O Str. ester), 1641 (CH=N, Str. azomethine), 2228 (−N≡C). **^{1}H NMR** (400 MHz, $CDCl_3$): Δ/ppm 0.86–0.89 (t, CH_3), 1.25–1.84 (m, CH_2), 4.03–4.06(t, OCH_2), 6.63–8.12 (m, Ar-H), 8.54 (s, CH=N). **^{13}C NMR ($CDCl_3$):** Δ/ppm 14.15 ($\underline{C}H_3$), 23.71–31.94 ($\underline{C}H_2$) 68.04 ($O\underline{C}H_2$), 114.45–163.15 (Ar-$\underline{C}$), 159.95(−$\underline{C}$H = N), 164.41 (−$\underline{C}$=O−), 115.63 (−N≡$\underline{C}$) TOF MS ES+ m/z (rel.int%): 488.5 $(M)^+$m/z.

2.3.4 4-n-alkoxy benzaldehydes. These were synthesized by alkylation of 4-hydroxy benzaldehyde using the reported method of Vyas and Shah [53]. The clearing points of these compounds were compared with the reported one and they are almost similar to reported values.

2.3.5 4-n-alkoxy cinnamic acid. 4-*n*-alkoxy cinnamic acid were prepared by the method of Gray and Jones [54].

2.3.6 4-(4′-n-alkoxy cinnamoyloxy) benzaldehydes. The compound has been prepared by esterification of a mixture of the appropriate 4′-*n*-alkoxy acid and the appropriate 4-hydroxy benzaldehydes (0.246 g, 2.02 mmol), dicyclohexylcarbodiimide (0.457g, 2.22 mmol), dimethylaminopyridine (0.002g, 0.2 mmol) and dry CH_2Cl_2 (20 mL) was stirred at room temperature overnight. The ensuing white precipitate was isolated by Buchner filtration and discarded, while the filtrate was evaporated to dryness in vacuo. The resultant crude residue was purified by column chromatography on silica gel eluting with dichloromethane, followed by repeated recrystallization from ethanol until constant transition temperatures were achieved [50–52].

2.3.7 2-[4-(4′-n-alkoxy cinnamoyloxy) benzylidenamino] 3-cyano thiophene. A mixture of 4-(4′-n-alkoxy cinnamoyloxy) benzaldehydes (10 mmol) and 2-amino 3-cyano thiophene (1.241g, 10 mmol) and three drops of acetic acid in absolute ethanol (10 mL) was refluxed for 4 h. The reaction mixture was allowed to cool and was stirred at room temperature overnight. The residue obtained on removal of solvent was chromatographed on silica gel (100–200 mesh) using petroleum ether (60°C–80°C) ethyl acetate mixture (80:20) as eluant. Removal of solvent from the eluant afforded a solid material, which was crystallized repeatedly from ethanol until constant transition temperatures were obtained. The purity of these compounds was checked by thin layer chromatography (Merck silica gel 60 F254 precoated plates).

Data:

B_6: Yield 80%. **Clearing Point (C.P.)** 90°C, **UV-Visible ($CHCl_3$)** λmax: 322 nm, Found C, 72.44; H, 6.59; N, 5.41; Calc. for $C_{31}H_{34}N_2SO_3$ (514 gm/mol), C72.37; H, 6. 61; N, 5.44;%. **IR (KBr)** υmax cm^{-1}3096 (C−H Str. aromatic), 2970, 2884 (C−H Str. aliphatic), 1725 (C=O Str. ester), 1630 (CH=N, Str. azomethine), 2232 (−N≡C). **^{1}H NMR** (400 MHz, $CDCl_3$): Δ/ppm 0.86–0.89(t, CH_3), 1.25–1.78 (m, CH_2), 4.03–4.07 (t, OCH_2), 6.63–8.12 (m, Ar-H), 8.53 (s, CH=N). **^{13}C NMR ($CDCl_3$):** Δ/ppm 14.21 ($\underline{C}H_3$), 22.77–32.00 ($\underline{C}H_2$) 68.47 ($O\underline{C}H_2$), 114.52–163.22 (Ar-$\underline{C}$), 160.02 (−$\underline{C}$H=N), 164.48 (−$\underline{C}$=O−), 114.49, 147.21 (−$\underline{C}$H=$\underline{C}$H−), 114.70 (−N≡$\underline{C}$) TOF MS ES+ m/z (rel.int%): 514.4 $(M)^+$ m/z.

