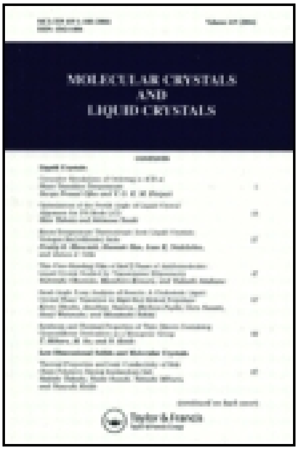

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Synthesis, Mesophase Behavior and Thermal Stability of Liquid Crystals Based on Different Central Linkages with Lateral Substitution and Terminal Heterocyclic Moieties

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Synthesis, Mesophase Behavior and Thermal Stability of Liquid Crystals Based on Different Central Linkages with Lateral Substitution and Terminal Heterocyclic Moieties

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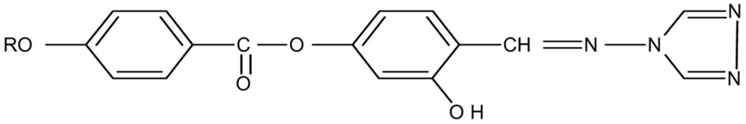
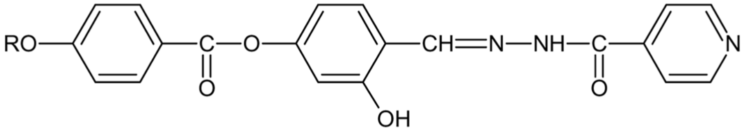
The synthesis and evaluation of thermal behavior of two new mesogenic homologous series of liquid crystalline compound containing 1,2,4-triazole and isonicotinic acid ring at the terminus of the molecule have been reported, viz. 3-hydroxy-4-[(4-1,2,4-triazol-4-ylimino)methyl] phenyl 4-alkoxybenzoate (Series-I) and 3-hydroxy-4 (isonicotinoyl carbonohydrazonoyl) phenyl 4-alkoxy benzoate (Series-II).



Series-I



Series-II

We are thankful to I.I.T.Bombay, CDRI Lucknow and Garda chemicals Ltd., Ankleshwar (Gujarat) to providing an elemental analysis, FT-IR, ^{1}H-NMR,^{13}C NMR Mass and Thermal studies.

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The compounds of both the series have been characterized by elemental Analysis, FT-IR, mass spectrometry, ^{1}H-NMR and ^{13}C-NMR. Phase transition temperatures and the thermal parameters were obtained from differential scanning calarimetry (DSC). The texture observation was performed under polarizing optical microscopy (PMO) attached with Mettler hot stage. All the derivatives are mesomorphic in nature showing nematic phase as well as higher members of both the series show smectic phase. The use of triazole and isonicotinic acid as a terminal group has a very dramatic effect on the melting and clearing points. Similarly lateral –OH substitution on central phenyl ring shows higher clearing temperature due to intermolecular hydrogen bonding. The mesomorphic behavior has been analyzed in terms of structural property relation.

Keywords: ester; isonicotinic acid hydrazide; lateral group; mesophase; nematic phase; Schiff base; smectic phase; triazole

1. INTRODUCTION

Thermotropic liquid crystals are of great technological importance [1]. Many series of liquid crystalline compounds containg heterocyclic groups have been synthesized because of their interesting properties [2].

There have been a variety of compounds reported with liquid crystalline properties, but heterocyclic moieties [3,4] are less explored, compared to homocyclic moieties. The introduction of heteroatom causes considerable changes in chemical and physical properties and influences the type of liquid crystal phase, also phase transition temperatures and other properties of the mesogens [5]. Usually five or six membered heterocycles are involved, and they form part of the core in rod-shape (calamitic), bent-shape or disc-shape (discotic) molecules. However, few mesogenic five membered and six membered heterocycles have been reported.

