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New hockey stick shaped amino allylidene (–N=CH–CH=CH) based compounds: Effect of linkage group on mesomorphic properties

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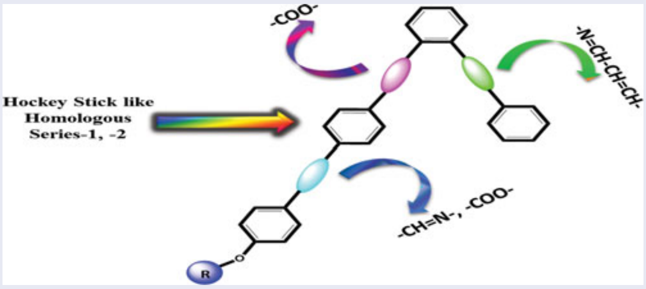
ABSTRACT

Two nonlinear hockey stick shaped homologous series based on three linking groups have been synthesized and characterized by elemental analyses and spectroscopic techniques. The mesomorphic properties of these compounds were observed by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). In this present investigation, we have synthesized two homologous series viz. 2-((3-phenyl allylidene) amino) phenyl 4-((4-n-alkoxy benzylidene) amino) benzoate (series-1) and 4-((2-((3-phenyl allylidene) amino) phenoxy) carbonyl) phenyl-4-n-alkoxy benzoate (series-2). Both the series are differing with respect to first linking group. In series-1, comp.C_4–C_{18} shows nematic as well as smectic phase while in series-2, comp.C_{10}–C_{16} shows smectic and nematic phase while comp.C_4–C_{18} shows only nematic phase.

KEYWORDS
Hockey-stick; liquid crystals; nematic; smectic

GRAPHICAL ABSTRACT



1. Introduction

The design of novel thermotropic liquid crystals as advanced functional materials involves suitable selection of a core fragment, linking group, and terminal functionality. However, anisometric rodlike or disk-like shaped molecules used to be a fundamental prerequisite for conventional thermotropic liquid crystal formation, because steric packing considerations play an important role in this interesting state of soft matter [1–2].

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A large number of bent-core or banana-shaped mesogens have been synthesized to examine their mesophase structures [3–4]. Afterwards, several groups reported the synthesis of new liquid crystal compounds with various molecular shapes like T, H, and W [5–6]. In the last period, a special kind of nonsymmetrical bent-shaped liquid crystal of hockey stick form was developed and these compounds are considered at the borderline between bent-core and rodlike mesogens [7]. A helical chiral smectic A phase undergoing a first order transition to a ferroelectric smectic C phase was observed for a hockey stick molecule of a four phenyl ring system having an ester of chiral 2-octanol pointing to the lateral side group direction [8].

Samulski et al. studied the structural variations on a series of all aromatic liquid crystals derived from p-quinquephenyl, including hockey stick and boomerang shaped liquid crystals [9]. Choi and his groups reported asymmetric bent-core liquid crystals with 1,6-napthalene central unit to form B_2 mesophase [10]. Sedative's group reported that asymmetric banana-shaped molecules with a strongly polar terminal cyano/nitro group showed a polar biaxial smectic A phase [11]. Gallardo et al. reported unsymmetrical luminescent hockey stick shaped compounds and studied their LCs properties [12]. Subsequently, Dhara and his coworkers studied the measurement of birefringence, dielectric constant, splay, bend elastic constant, and rotational viscosity in the nematic phase (N) of a hockey stick shaped compound exhibiting smectic A and anticlinic smectic C phase [13]. Scutaru reported the hockey stick shaped liquid crystals based on a 2,5-asymmetric disubstituted [1,3,4] oxadiazole core [14]. Seltmann et al. reported low temperature enantiotropic nematic phase from V-shaped molecules [15]. Afterward, Yoshizawa reported synthesis and physical properties of T-shaped chiral liquid crystal oligomers having terminal cyano (−CN) groups [16]. Stannarius and other groups studied the several unusual behaviors in the LC phase formed by hockey stick molecules. An anticlinic structure is confirmed for a lower temperature smectic C phase on free standing films of hockey stick molecules consisting of schiff base and cinnamate or benzoate linkage groups [17]. Yu et al. reported enantiotropic anticlinic smectic C (SmCa), smectic C (SmC), smectic A (SmA), and nematic (N) phases of hockey stick shaped molecules [18]. Sadashiva and his groups synthesized a series of five ring compounds composed of hockey stick shaped molecules and studied their mesomorphic properties. They have reported all the synthesized compounds display anticlinic smectic C phase [19]. Furthermore, Svoboda et al. reported hockey stick mesogens and identified nematic, synclinic, and anticlinic smectic C phase [20]. Prasad et al. reported azo based hockey stick shaped compounds and studied the effect of different types of linkages and their direction of linking on the mesomorphic properties [21]. Consequently, Das et al. reported hockey stick shaped compounds with lateral methyl group showing nematic, synclinic, and anticlinic smectic C phases [22]. Clark et al. reported chiral random grain boundary phase of achiral hockey stick liquid crystals [23]. Recently, Jasinski et al. reported a series of hockey stick shaped 6-oxoverdazyl radicals containing $-CF_3$ and −CN group to exhibited nematic phase [24].

In this work, we present the synthesis of unsymmetrical hockey stick shape type two homologous series-1 and series-2 along with their mesomorphic properties. The structure of final target compounds of series-1 and series-2 is shown in below Fig. 1.

2. Experimental

2.1. General

For the synthesis of target compounds in homologous series-1 and series-2, the following materials were used: 4-hydroxy benzoic acid, 4-hydroxy benzaldehyde were purchased from

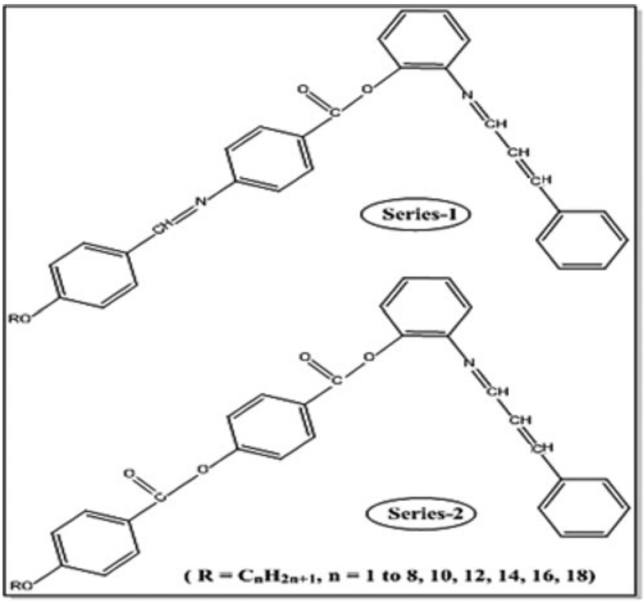


Figure 1. Chemical structure of final synthesized series-1 and series-2.