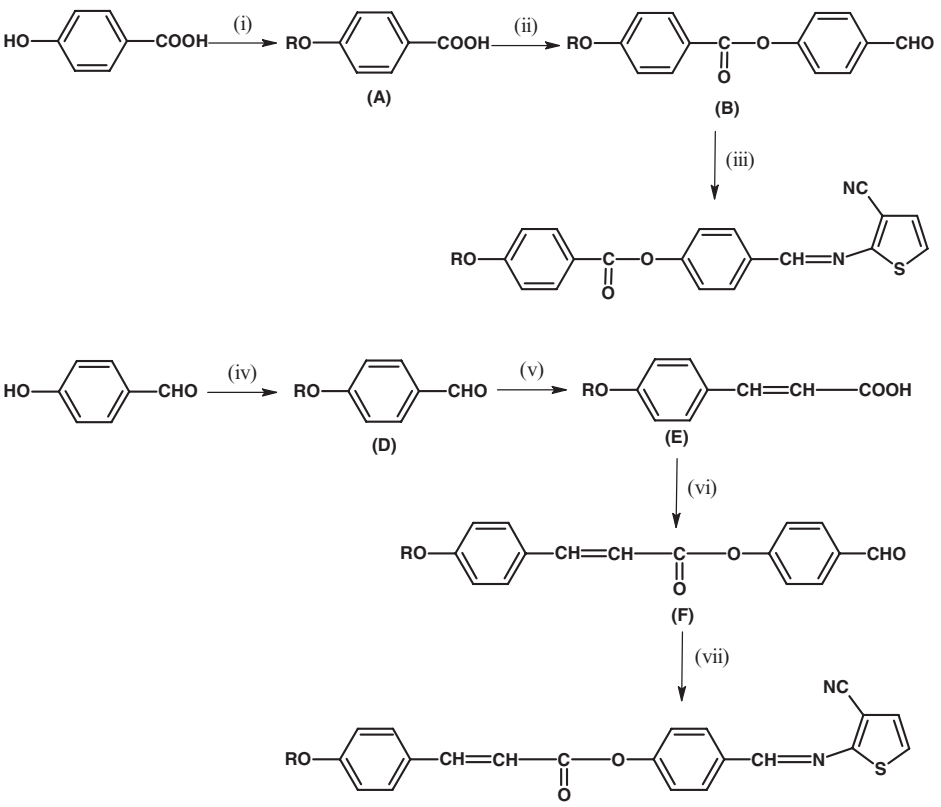
3. Results and Discussion

The synthetic route used for the preparation of Series-A and B is shown in Scheme 1. All compounds were characterised by elemental analysis, ^{1}H-NMR, ^{13}C-NMR, FT-IR spectroscopy. The mesomorphic properties of all the synthesized compounds have been investigated by differential scanning calorimetry (DSC) and polarizing optical microscope (PMO) attached with a Linkam hot stage.

3.1 The phase Behavior of Series A and B

All the thirteen members of Series-A exhibit an enantiotropic nematic phase. The SmC mesophase commences from the *n*-dodecanoyloxy derivative along with the nematic phase. The transition temperatures are recorded in Table 1 and a plot of transition temperatures against the number of carbon atoms in the alkoxy chain is given in Fig. 1. It can be noticed that the nematic-isotropic transition temperature shows a smooth falling tendency and does not exhibit an odd–even effect. It also exhibits a tendency for rising smectic-nematic transition temperatures in the ascending Series-A.

All the compounds synthesized in Series-B exhibit enantiotropic nematic phase. The transition temperatures are recorded in Table 2 and a plot of transition temperatures against



Where, R=C $_nH_{2n+1}$, n=1 to 8,10,12,14,16,18.

Scheme 1. Synthetic route to Series-A and B. Reagents and conditions: (i) R-Br, KOH, Ethanol; (ii) DCC, DMAP, CH_2Cl_2, 4-Hydroxy benzaldehyde stirred at 0°C for 1 h, stirred at room temperature for 24 h; (iii) Ethanol, 2 to 3 drop AcOH reflux for 4 h; (iv) RBr, K_2CO_3, Dry acetone; (v) Malonic acid, Piperidine reflux for 6–8 h; (vi) DCC, DMAP, CH_2Cl_2, 4-Hydroxy benzaldehyde stirred at 0°C for 1 h, stirred at room temperature for 24 h; (vii) Ethanol, 2 to 3 drop AcOH reflux for 4 h.

the number of carbon atoms in the alkoxy chain is given in Fig. 2. It can be noticed that the crystal to mesophase transition temperatures increase with the usual old-even effect for lower members. The nematic-isotropic transition temperatures also show no odd–even effect.