In our present work we introduce 4-amino-1,2,4-triazole and Isonicotinic acid hydrazide as terminal groups and synthesized two homologues series, viz., 3-hydroxy-4-[(4-1,2,4-triazole-4-ylimino)-methyl] phenyl 4-alkoxy benzoate (Series-A) and 3-hydroxy-4-(isonicotinoyl carbonohydrazonoyl) phenyl 4-alkoxy benzoate (Series-B).

1,2,4-triazoles have been reported as potential biologically active agent [6,7]. 1,2,4-triazole and their derivatives constitute an important class of organic compounds with diverse agricultural, industrial and biological activities [8,9,10], including anti inflammatory [11]. Acid hydrazide and hydrazones are useful chelating agents and are of biological importance [12]. Isonicotinic acid hydrazide (inh) and its derivatives are antibacterial agents that have been used to treat tuberculosis, interacting with microbial cell walls [13,14].

In our recent work series-A contains triazole ring as terminal group and due to triazole ring melting point of compound are increases. The entire compound in series-A show mesomorphic properties. In each case an enantiotropic nematic mesophase is observed in lower member where higher member of series -A (A_{12}, A_{14}, A_{16}) shows an enantiotropic smectic C phase and nematic phase whereas in series -B isonicotinic acid hydrazide as terminal group is shows nematic phase as well as smectic C phase for heptyl derivative and smectic A phase for decyl and tetradecyl derivatives. All the compound of both the series have been characterized by elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, Mass spectrometry. The liquid crystalline behaviors of these compounds were observed by DSC study and polarizing microscope.

2. EXPERIMENTAL

2.1. Reagents and Technique

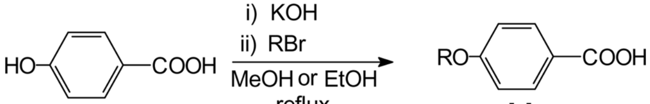
The solvents were used after purification using the standard method described in literature [15]. 4-hydroxy benzoic acid, 2,4-dihydroxy benzaldehyde and DMAP (4-dimethylaminopyridine) were obtain from Merck (Germany). 4-amino-1,2,4-triazole, Isonicotinic acid hydrazide and DCC (Dicyclohexylcarbodiimide) was purchased from Fluka Chemie (Switzerland). Elemental analyses (C, H, N) were performed at CDRI, Lucknow. Infrared spectra were recorded with a Perkin-Elmer2000 FT-IR spectrophotometer in the frequency range 4000–400 cm^{-1} with samples embedded in KBr discs. ^{1}H-NMR spectra of the compound were recorded with JEOL-GSX-400 using $CDCl_3$ as a solvent and TMS as an internal reference at SAIF, IIT Madras, Chennai. ^{13}C NMR spectra of the compound were recorded with BRUKER AVANCE II 400 NMR Spectrometer, SAIF, Chandigarh. Mass spectra (EI) of the compounds were recorded at SAIF, IIT Madras, Chennai. Thin-layer chromatography analyses were performed by using aluminium-backed silica-gel plates (Merck 60 F524) and examined under short-wave UV light.

The phase-transition temperatures were measured using a shimadzu DSC-50 at heating and cooling rates of 5°C min^{-1}, respectively. The optical microscopy studies were carried out with a Carl Zeiss polarizing microscope equipped with a Mettler FP52 hot stage. The textures of the compounds were observed using polarized light with crossed polarizers with sample in thin film sandwiched between a glass slide and cover slip.

2.2. Synthesis

2.2.1. *Synthesis of 4-n-alkoxy benzoic acid* [16]

These were prepared by the reported method. A mixture of 4-hydroxy benzoic acid (1 mmole) and KOH (1.5 mmol) in 250 ml of Methanol or Ethanol was stirred and heated at 70°C while 1-bromo alkane (1.02 mmol) was added slowly (1–2 hrs), after which mixture was refluxed for 11–13 hrs. The reaction mixture was cooled to room temperature and poured into acidic crushed ice. The product obtained was filtered off and purified as reported. The molecular structure of these acids were confirmed by spectroscopic analysis and found to be in agreement with the reported data.