SRL (Mumbai), alkyl halides were purchased from Lancaster (England), 4-amino benzoic acid was purchased from Sigma Aldrich, anhydrous K_2CO_3, KOH, 4-amino phenol, cinnamaldehyde were purchased from SRL (Mumbai, India), DCC (Dicyclohexyl carbodimide) was purchased from Fluka Chemie (Switzerland), Dimethyl amino pyridine DMAP (4,4′-dimethylamino pyridine) was purchased from Finar chemicals (India), dichloro methane, ethanol, MeOH, acetone required for synthesis were used as received except solvents which were dried and distilled prior to use. The molecular structures of the target products and the intermediates were confirmed by spectroscopic analysis and elemental analysis. Representative homologous series were characterized by elemental analysis, infrared spectroscopy, ^{1}H NMR spectra. IR spectra were recorded by Perkin–Elmer spectrum GX, ^{1}H NMR spectra were recorded on Bruker (400 MHz) using $CDCl_3$ as solvent. Microanalysis was performed on Perkin–Elmer PE 2400 CHN analyzer. Texture image of nematic phase was determined by using miscibility method. Transition temperature and LC properties (textures) were determined using an polarizing optical microscopy (POM) equipped with heating stage attached with camera. Decomposition temperatures were determined using Shimadzu differential Scanning Calorimeter (DSC) with a heating rate of 5 °C–10.0 °C min^{-1}.

2.2. Synthesis of series-1 and series-2 compounds

2.2.1. Synthesis of 2-((3-phenyl allylidene amino) phenol (1a)

2-((3-phenyl allylidene amino) phenol was prepared by reported method [25]. (Brownish yellow color, Yield: 78%), IR (KBr): ν_{max} cm^{-1} 3030 (C–H str.), 1590 (CH=N), 961 (–CH=CH–), 3280 (–OH str.). Elemental analysis: calculated for $C_{15}H_{13}ON$: C, 80.71; H, 5.82; N, 6.27%; found: C, 80.62; H, 5.73; N, 6.23%.

2.2.2. Synthesis of 4-n-alkoxy benzoic acid (2a)

4-n-alkoxy derivatives of benzoic acid were prepared by reported method [26].

2.2.3. Synthesis of Methyl-4-hydroxy benzoate (3a)

Equimolar proportion of p-hydroxy benzoic acid and absolute methanol shacked well in presence of two drops of concentrated H_2SO_4 and reaction mixture was refluxed for 2–3 hr. Then reaction mixture was dumped into ice, and allowed it to settle down. Solid white precipitate of methyl-4-hydroxy benzoate was obtained. Product was filtered, washed, dried, and then purified by alcohol. Fine crystals were obtained (M.P.126 °C, yield 72%) [27].

2.2.4. Synthesis of 4-(methoxy carbonyl) phenyl 4′-n-alkoxy benzoate (3b)

4-(methoxy carbonyl) phenyl 4′-n-alkoxy benzoate has been prepared by esterification of the appropriate 4-n-alkoxy benzoic acid (2a) (2.02 mmol) and methyl-4-hydroxy benzoate (3a) (0.246 g, 2.02 mmol); dicyclohexyl carbodiimide (DCC) (0.457 g, 2.22 mmol) and dimethylaminopyridine (DMAP) in catalytic amount (0.002 g, 0.2 mmol) in dry CH_2Cl_2 (DCM) (60 ml) was stirred at room temperature for 48 hr. The white precipitate of DCU was obtained which was isolated by filtration and removed, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol:chloroform as eluent (2:4) [28].

Comp. 3b$_4$: IR (KBr): ν_{max} cm^{-1} 3033 (C–H str.), 679 polymethylene group of $-OC_4H_9$ chain group, 1740 (–COO– group), 1240 (C–O str.). ^1H NMR: 0.88 (t, 3 H, $-OC_4H_9$), 4.06 (t, 2 H, $-OC_4H_9$), 3.82 (s, 3 H, $-OCH_3$), 1.43–1.72 (p, 4 H, $-OC_4H_9$), 7.12 & 8.01 (d, 4 H, first phenyl ring), 7.38 & 8.11 (d, 4 H, second phenyl ring). Elemental analysis: calculated for $C_{19}H_{20}O_5$: C, 69.51; H, 6.09; found: C, 69.41; H, 5.91; O, 5.89%.

2.2.5. Synthesis of 4-((4′-n-alkoxy benzoyl) oxy) benzoic acid (3c)

4-((4′-n-alkoxy benzoyl) oxy) benzoic acid were prepared by dissolving compound 3b in ethanol (40 ml) and 10% aq. NaOH (2 ml) was added. The resultant mixture was heated at reflux for 6–7 hr, then cooled to room temperature, poured into ice cold water (80 ml), and then acidified with dil. HCl. The crude product obtained by filtration was recrystallized by using MeOH/DCM [29].

Comp. 3c$_4$: IR (KBr): ν_{max} cm^{-1}, 3071 (C–H str.), 3301 (–OH of carboxylic group), 1680 (C=O str. of carboxylic group), 1750 (–COO– group), 648 polymethylene group of $-OC_4H_9$ group. ^1H NMR: 0.88 (t, 3 H, $-OC_4H_9$), 4.06 (t, 2 H, $-OC_4H_9$), 10.8 (s, 1 H, –COOH group), 1.43–1.72 (p, 4 H, $-OC_4H_9$), 7.11 & 8.01 (d, 4 H, first phenyl ring), 7.58 & 8.23 (d, 4 H, second phenyl ring). Elemental analysis: calculated for $C_{18}H_{18}O_5$: C, 68.78; H, 5.73%; found: C, 68.69; H, 5.68%.

2.2.6. Synthesis of 4-n-alkoxy benzaldehyde (4a)

4-n-alkoxy benzaldehyde (4a) were synthesized by refluxing the mixture of 4-hydroxy benzaldehyde (1 equiv.) with corresponding n-alkyl bromide (R-Br) (1 equiv.) in presence of anhydrous K_2CO_3 (1.2 equiv.) in dry acetone as a solvent [30]

2.2.7. Synthesis of 4-((4′-n-alkoxy benzylidene) amino) benzoic acid (4b)

4-((4-alkoxy benzylidene) amino) benzoic acid were prepared by refluxing the mixture of 4a and 4-amino benzoic acid at 3–4 hr in presence of ethanol and few drops of glacial acetic acid. The resultant mixture was filtered, dried, and recrystallized from ethanol [25].