All the compounds of Series-A and Series-B exhibit mesomorphism. On cooling the isotropic liquid of Series-A the compounds form small droplets that coalesce to classical Schlieren textures characteristic of the nematic phase. On further cooling, higher members show the focal-conic texture characteristic of the SmC mesophase. For Series-B on cooling the isotropic liquid, all the members exhibit the Schlieren texture of the nematic phase, and no smectic mesophase is observed even in higher homologues. It is consistent with the assignment of each mesophase type using the classification system reported by Sackmann and Demus [55] and Gray and Goodby [56].

DSC is a valuable method for the detection of phase transition. It yields quantitative results; therefore, we may draw concerning the nature of the phase that occurs during the transition. The phase transition temperatures and corresponding enthalpy changes of

Table 1. Transition temperatures (°C) data of 2-[4-(4′-*n*-alkoxy benzoyloxy) benzylidenamino] 3-cyano thiophene (Series-A)

		Transition temperatures °C						
Compounds	R = *n* alkoxy	Cr		SmC		N		I
A_1	Methyl	•	–	–	126	•	165	•
A_2	Ethyl	•	–	–	118	•	162	•
A_3	Propyl	•	–	–	121	•	160	•
A_4	Butyl	•	–	–	114	•	156	•
A_5	Pentyl	•	–	–	110	•	153	•
A_6	Hexyl	•	–	–	105	•	150	•
A_7	Heptyl	•	–	–	94	•	127	•
A_8	Octyl	•	–	–	78	•	110	•
A_{10}	Decyl	•	–	–	69	•	94	•
A_{12}	Dodecyl	•	(49)*	•	72	•	91	•
A_{14}	Tetradecyl	•	47	•	74	•	88	•
A_{16}	Hexadecyl	•	52	•	67	•	86	•
A_{18}	Hexadodecyl	•	54	•	64	•	83	•

()* monotropic.

compounds A_6, A_{10}, B_6, B_{10} were determined using a DSC. The data obtained from the DSC analysis and from POM are summarized in Table 3, which helps to further confirm the mesophase type. Table 3 shows the phase transition temperatures, associated enthalpy (ΔH) and molar entropy ΔS for compounds of Series-A (A_6, A_{10}) and Series-B (B_6, B_{10}). The DSC curves of representative compounds are shown in Figs. 3–6. Microscopic transition temperature values are almost similar to DSC data. 7

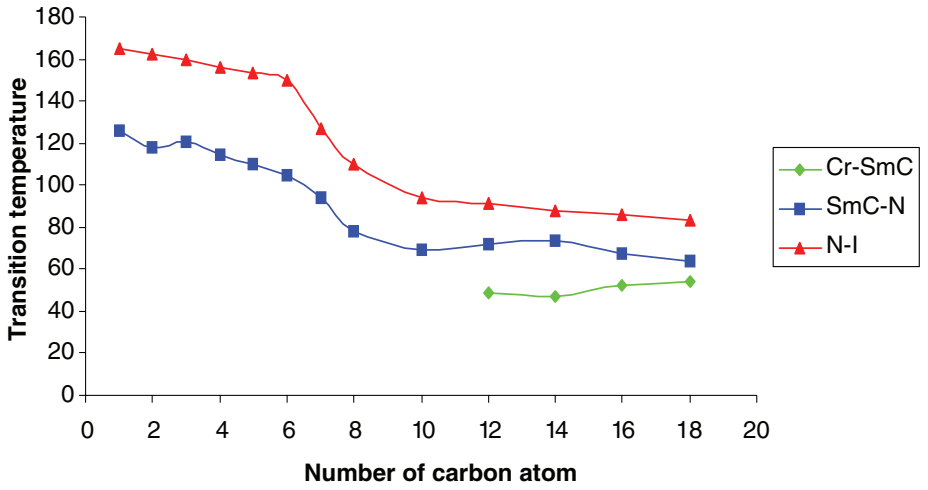


Figure 1. Transition temperature curve of Series-A.

Table 2. Transition temperatures (°C) data of 2-[4-(4′-*n*-alkoxy cinnamoyloxy) benzylidenamino] 3-cyano thiophene (Series-B)

		Transition temperatures °C						
Compounds	R = *n* alkoxy	Cr		Sm		N		I
B_1	Methyl	•	–	–	148	•	197	•
B_2	Ethyl	•	–	–	151	•	202	•
B_3	Propyl	•	–	–	154	•	191	•
B_4	Butyl	•	–	–	143	•	180	•
B_5	Pentyl	•	–	–	147	•	185	•
B_6	Hexyl	•	–	–	139	•	171	•
B_7	Heptyl	•	–	–	116	•	153	•
B_8	Octyl	•	–	–	95	•	134	•
B_{10}	Decyl	•	–	–	81	•	99	•
B_{12}	Dodecyl	•	–	–	77	•	96	•
B_{14}	Tetradecyl	•	–	–	74	•	95	•
B_{16}	Hexadecyl	•	–	–	72	•	92	•
B_{18}	Hexadodecyl	•	–	–	69	•	88	•