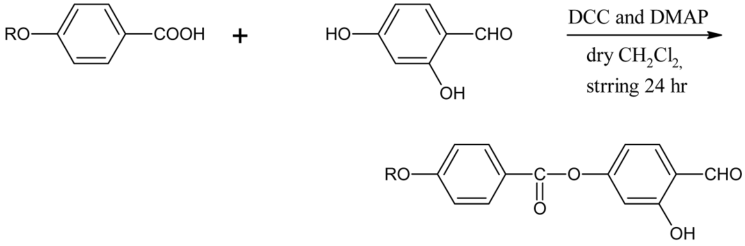


[a]

R=C_nH_{2n+1}; n=1,2,3,4,5,6,7,8,10,12,14,16.

2.2.2. *Synthesis of 4-formyl-3-hydroxyphenyl 4-alkoxy benzoate* [17,18]

To a mixture of 4-n-alkoxy benzoic acid (1 mmol) and p-hydroxy benzaldehyde (1 mmol) in 150 ml of distilled dichloromethane were added 0.1 mmol of dimethyl aminopyridine (DMAP) under an argon atmosphere. The mixture was cooled in an ice/water bath and, after 10 min, 1 mmol of dicyclohexylcarbodiimide (DCC) were added under an argon atmosphere. The mixture was stirred overnight at room temperature, the salts were filtered off and the solvent was evaporated. The crude product was purified by flash chromatography using a mixture of hexanes/ethyl acetate (7/1) as eluent.



[b]

R = C_nH_{2n+1}; n=1 – 8, 10, 12, 14, 16.

Data

Compound B

Yield 79%. Found: C, 75.12; H, 7.68; Calc. for $C_{24}H_{30}O_4$; C, 75.39; H, 7.85%. IR (KBr): Vmax/cm^{-1} 2953, 2919, 2850 cm^{-1}(C–H aliphatic), 1729 cm^{-1}(C=O of ester), 1702 (C=O of aldehyde), 3441 cm^{-1}(OH).

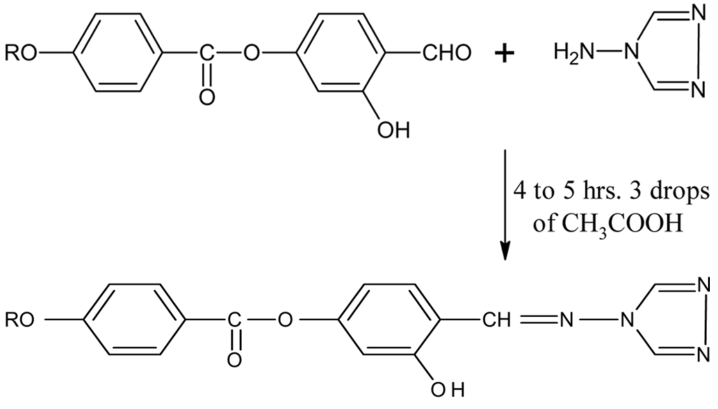
2.2.3. *Synthesis of Compound 3A and 3B* [17,19]

2.2.3A. Synthesis of 3-hydroxy-4-[(4-1,2,4-triazol-4-ylimino) methyl] phenyl 4-alkoxy benzoate. A mixture of 1 mmol 4-formyl-3-hydroxyphenyl 4-alkoxybenzoate and 1 mmol of 4-amino-1,2,4-triazole, and three drops of acetic acid in absolute ethanol was heated at reflux for 4 h. The reaction mixture was allowed to cool and was stirred at room temperature overnight. The solid was collected and recrystallized from technical ethanol.

Data

Compound A_{10}

Yield 78%. M.P. 188°C. Found: C, 67.29; H, 6.90; N, 12.06. Calc. for $C_{26}H_{32}O_4N_4$; C, 67.24; H, 6.89; N, 12.06%. EI-MS m/z (rel.int%): 464(2) $(M)^+$. IR (KBr): Vmax/cm^{-1} 3425 cm^{-1}(OH), 2948, 2853 cm^{-1} (C–H aliphatic), 1729 cm^{-1}(C=O of ester), 1619 cm^{-1} (CH=N),



[3A]

R = C_nH_{2n+1}; n= 1 – 8, 10, 12, 14, 16.