Comp.4b$_1$: FT-IR (KBr) in cm^{-1}: 3032 (–C–H– str in aromatic), 2825(C–H str. $-OCH_3$), 1365 and 1236 (–C–O Str), 806 (disubstituted aromatic ring -para), 1630 (–CH=N, str. azomethine group), 1667 (–C=O Str.), 2550 (–OH of –COOH group). ^1H NMR: δH ($CDCl_3$, 400 MHz): 3.80 (s, 3 H, $-CH_3$ of $-OCH_3$ group), 10.32 (s, 1 H, –OH group of –COOH), 8.23

(s, 1 H, –CH=N– group), 7.01–7.82 (4 H, first phenyl ring), 7.42–8.14 (4 H, second phenyl ring); Elemental analysis of $C_{15}H_{13}NO_3$: Calculate: C, 70.58%; H, 5.09%; O, 18.82%; N, 5.49%; found: C, 69.62%; H, 4.96%; O, 18.74%; N, 5.42%.

Comp.4b$_{10}$: FT-IR (KBr) in cm^{-1}: 3031 (–C–H– str in aromatic), 681 (Polymethylene (–CH_2-)n of –$OC_{10}H_{21}$), 1355 and 1230 (–C–O str), 821 (disubstituted aromatic ring -para), 1630 (–CH=N, Str. azomethine group), 1661 (–C=O Str.), 2556 (–OH of –COOH group). ^{1}H NMR: δH ($CDCl_3$, 400 MHz): 0.88 (t, 2 H, –$OC_{10}H_{21}$ group), 1.31 (q, 3 H, –$OC_{10}H_{21}$ group), 1.26–1.29 (m, 12 H, –$OC_{10}H_{21}$ group), 1.71 (P, 2 H, –$OC_{10}H_{21}$ group), 4.06 (t, 2 H, –$OC_{10}H_{21}$ group), 10.48 (s, 1 H, –OH group of –COOH), 8.23 (s, 1 H, –CH=N– group), 7.06–7.82 (4 H, first phenyl ring), 7.43–8.14 (4 H, second phenyl ring); Elemental analysis of $C_{24}H_{31}NO_3$: Calculate: C, 75.59%; H, 8.13%; O, 12.59%; N, 3.67%; found: C, 75.32%; H, 8.02%; O, 12.52%; N, 3.62%.

Comp.4b$_{12}$: FT-IR (KBr) in cm^{-1}: 3032 (–C–H– str in aromatic), 1365 and 1236 (–C–O str), 644 Polymethylene (–CH_2-)n of –$OC_{12}H_{25}$, 808 (disubstituted aromatic ring -para), 1631 (–CH=N, str. azomethine group), 1672 (–C=O Str.), 2558 (–OH of –COOH group); ^{1}H NMR: 0.88 (t, 2 H, –$OC_{12}H_{25}$ group), 1.31 (q, 3 H, –$OC_{12}H_{25}$ group), 1.26–1.29 (m, 14 H, –$OC_{12}H_{25}$ group), 1.71 (P, 2 H, –$OC_{12}H_{25}$ group), 4.06 (t, 2 H, –$OC_{12}H_{25}$ group), 10.68 (s, 1 H, –OH group of –COOH), 8.21 (s, 1 H, –CH=N– group), 7.04–7.81 (4 H, first phenyl ring), 7.43–8.14 (4 H, second phenyl ring); Elemental analysis of $C_{26}H_{35}NO_3$: Calculate: C, 76.28%; H, 8.55%; O, 11.73%; N, 3.42%; found: C, 76.23%; H, 8.48%; O, 11.68%; N, 3.37%.

2.2.8. General procedure for the synthesis of (series-1)

The compound has been prepared by esterification of the appropriate compound 4b (2.02 mmol) and compound 1a (0.246 g, 2.02 mmol); dicyclohexyl carbodiimide (DCC) (0.457 g, 2.22 mmol) and dimethylaminopyridine (DMAP) in catalytic amount (0.002 g, 0.2 mmol) in dry CH_2Cl_2 (DCM) (40 ml) was stirred at room temperature for 48 hr. The slightly yellowish white precipitate of DCU was obtained which was isolated by filtration and removed, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol:chloroform as eluent (1:4) [31]. The synthesis route of derivatives for series-1 and series-2 were mentioned in Schemes 1 and 2.

C_4 (series-1): IR (KBr): ν_{max} cm^{-1} 3066 (C–H str. of alkane), 1601 (C=C str. of alkene in amino allylidene), 1630 (–CH=N-), 1740 (–COO– group), 992 (C–H bending of alkene), 1170 (C–O str. of ether linkage of butoxy group), 791 (polymethylene group of –OC_4H_9). ^{1}H NMR: 0.90 (t, 3 H, –CH_3 of polymethylene –OC_4H_9), 1.45 (p, 2 H, –OC_4H_9), 1.76(p, 2H, –OC_4H_9), 4.06 (t, 2H, –OC_4H_9), 8.02 (s, 1H, –CH=N-), 7.48 (s, 1H, –N=CH–CH=C–), 6.84 & 7.21 (d, 2H, –N=CH–CH=CH–), 7.07 & 7.82 (d, 4H, first phenyl ring), 7.34 & 8.21 (d, 4H, second phenyl rin), 7.37, 7.40 & 7.51 (d, 4H, third phenyl ring), 7.60, 7.33, 7.40 (d, 5H, fourth phenyl ring). Elemental analysis: calculated for $C_{33}H_{30}N_2O_3$: C, 78.88; H, 5.97; N, 5.57%; found: C, 78.81; H, 5.91; N, 5.51%.

C_5 (series-1): IR (KBr):: IR (KBr): ν_{max} cm^{-1} 3063 (C–H str. of alkane), 1601 (C=C str. of alkene in amino allylidene), 1630 (–CH=N-), 1740 (–COO– group), 991 (C–H bending of alkene), 1170 (C–O str. of ether linkage of pentoxy group), 761 (polymethylene group of –OC_5H_{11}). ^{1}H NMR: 0.90 (t, 3H, –CH_3 of polymethylene –OC_5H_{11}), 1,29–1.45 (m, 4H, –OC_5H_{11}), 1.76(p, 2H, –OC_5H_{11}), 4.06 (t, 2H, –OC_5H_{11}), 8.01 (s, 1H, –CH=N-), 7.47 (s, 1H, –N=CH–CH=C–), 6.84 & 7.20 (d, 2H, –N=CH–CH=CH–), 7.07 & 7.81 (d, 4H, first phenyl ring), 7.34 & 8.21 (d, 4H, second phenyl ring), 7.37, 7.40 & 7.52 (d, 4H, third phenyl ring), 7.60, 7.33, 7.40 (d, 5H, fourth phenyl ring). Elemental analysis: calculated for $C_{33}H_{27}N_2O_3$: C, 79.06; H, 6.20; N, 5.42%; found: C, 78.98; H, 6.14; N, 5.39%.