3.2 Mesomoxrphic Behavior

In Series-A, as the length of the carbon chain increased, an enantiotropic smectic C phase was observed from the A_{14} derivative. In fact, the smectic phase observed as monotropic on cooling for the compound A_{12}. The crystal to nematic mesophase transition temperature gradually decreased from the C_4 members. Clearing points descended with the increase in

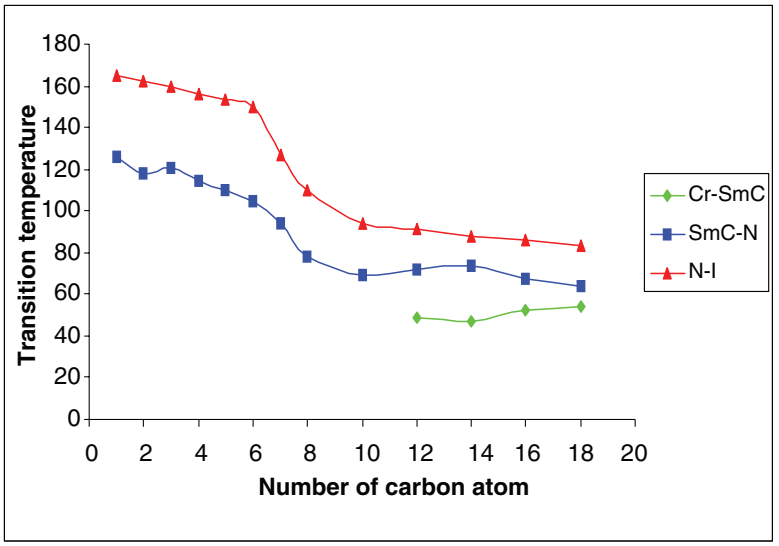


Figure 2. Transition temperature curve of Series-B.

Table 3. DSC data of the Series-C and D

Series	Compound No.	Transition	Peak/POM Temp. °C	ΔH J/g	ΔS J/g°K
A	A_6	Cr-N	104.67(105)	32.05	0.3062
		N-I	150.67(150)	11.87	0.0787
	A_{10}	Cr-N	69.31(69)	12.70	0.1832
		N-I	94.17(94)	4.93	0.0523
B	B_6	Cr-N	139.18(139)	36.29	0.2607
		N-I	170.80(171)	15.47	0.0905
	B_{10}	Cr-N	80.81(81)	10.37	0.1283
		N-I	99.29(99)	24.93	0.2510

length of the carbon chain due to the dilution of the mesogenic core resulting from the flexibility provided by the terminal alkanoyloxy chain. Generally, short-chain members favor nematic formation, whereas the smectic phase is more favorable in long-chain members [57]. This general trend was obeyed by the Series-A depicted in Figure 1 in which the nematic phase range reduced as the length of the terminal chain increased.

In Series-B, all synthesized compounds show only the nematic mesophase, the nematic transition temperature does not show the odd–even effect in the short-chain members ($n =$ 1 to 6). Then Clearing points descended with the increase in length of the carbon chain due to the dilution of the mesogenic core resulting from the flexibility provided by the terminal alkanoyloxy chain [58].

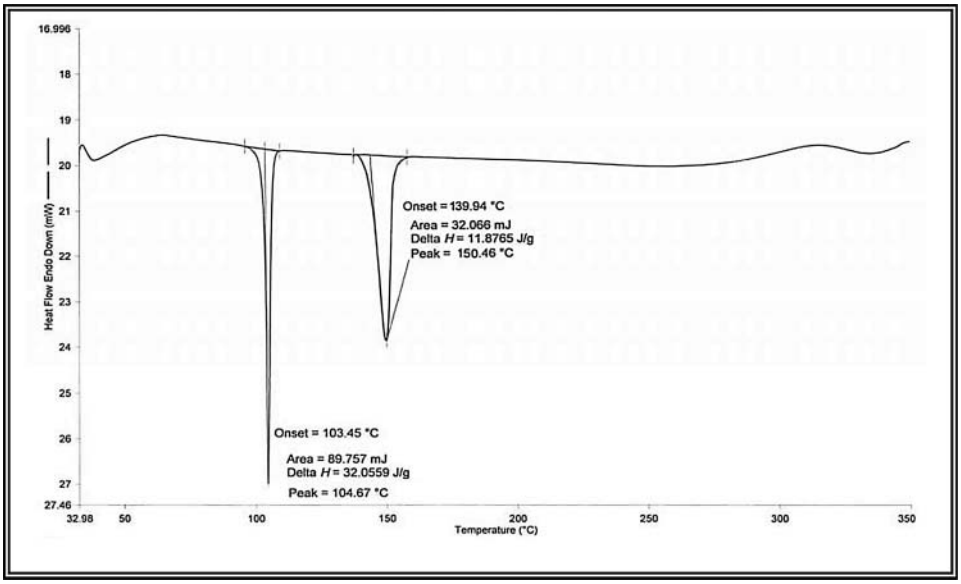


Figure 3. DSC thermogram for compound A_6 (Series-A).