(Scheme-I)

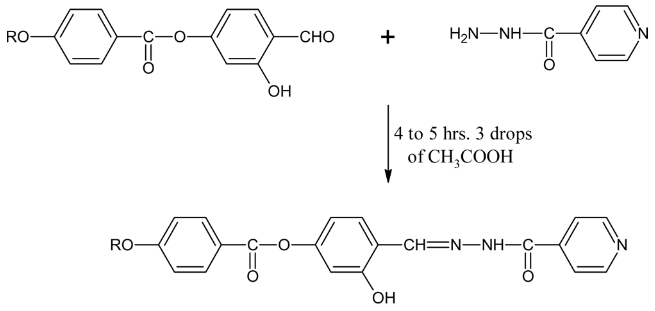
1600 cm^{-1}(C=C aromatic), 1276 cm^{-1}(C–O), 1589, 1600 cm^{-1}(C=N, triazole), 1622 cm^{-1}(N–N=C, triazole). ^1H NMR ($CDCl_3$): δ 0.91–0.93 ppm (CH_3), 1.23–1.47 ppm (CH_2), 4.03–4.07 ppm (OCH_2), 6.89–8.07 ppm (Ar–H), 9.10–9.30 ppm (CH=N), 8.2 ppm (triazole-H). 12.82 ppm (OH). ^{13}C NMR ($CDCl_3$), 14.40 ppm (CH_3), 23.00–34.70 ppm (CH_2), 110.00–162.25 ppm (Ar–C), 161.21 ppm (C=N), 171 ppm (C=O ester), 142.00–160.00 ppm (triazole-C).

2.2.3B. Synthesis of 3-hydroxy-4 (isonicotinoyl carbonohydrazonoyl) phenyl 4-alkoxy benzoate. A mixture of 1 mmol 4-formyl-3-hydroxyphenyl 4-alkoxybenzoate and 1 mmol of isonicotinic acid hydrazide, and three drops of acetic acid in absolute ethanol was heated at reflux for 4 h. The reaction mixture was allowed to cool and was stirred at room temperature overnight. The solid was collected and recrystallized from technical ethanol.

Data

Compound B_{10}

Yield 91%. M.P.183°C. Found: C, 69.67; H, 6.77; N, 8.14. Calc. for $C_{30}H_{35}O_5N_3$; C, 69.64; H, 6.76; N, 8.12%. EI-MS m/z (rel.int%): 517(2) $(M)^+$. IR (KBr): Vmax/cm^{-1} 3434 cm^{-1} (OH), 2947, 2919, 2847 cm^{-1}(C–H aliphatic), 1738 cm^{-1} (C=O of ester), 1614 cm^{-1} (CH=N), 1602 cm^{-1} (C=C aromatic), 1271 cm^{-1}(C–O), 1667 cm^{-1} (C=O of hydrazone linkage), 3179–3240 cm^{-1} (NH), 1556 cm^{-1} (C=N,



[3B]

R = C_nH_{2n+1}; n= 1 – 8, 10, 12, 14, 16.

(Scheme-II)

pyridyl ring), ^{1}H NMR ($CDCl_3$): δ 0.90–0.92 ppm (CH_3), 1.30–2.61 ppm (CH_2), 4.03–4.07 ppm (OCH_2), 6.68–7.35 ppm (Ar–H), 8.58–8.90 ppm (CH=N), 12.82 ppm (OH), 10.98 ppm (NH), 8.7–8.9 ppm (pyridyl-H) ^{13}C NMR ($CDCl_3$), 14.28 ppm (CH_3), 22.92–34.86 ppm (CH_2), 110.00–163.00 ppm (Ar-C),158.99 ppm (C=N), 172.05 ppm (C=O, ester). 155.00–165.00 ppm (–C=O–NH), 148.44, 149.25 ppm (pyridyl-C).