2.2.9. General procedure for the synthesis of (series-2)

The compound has been prepared by esterification of the appropriate compound 3c (2.02 mmol) and compound 1a (0.246g, 2.02 mmol); dicyclohexylcarbodiimide (DCC) (0.457 g, 2.22 mmol) and dimethylaminopyridine (DMAP) in catalytic amount (0.002 g, 0.2 mmol) in dry CH_2Cl_2 (DCM) (40 mL) was stirred at room temperature for 48 hr. The slightly off white precipitate of DCU was obtained which was isolated by filtration and discarded, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting methanol:chloroform (1:4) [31].

C_6 (series-2): IR (KBr): IR (KBr): ν_{max} cm^{-1} 3040 (C–H str. of alkane), 1604 (C=C str. of alkene in amino allylidene), 1640 (–C=O str.), 1730 (–COO– group), 991 (C–H bending of alkene), 1130 (C–O str. of ether linkage of hexyloxy group), 663 (polymethylene group of $-OC_6H_{13}$). ^1H NMR: 0.88–0.90 (t, 3H, $-CH_3$ of polymethylene $-OC_6H_{13}$), 1.29–1.43 (m, 6H, $-OC_6H_{13}$), 1.76 (p, 2H, $-OC_6H_{13}$), 4.06 (t, 2H, $-OCH_2-CH_2-$ of $-OC_6H_{13}$), 7.48 (s, 1H, –N=CH–CH=C–), 6.83 & 7.21 (d, 2H, –N=CH–CH=CH–), 7.12 & 8.12 (d, 4H, first phenyl ring), 7.52 & 8.27 (d, 4H, second phenyl ring), 7.31, 7.40 & 7.52 (d, 4H, third phenyl ring), 7.33, 7.40, 7.58 (d, 5H, fourth phenyl ring). Elemental analysis: calculated for $C_{35}H_{33}NO_5$: C, 76.78; H, 6.03; N, 2.55%; found: C, 76.71; H, 5.97; N, 2.48%.

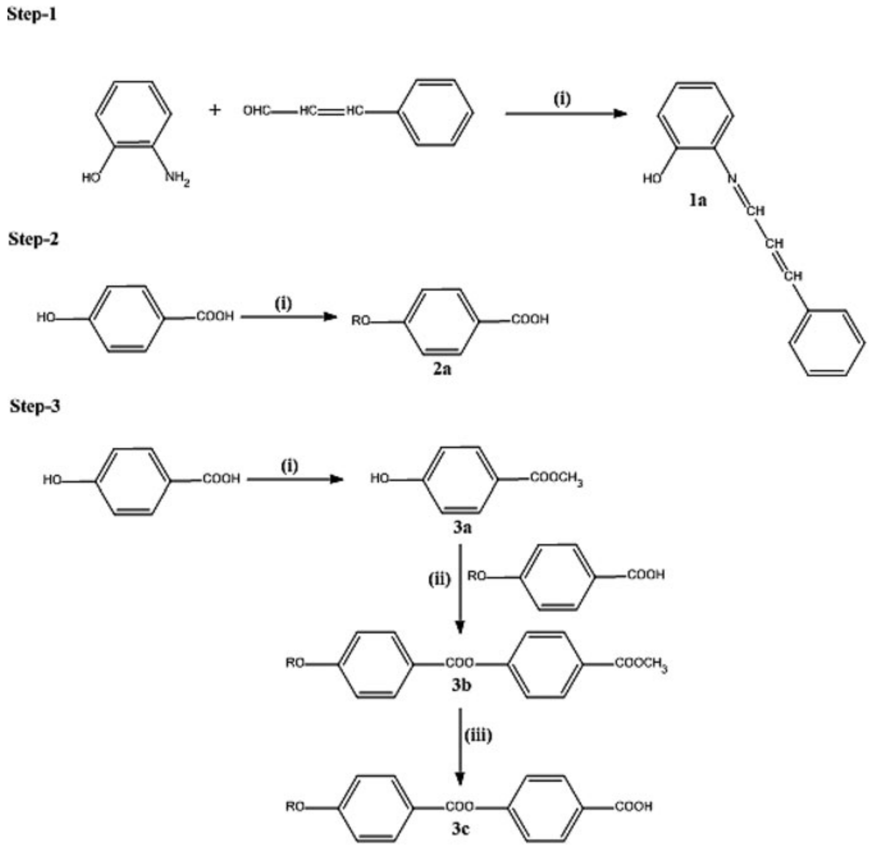
C_8 (series-2): IR (KBr): IR (KBr): ν_{max} cm^{-1} 3040 (C–H str. of alkane), 1610 (C=C str. of alkene in amino allylidene), 1640 (–C=O str.), 1750 (–COO– group), 991 (C–H bending of alkene), 1130 (C–O str. of ether linkage of octyloxy group), 781 (polymethylene group of $-OC_8H_{17}$). ^1H NMR: 0.88–0.90 (t, 3H, $-CH_3$ of polymethylene $-OC_8H_{17}$), 1.26–1.43 (m, 10H, $-OC_8H_{17}$), 1.76 (p, 2H, $-OC_8H_{17}$), 4.06 (t, 2H, $-OCH_2-CH_2-$ of $-OC_8H_{17}$), 7.49 (s, 1H, –N=CH–CH=C–), 6.84 & 7.21 (d, 2H, –N=CH–CH=CH–), 7.12 & 8.10 (d, 4H, first phenyl ring), 7.52 & 8.27 (d, 4H, second phenyl ring), 7.31, 7.40 & 7.52 (d, 4H, third phenyl ring), 7.33, 7.40, 7.58 (d, 5H, fourth phenyl ring). Elemental analysis: calculated for $C_{37}H_{37}NO_5$: C, 77.21; H, 6.43; N, 2.43%; found: C, 77.19; H, 6.41; N, 2.39%.

C_{10} (series-2): IR (KBr): ν_{max} cm^{-1} 3030 (C–H str. of alkane), 1604 (C=C str. of alkene in amino allylidene), 1630 (–C=O str.), 1750 (–COO– group), 991 (C–H bending of alkene), 1140 (C–O str. of ether linkage of decyloxy group), 804 (polymethylene group of $-OC_{10}H_{21}$). ^1H NMR: 0.88–0.90 (t, 3H, $-CH_3$ of polymethylene $-OC_{10}H_{21}$), 1.26–1.43 (m, 14H, $-OC_{10}H_{21}$), 1.76 (p, 2H, $-OC_{10}H_{21}$), 4.06 (t, 2H, $-OCH_2-CH_2-$ of $-OC_{10}H_{21}$), 7.50 (s, 1H, –N=CH–CH=C–), 6.85 & 7.21 (d, 2H, –N=CH–CH=CH–), 7.12 & 8.10 (d, 4H, first phenyl ring), 7.51 & 8.27 (d, 4H, second phenyl ring), 7.31, 7.40 & 7.52 (d, 4H, third phenyl ring), 7.33, 7.40, 7.58 (d, 5H, fourth phenyl ring). Elemental analysis: calculated for $C_{39}H_{41}NO_5$: C, 77.61; H, 6.79; N, 2.52%; found: C, 77.56; H, 6.73; N, 2.48%.