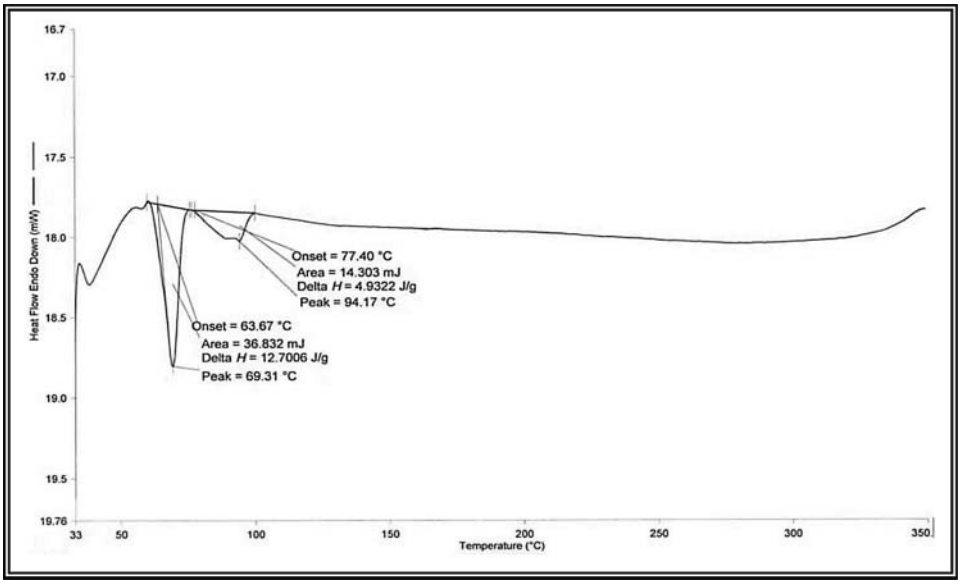


Figure 4. DSC thermogram for compound A_{10} (Series-A).

3.3 Chemical Structure-Mesomorphic Property Relationship

There is close relation between mesomorphism and molecular constitution of organic compounds. Hence, transition temperatures and mesophase range as measures of mesomorphism can be correlated with the molecular constitution of the compounds. Table 4 summarizes the average thermal stabilities, mesophase range, and comparative geometry

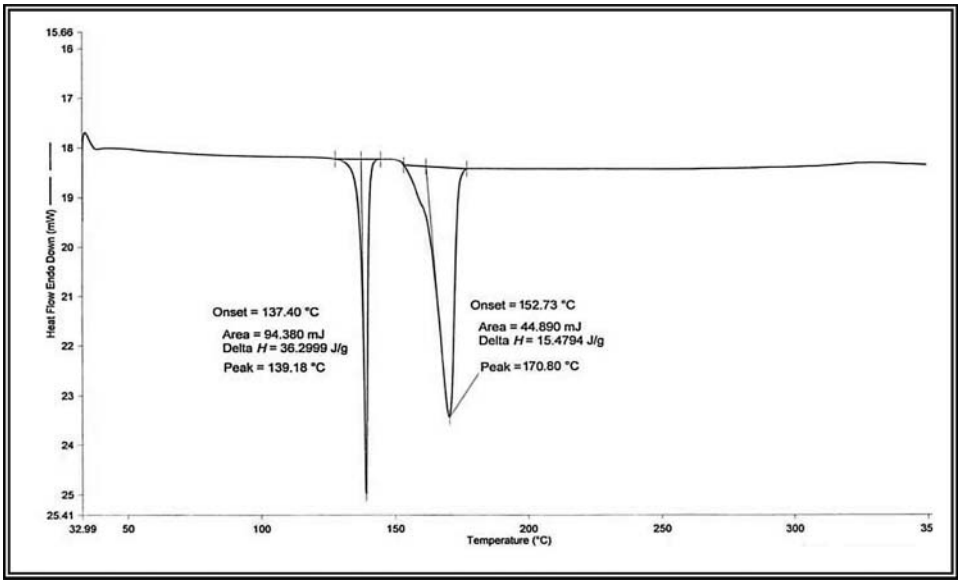


Figure 5. DSC thermogram for compound no B_6 (Series-B).