3. RESULTS AND DISCUSSION

In our recent work, 12 homologous from each of the two series, 3-hydroxy-4-[(4-1,2,4-triazol-4-ylimino) methyl] phenyl 4-alkoxy benzoate (series-A) and 3-hydroxy-4 (isonicotinoyl carbonohydrazonoyl) phenyl 4-alkoxy benzoate (series-B) are synthesized and their mesomorphic properties are studied. The common structural features of the compounds are that they consist of two phenyl rings and linkages with different terminal groups at one end. The mesomorphic properties of all the synthesized compounds have been characterized by differential scanning calorimetry (DSC) and polarizing optical microscope (PMO) attached with Mettler hot stage.

In series-A, it is observed that the lower n-alkoxy derivatives. i.e., From n-methyloxy to n-propenyloxy members, are gives sharp melting point and directly convert to isotropic mesophase whereas n-butyloxy to n-decyloxy members are nematogens. The higher n-alkoxy derivatives viz. n-decyloxy and n-hexadecyloxy, exhibit an additional smectic C phase along with nematic mesophase, which can be attributed to the increase in alkoxy chain length at one end. It is consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus [20], Gray and Goodby [21]. In series -B, where pyridyl ring as terminal group and (–CH=N–NH–CO–) linkage as spacer group with ester linkage. Compound of series-B are mesomorphic in nature. n-heptyloxy derivative shows Sm C mesophase and n-dodecyloxy and n-tetradecyloxy derivatives shows Sm A mesophase along with nematic phase. A nematic marble texture was first observed when it was cooled down from the isotropic phase and upon further cooling the texture characteristic of nematic phase has gradually changed to a phase identified as Sm A phase. All the compounds exhibit enantiotropic behavior. The appearance of Sm A phase is found to conform to earlier reported Schiff base – ester [22]. From n-methyloxy to n-butyloxy derivatives melting peaks are sharp and no mesomorphism. In both the series melting point decreasing with increasing length of alkoxy chain. One of the noticeable features is that the clearing temperature of compounds of series-A are considerably higher than compounds of series-B. This information indicates that the introduction of hydroxy group at the *ortho* position in the aldehyde fragment increases the degree of anisotropy of the molecular polarizability of compounds in both the series and hence increases the degree of molecular order, causing the smectic phase to be more stable [23]. Structural feature which has been varied in the dimeric architecture is the type of linking group between the spacer and mesogenic units including ethers [24], esters [25], thioesters [26] and thioethers [27]. The family of Schiff's bases exhibiting liquid crystalline behavior offers wide scope [28,29]. In series-B the presence of an additional amino group in the hydrazides causes delocalization of electrons with subsequent changes in energy level associated with the carbonyl oxygen which acts as donor in acid amides. The hydrazone derivatives are used as fungicides and in the treatment of diseases such as tuberculosis, leprosy and mental disorders [30]. The remarkable biological activity of acid hydrazides, R–CO–NH–NH_2, their corresponding hydrazones R–CO–NH–N=CH–R′ present in the living system have offered significant interest in recent years [12]. The remarkable biological activity of acid hydrazides R–CO–NH–NH_2, a class of Schiff base, their corresponding aroylhydrazones R–CO–NH–N=CH–R′ and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest in the past [31,32]. In the past many compounds containg ester-Schiff's base central linkage shows mesomorphism [18]. Ester derivatives are more stable compound to Schiff's base derivatives.

TABLE 1 Transition Temperature of Series-A

		Transition temperature °C		
Compounds	R = n alkoxy	SmC	N	I
A_1	Methyl	–	–	289
A_2	Ethyl	–	–	285
A_3	Propyl	–	–	279
A_4	Butyl	–	202	263
A_5	Pentyl	–	189	247
A_6	Hexyl	–	177	233
A_7	Heptyl	–	166	217
A_8	Octyl	–	156	199
A_{10}	Decyl	–	147	188
A_{12}	Dodecyl	109	141.14	173
A_{14}	Tetradecyl	86	132	160
A_{16}	Hexadecyl	72	124.92	146

Note: Sm C, smectic C; N, nematic; I, isotropic.