2.3. Reaction scheme

3. Result and discussion

In the present study, we have synthesized thirteen compounds for each two series, 2-((3-phenyl allylidene) amino) phenyl 4-((4′-n-alkoxy benzylidene) amino) benzoate (series-1) and 4-((2-((3-phenyl allylidene) amino) phenoxy) carbonyl) phenyl 4′-n-alkoxy benzoate (series-2) were synthesized and their mesomorphic properties were studied by using DSC and POM.



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

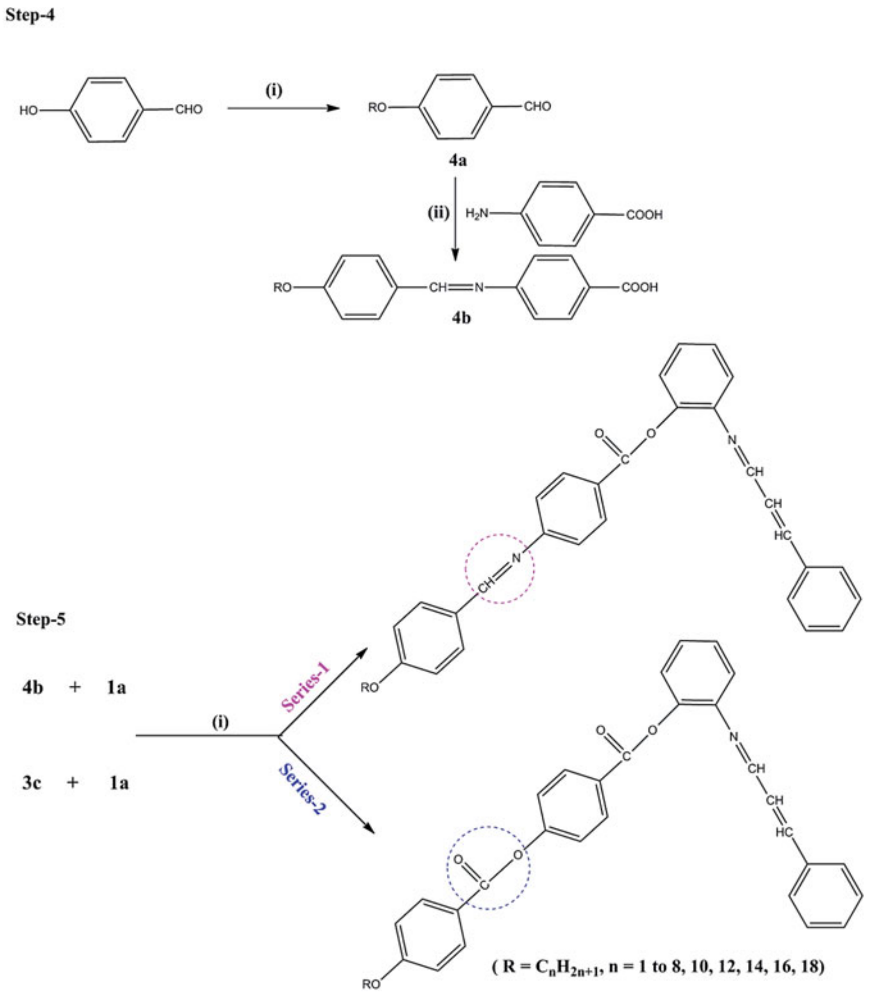
Step-1: ETOH, glacial acetic acid, Reflux; Step-2: (i) R-Br, KOH, MeOH, Reflux; Step-3: (i) MeOH, Conc.H_2SO_4, Reflux; (ii) DCC/DMAP, DCM, 48 stirring(R.T.) (iii) KOH, ETOH, Reflux.

Scheme 1. Synthetic route of some derivatives of series-1 and series-2.

3.1. POM investigation

We have studied comprehensively the effect of linking group as well as alkyl aliphatic chain length to form mesogens having hockey stick type shape. It has been proven that altering the length of alkyl chain effects the LC property. Here, in present, we have synthesized and studied the effect of linking group as well as the effect of varying aliphatic side alkyl chain length from small spacer (–OCH_3) to higher spacer (–$OC_{18}H_{37}$) in presence of four benzene ring connect by three linking groups. We have synthesized thirteen homologous compounds (C_1–C_8, C_{12}, C_{14}, C_{16}, C_{18}) in both homologous series-1 and series-2. All the synthesized compounds, except for three derivatives (C_1–C_3) exhibit LC phases in both series. However, the type of the mesophases depends on the number of carbon atoms in the aliphatic spacer and terminal alkyl chain. Nematic mesophase commences from C_4 homologue in both synthesized series. Smectic mesophase commences early in series-1 as compared to series-2. The transition temperature of series-1 and series-2 are listed below in Tables 1 and 2.

Compounds C_1–C_3 in both series do not show in LC property. This is due to the presence of short alkyl spacer or tail group in left side chain which causes more crystallinity tendency and directly passes isotropic without displaying LC phase. The nonmesomorphicity of compound is mainly attributed to the low magnitudes of intermolecular dispersion forces and



Srep-4: (i) R-Br, Anhy.K_2CO_3, Dry Acetone, Reflux; (ii) KOH, EtOH, Reflux; Step-5: DCC/DMAP; DCM, 48 hour stirring(R.T).

Scheme 2. Synthetic route of series-1 and series-2.

Table 1. Transition Temperature in °C by POM (series-1).

		Transition temperatures in ^{0}C						
Sr.no	R = n-alkyl group	Cr	Smectic		Nematic		Isotropic	
1	C_1	·	—	—	—	—	159.0	·
2	C_2	·	—	—	—	—	157.0	·
3	C_3	·	—	—	—	—	152.0	·
4	C_4	·	108.0	·	128.0	·	148.0	·
5	C_5	·	104.0	·	139.0	·	147.0	·
6	C_6	·	102.0	·	135.0	·	144.0	·
7	C_7	·	110.0	·	142.0	·	151.0	·
8	C_8	·	98.0	·	136.0	·	142.0	·
9	C_{10}	·	97.0	·	131.0	·	137.0	·
10	C_{12}	·	92.0	·	122.0	·	134.0	·
11	C_{14}	·	91.0	·	119.0	·	128.0	·
12	C_{16}	·	89.0	·	107.0	·	118.0	·
13	C_{18}	·	78.0	·	98.0	·	110.0	·

Table 2. Transition Temperature in °C by POM (series-2).