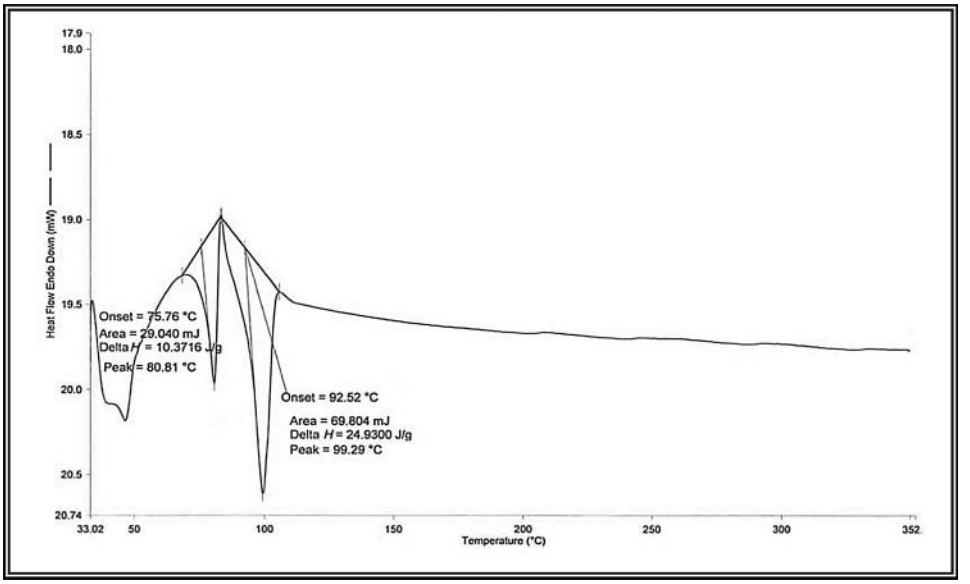


Figure 6. DSC thermogram for compound no B_{10} (Series-B).

of the present Series-A, B, and structurally related Series-I [59], II [60], III, and IV [61] reported in the literature. The average nematic mesophase range of Series-B is higher by 0.32°C and the N-I mesophase thermal stability is higher by 19.84°C compared to the respective mesophase ranges of Series-A. This is understandable, as the molecules of Series-B are longer and more polarizable compared to the molecules of Series-A due to the presence of additional cinnamoyloxy (−CH=CH−COO−) central linkage. The molecules of Series-A and B differ only at the central linkages. The molecules of Series- B have cinnamoyloxy (−CH=CH−COO−) central linkage, while Series-A have ester (−COO−) central linkage.

Gray [62] has explained that the addition of double bond in the system increases the polarizability and length of the rod-like molecules. Therefore, the greater mesophase thermal stability of the present Series-B must be explained in terms of the greater molecular

Table 4. The mesophase range and thermal stabilities of Series-A, B, and structurally related series-I to IV

	Mesophase range (°C)		Thermal stabilities (°C)		
Series	Smectic	Nematic	Sm-N	N-I	Commencement of Smectic phase
A	18.75	31.76	93.23	125.00	C_{12}
I	89.0	39.58	181.33	221.00	C_{12}
II			Nonmesogenic		
B	—	32.08	—	144.84	—
III	16.0	69.0	133.69	202.23	C_{10}
IV	—	82.28	—	212.08	—