		Transition temperatures in ^{0}C						
Sr.no	R = n-alkyl group	Cr	Smectic		Nematic		Isotropic	
1	C_1	·	—	—	—	—	179.0	·
2	C_2	·	—	—	—	—	174.0	·
3	C_3	·	—	—	—	—	168.0	·
4	C_4	·	—	—	136.0	·	160.0	·
5	C_5	·	—	—	129.0	·	158.0	·
6	C_6	·	—	—	128.0	·	149.0	·
7	C_7	·	—	—	132.0	·	152.0	·
8	C_8	·	—	—	126.0	·	148.0	·
9	C_{10}	·	116.0	·	123.0	·	150.0	·
10	C_{12}	·	114.0	·	121.0	·	148.0	·
11	C_{14}	·	108.0	·	116.0	·	142.0	·
12	C_{16}	·	102.0	·	112.0	·	137.0	·
13	C_{18}	·	—	·	104.0	·	128.0	·

low magnitudes of dipole-dipole interactions leading to its high crystallizing tendency which origins abrupt breaking of crystal lattices due to unsuitable and unfavorable magnitudes of anisotropic forces of intermolecular attractions. Thus, irregular breaking of crystal lattices suddenly takes place at relatively higher temperature. As a result, crystalline solid state directly passes into isotropic state without displaying LC phase. The phase diagram of both the series are listed in Figs. 2 and 3.

A phase diagram (Fig. 2) of new series-1 consisted of Cr-N/I, Sm-N, and N-I transition curves showing phase behaviors of series. The Cr-N/I transition curve starts decreasing from first C_1 homologue to C_6 homologue, increasing at C_7 homologue, and again decreasing upto last C_{18} homologue. Odd-even effect is present between C_6 to C_7 homologue in series-1, respectively. Sm-N transition curve show increasing tendency at C_5 and C_7 homologue with overall downward tendency. N-I transition curve shows decreasing tendency from C1 to C_6 homologue and then increases at C_7 homologue and then continue to decreases upto last C_{18} homologue. It is interesting to note that the altering of alkyl chain length on alkoxy side group (–OR) effects the mesomorphic properties of synthesized compounds.

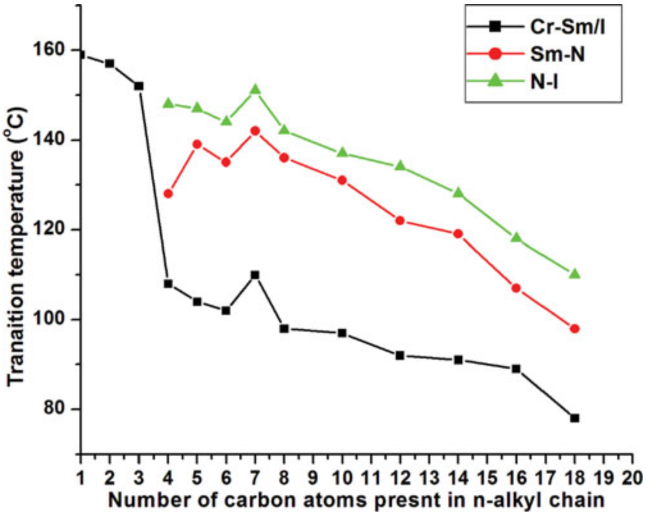


Figure 2. Phase diagram of series-1.

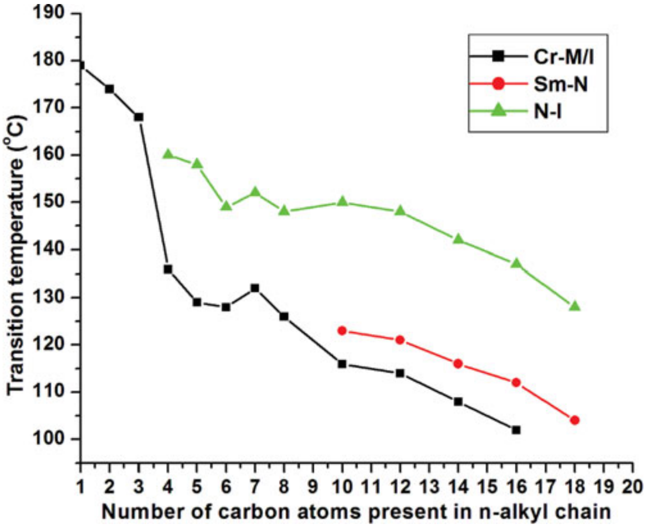


Figure 3. Phase diagram of series-2.

The phase diagram of series-2 is mentioned in below Fig. 3. Cr-M/I and N-I transition curves show decreasing tendency from lower member (C_1) to higher member (C_{18}) compounds except C_7 homologue in series-2. Odd-even effect is observed in Cr-M/I and N-I transition curve at C_6–C_7 homologue. Sm-N transition curve starts from C_{10} homologue and shows decreasing tendency upto last C_{16} homologue. The exhibition of nematic mesophase in C_4–C_{18} (series-1, series-2) is attributed to the appropriate magnitudes of end to end intermolecular anisotropic forces of attractions and closeness as a significance of favorable molecular rigidity, linearity due to the presence of linking group, and flexibility caused by the presence of left side chain generate permanent dipole-moment across the long molecular axis, suitable magnitudes of dispersion forces and dipole-dipole interactions, molecular polarizability, and polarity which facilitate the molecules under microscopic study to float on the surface with statically parallel orientational order within certain range of temperature as nematic phase [32].

3.2. Nematic mesophase study by miscibility method

The nematic mesophase in comp. C_4–C_{18} were also confirmed by using miscibility method which was listed in Table 3. Comp.C_{10} shows threaded type nematic phase whereas in comp.C_{12}, rod type textural image was seen. Comp. C_{14} homologue shows rod type textural pattern of nematic phase. Comp.C_{16}–C_{18} shows threaded type textural pattern of nematic mesophase.

Table 3. Texture of Nematic Phase of C_{12}, C_{14}, $C_{16,}$ and C_{18} by miscibility method.

Sr. No.	Homologue	Texture (Series-1)	Texture (Series-2)
1	C_{12}	Threaded	Threaded
2	C_{14}	Threaded	Threaded
3	C_{16}	Schlieren	Threaded
4	C_{18}	Schlieren	Rodlike

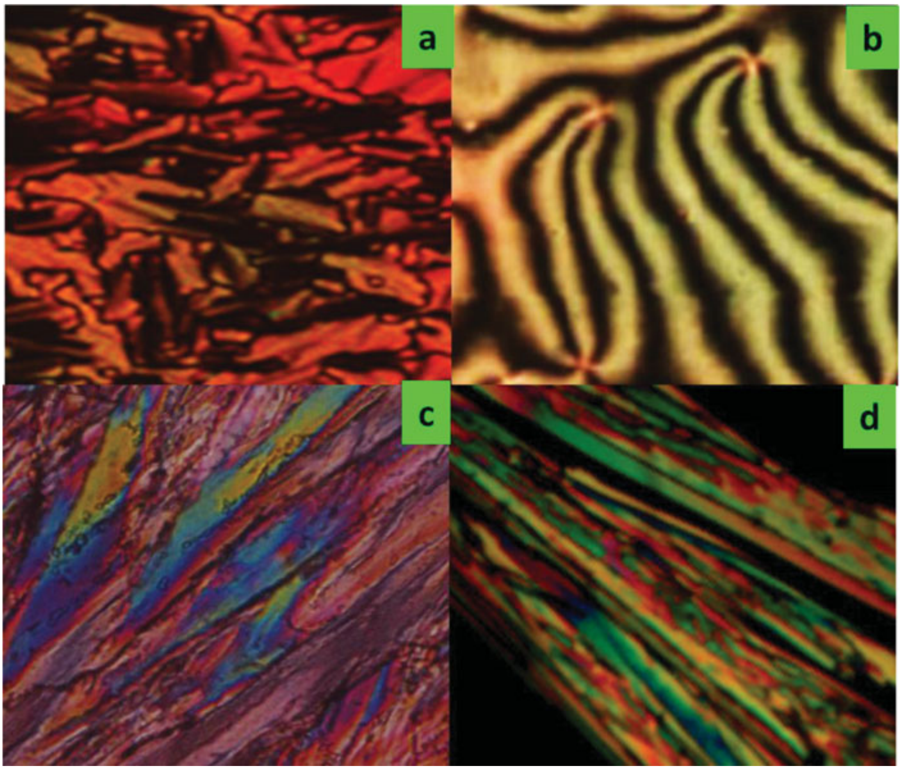


Figure 4. Photomicrograph of optical texture of (a) **C_{10}** at 131.0 °C (series-1); (b) **C_{16}** at 107.0 °C (series-1); (c) **C_{14}** at 91.0 °C (series-1); (d) **C_6** at 102.0 °C (series-1).

3.3. Textural study

The solid samples held between an untreated glass slide and a coverslip were heated to their isotropic phase and cooled slowly. As shown in Figs. 4 and 5, a schlieren type nematic texture pattern of compound C_{10} (series-1) is seen at 131.0 °C. Compound C_{16} show schlieren type texture image of nematic pattern at 107.0 °C on heating condition. Compound C_6 (series-1) shows textural pattern of smectic A phase at 102.0 °C on heating condition. Compound C_{14} (series-1) shows feather like textural pattern of smectic A phase at 91.0 °C on cooling condition. Compound C_{10} (series-2) shows broken focal type textural pattern of smectic

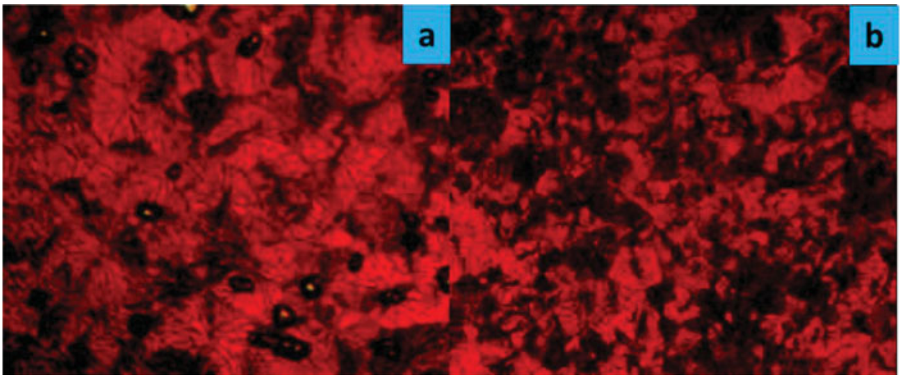


Figure 5. Photomicrograph of optical texture of (a) **C_{10}** at 116.0 °C (series-2); (b) **C_{14}** at 108.0 °C (series-2).

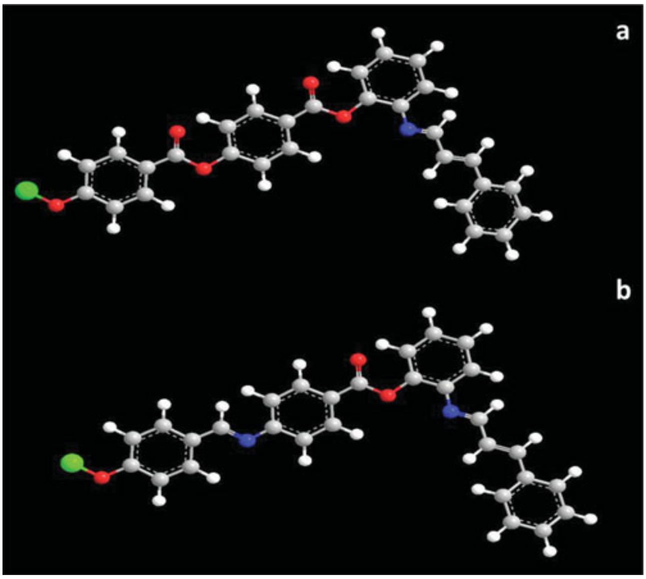


Figure 6. Space filling diagram of structurally similar analogous series.

A phase at 116.0 °C on heating condition, while compound C_{14} shows typical textural pattern of smectic C phase at 108.0 °C on heating condition. The focal conic texture pattern appears broken in the SmC mesophase because of the disruption of the lamellar packing due to the tilt of the molecules [33].

3.4. Comparative study

Here, we have compared the geometry and molecular shape with respect to linking and terminal groups of presently synthesized series-1 with series-2. The structure of both the series is mentioned in above Fig. 1. The hockey stick shaped homologous series-1 and series-2 are identical with respect to four phenyl rings and three linkage groups that connect one part of a core to another part. But they differ with respect to each other at first linkage group between first and second phenyl ring. In series-1, schiff base (–CH=N-) linkage group is present while in series-2, ester (–COO–) group is present. The geometrical shape of series-2 is more steady as compared to series-1 because of the presence of ester (–COO–) unit which confers a stepped structure and maintain the linearity of molecule and due to its high polarity mesophase observed at higher temperature as compared to series-1. There is conjugation in imine (–CH=N-) linkage group which extended over the longer molecule and enhance the polarizability anisotropy of molecule. Thus, variations in mesomorphic (LC) properties are ascribed to the magnitudes of differing features like (shapes and left terminal tail groups) in both series from lower chain containing homologue to higher chain containing homologue.

The space-filling diagram indicate the energy minimize in series-1 and series-2 as shown in Fig. 6. The geometrical shapes of both series are nonlinear. Presence of allylidene amino unit (-N=CH–CH=CH–) and second ester (–COO–) part unit is common in both series. Therefore, it proves that, the changing in first linking unit ester (–COO–, series-1) by schiff base (–CH=N–, series-2) as a result variation is arrised in LC properties. The ester (–COO–) linkage group is a polar group that can aid lamellar packing and create smectic phase in both series [34].

Table 4. Relative thermal stability in °C.