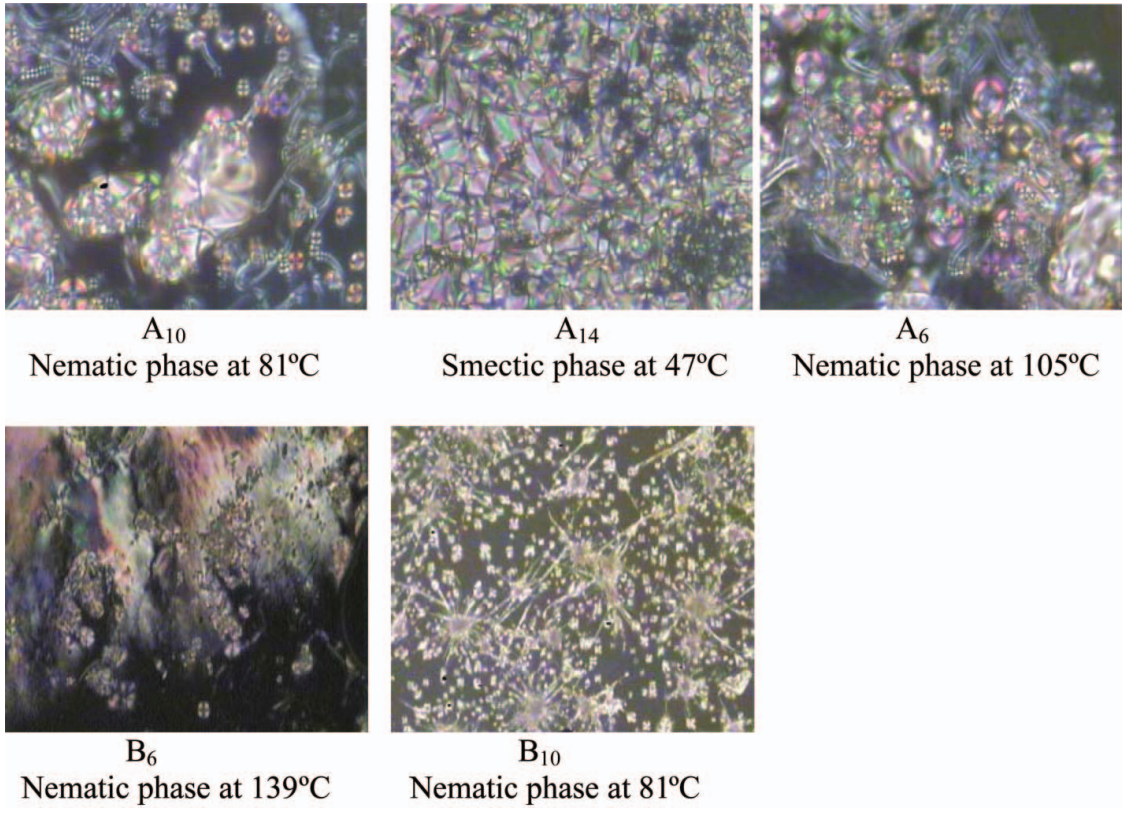
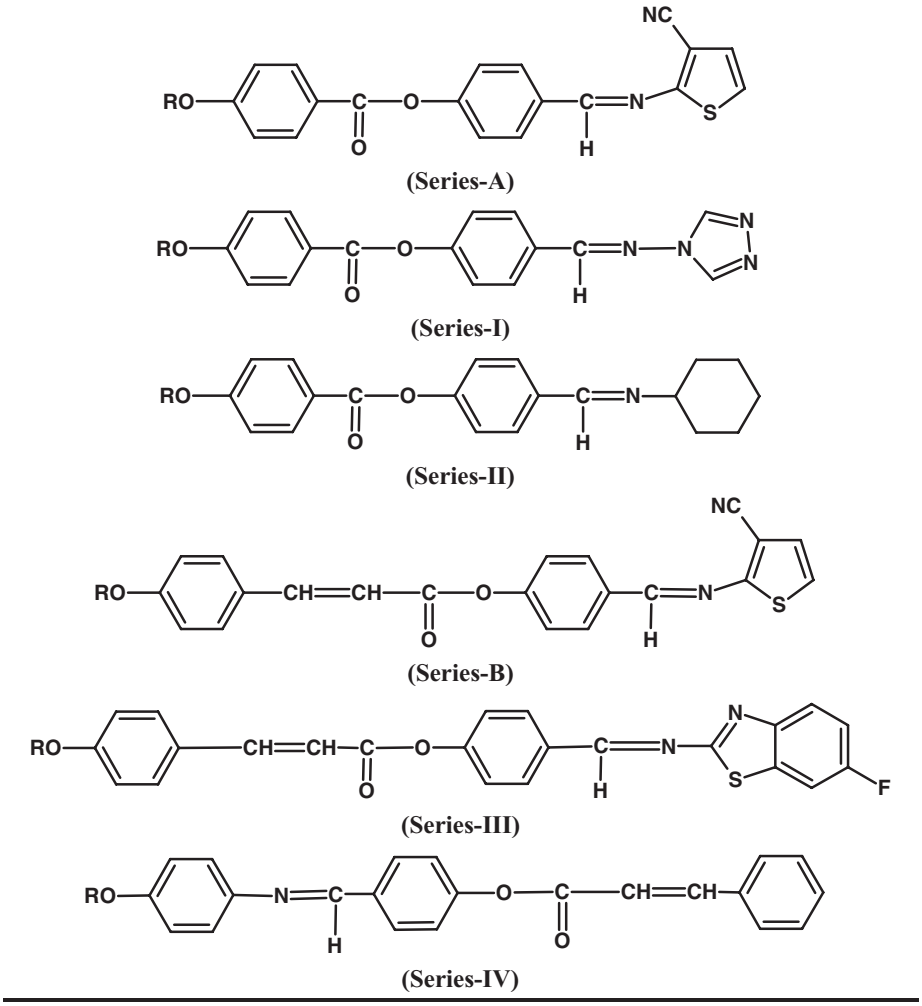


Figure 7. Micro photograph of liquid crystalline compounds.

length and polarizability of the molecule resulting from additional −CH=CH− units in the central linkage.