Series	Series-1	Series-2
Sm-N	125.7	118.0
N-I	135.9 °C	147.2 °C
Commencement of nematic phase	C_4–C_{18}	C_4–C_{18}
Commencement of smectic phase	C_4–C_{18}	C_{10}–C_{16}
Total temperature range of mesophase	40.0–32.0 C_4 C_{18}	24.0–35.0 C_4 C_{18}

3.5. Thermal stability and temperature range of mesophase

Table 4 represents some thermometric data of series-1 and series-2 in comparative manner. Thermal stability of nematic mesophase of series-1 is lower as compared to series-2. Thermal stability of smectic phase of series-1 is greater as compared to series-2. Temperature range of mesophase is in increasing order of lower to higher homologue in series-1 and series-2. The early or late commencement of mesophase depends upon the extent of molecular noncoplanarity caused by the presence of linkage group and their magnitudes like polarity, polarizability, and linearity.

3.6. DSC analysis

The phase transition temperatures and enthalpies were measured by carrying out DSC thermal analysis. All compounds are thermally stable as confirmed by the reproducibility of thermograms on several heating and cooling cycles. In Fig. 7, compound C_4 (series-1) shows two endothermic peaks at 104.23°C and 146.92 °C in heating cycle, which designates the

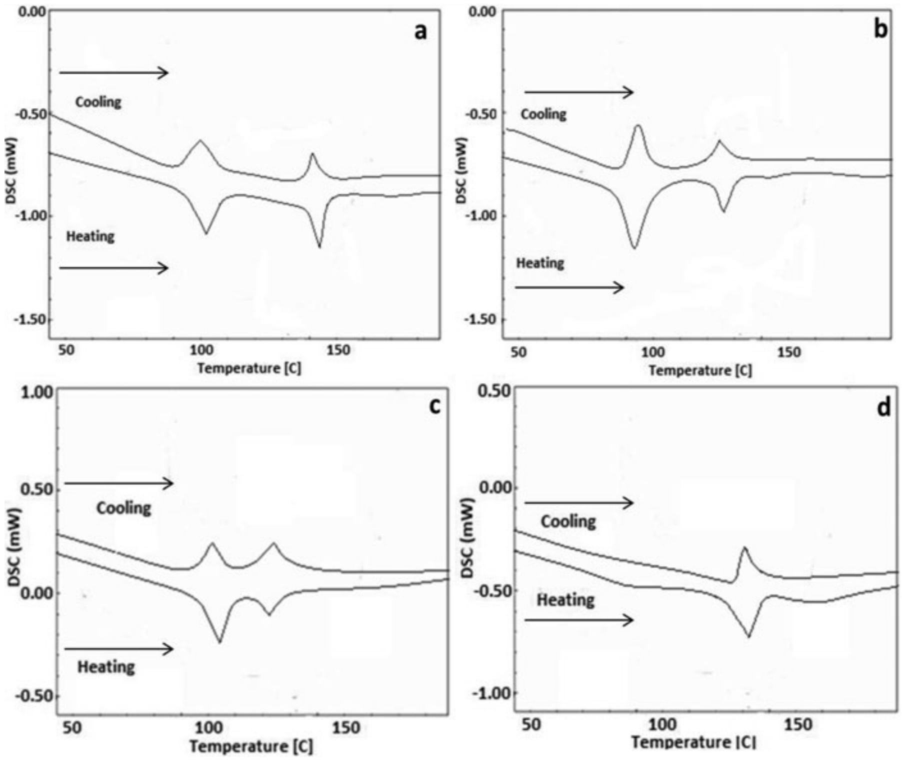


Figure 7. DSC thermograms of compound (a) C_4 (series-1); (b) C_{12} (series-1); (c) C_{10} (series-2); (d) C_4 (series-2).

Table 5. Transition temperature (°C) and enthalpy (J g^{-1}) and entropy change (J $g^{-1}k^{-1}$) by DSC measurement.

Comp.	Transition	Heating scan(°C)	Cooling scan(°C)	ΔH (−J g^{-1})	ΔH (J g^{-1})	ΔS (−J $g^{-1}k^{-1}$)	ΔS (J $g^{-1}k^{-1}$)
C_4	**Cr-SmC**	104.23	103.91	5.34	1.18	0.0141	0.0031
(series-1)	**SmC–N**	146.92	145.41	12.32	16.42	0.0293	0.0392
	N-I	>145	—	3.45	—	0.0082	—
C_{12}	**Cr-SmC**	92.61	93.67	6.28	1.91	0.0171	0.0052
(series-1)	**SmC–N**	126.32	125.53	11.32	9.42	0.0283	0.0236
	N-I	>130	—	4.56	—	0.0113	—
C_{10}	**Cr-SmC**	106.92	105.98	3.84	2.40	0.0101	0.0063
(series-2)	**SmC–N**	121.61	122.67	9.23	8.42	0.0233	0.0212
	N-I	>150	—	4.52	—	0.0106	—
C_4	**Cr-N**	131.52	130.48	8.45	5.35	0.0208	0.0132
(series-2)	**N-I**	>156	—	12.42	—	0.0289	—

presence of SmC and nematic phase. That was further confirmed by POM analysis. While on cooling condition, again two exothermic peaks were traced at 103.91°C and 145.41 °C. Compound C_{12} (series-1) shows two endothermic peaks at 92.61°C and 126.32 °C during heating cycle, while in cooling cycle, it appears at 93.67°C and 125.53 °C which was also confirmed by POM analysis which indicates the mesophase looked in enantiotropical manner. Compound C_{10} (series-2) exhibits two endothermic peak at 106.92 °C and 121.61 °C on heating cycle which reveals with POM study. On cooling cycle, again two exothermic peaks were traced at 105.98 °C and 122.67 °C. Compound C_4 (series-2) shows only one significant endothermic peak at 131.52°C in heating condition while it appears at 130.48 °C on cooling condition. On POM study, it confirms the presence of nematic phase in heating and cooling condition.

The phase transition temperatures and the value of enthalpy and entropy were measured by carrying out DSC thermal analysis. The phase transition temperatures, enthalpy and entropy values for the present synthesized series-1, -2 are summarized in Table 5. Molecules of every homologue arbitrarily oriented in all likely directions with high order of disorder or entropy ($\Delta S = \Delta H/T$) further than isotropic temperature and the enthalpy value (ΔH). But, at cooled condition, the matching from and lower isotropic temperature, the mesophase is continued to seem reversibly at the lower temperature as observed during heating condition. The mesophase attained in this present series is enantiotropically nematogenic.

4. Conclusion

A new nonlinear homologous series of imine (schiff base, series-1) and ester (series-2) containing ester and allylidene amino linking groups having left alkoxy side chains groups ($n =$ 1–8, 10, 12, 14, 16, 18) has been synthesized. The lower members C_1–C_3 in both the series showed nonliquid crystalline behavior while higher members of both the series exhibited enantiotropic nematic or smectic phase transition with higher thermal stabilities.

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