Series-A exhibits both smectic as well as nematic mesophases (texture of smectic and nematic phases shown in Figure-7), where as Series-B exhibits only the nematic mesophase (nematogenic). There is only one difference between Series-A and B. Series-A containing ester-azomethine central likage while Series-B having cinnamate-azomathine linkage. The ester group is more conducive for mesophase then cinnamate group. Therefore, Series-A exhibit both mesophase, i.e., smectic at higher homologus and nematic mesophase from methoxy group until the end. In case of length to breath ratio is higher, which shows nematic phase only. It can be seen that Series-B having higher length to breath ratio than Series-A. As a result of this, Series B exhibit only nematic phase (textures of compound B6 and B7 are shown in Figure 7) where as Series A exhibit both smetic as well nematic mesophase.

Comparison of Series-A with Series-I and Series-II, respectively, gives insight on the role played by the terminal ring. The structural difference between the series is one of the



terminal rings. The compounds of Series-A and Series-I are mesogenic, whereas Series-II is nonmesogenic in nature because of the presence of the cyclohexane ring.

Series-A is compared with related Series-I. All the members of Series-A exhibit an enantiotropic nematic phase. The SmC mesophase commences from the *n*-dodecyloxy derivative as a monotropic phase. *n*-Tetradecyloxy to *n*-octadecyloxy members exhibit an enantiotropic SmC phase, whereas in Series-I the *n*-dodecyloxy to *n*-hexadecyloxy derivatives exhibit the SmC phase along with an enantiotropic nematic phase. The lone pairs of electrons on the nitrogen atoms act to broaden the molecule and also introduce attractive forces, which aid smectic formation. Reference to Table 4 indicates that the nematic mesophase length and N-I phase thermal stability of Series-I are higher by 7.82°C and 96.0°C, respectively, than that of present Series-A. Both the series differ only at one terminus. Series-A has a 3-cyano thiophene ring at the terminus instead of the 1,2,4-triazole ring of Series-II. Owing to the inherent nature of thiophene, it nonlinearly reduces the efficiency of packing and thus lowers the mesophase thermal stability of members of Series-A than Series-I.

Reference to Table 4 indicates that the nematic mesophase length and N-I phase thermal stability of Series-B are lower by 36.92°C and 57.39°C, respectively, than that of present Series-III, similarly Series-B are lower by 50.2°C and 67.24°C, respectively, than that of present Series-IV. Both the series differ only at one terminus. Series-A has a 3-cyano thiophene ring at the terminus instead of the 6-fluro benzothiazole ring of Series-III and benzene ring of Series-IV. The fact that thermal stabilities of Series-III and IV are higher than that of Series-B (of present work) suggests that even though Series-B contains a five-membered thiophene ring, which normally imparts nonlinearity, the essential attracting forces are similar to one present in Series-IV benzene analogues. Oh [63] has reported that all the transition temperatures of pyridine analogues were lower compared to the benzene analogues. In the present study also shows that the thiophene derivatives have lower transition temperatures. The hetero atom has high electro negativity and, therefore, withdraws electron from the other atoms of the ring system, rendering the ring deactivated related to benzene.

4. Conclusion

In this paper, we have presented the synthesis and characterization of new mesogenic homologous series viz 2-[4-(4′-n-alkoxy benzoyloxy) benzylidenamino] 3-cyano thiophene (Series-A) which containing ester-azomethine central likage and 2-[4-(4′-n-alkoxy cinnamoyloxy) benzylidenamino] 3-cyano thiophene (Series-B), which contain a cinnamate-azomethine central linkage. Series-A with an ester-azomethine central linkage has lower thermal stabilites compared with Series-B with a cinnamate-azomethine central linkage. The ester central linkage is more conducive to conferring mesophases in the materials than the cinnamate central linkage. Series-A exhibits both smectic and nematic mesophases while Series-B exhibits only the nematic mesophase. The mesophase range of the Series-B analogues is higher than those of Series-A, which is attributed to the high polarizability of the molecules. Members of series-B with a cinnamoyloxy central linkage are more stable compared with the Series-A members containing ester-azomethine central linkage due to greater molecular length and polarizability of the molecule resulting from additional −CH=CH− units in the central linkage. Moreover, the terminal thiophene derivatives have lower transition temperatures due to high electro negative "S" atom. There is no much effect have been observed on the transition temperature by the presence of −CN group at lateral position in heterocyclic ring.

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