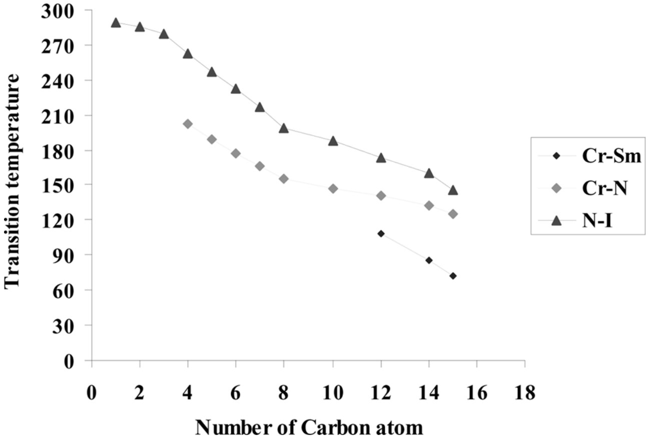


FIGURE 1 The phase behavior of series-A compounds.

In series-A twelve compounds have been synthesized and their mesogenic properties are evaluated. All the compounds synthesized exhibit enantiotropic smectic C and nematic mesophase. For series-A transition temperature are recorded in Table 1 and plot of transition temperatures against the number of carbon atom in the alkoxy chain (Fig. 1) show steady fall in N-I and Sm C-N transitions.

In series-B all the twelve members synthesized exhibit enantiotropic nematic mesophase. Smectic-C mesophase appears for the

TABLE 2 Transition Temperature of Series-B

		Transition temperature °C		
Compounds	R = n alkoxy	Sm	N	I
B_1	Methyl	–	–	238
B_2	Ethyl	–	–	231
B_3	Propyl	–	–	227
B_4	Butyl	–	–	215
B_5	Pentyl	–	183	206
B_6	Hexyl	–	174	198
B_7	Heptyl	129[†]	161	192
B_8	Octyl	116	149	187
B_{10}	Decyl	99[*]	139	183.59
B_{12}	Dodecyl	85	102	180
B_{14}	Tetradecyl	77[*]	83	178.01
B_{16}	Hexadecyl	62	70	162

Note: [†], Sm C; [*]Sm A; N, nematic; I, isotropic.

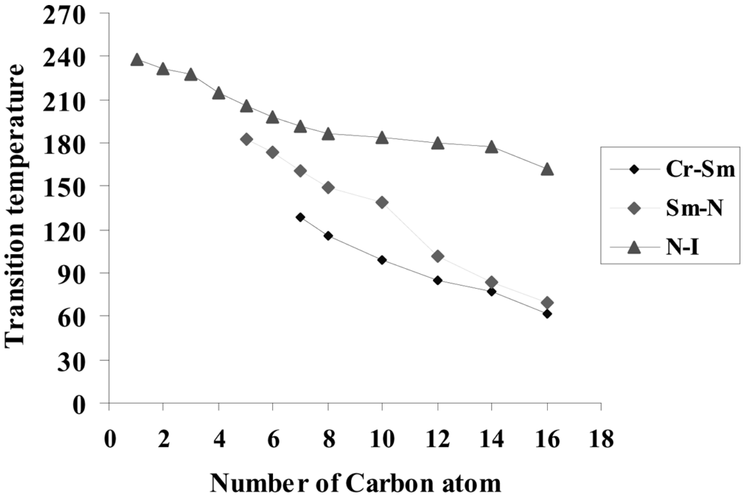


FIGURE 2 The phase behavior of series-B compounds.

n-heptyloxy derivative, but n-decyloxy and n-tetradecyloxy derivative shows Smectic A mesophase as an enantiotropic phase. The transition temperatures are recorded in Table 2. The entire homologous series-B exhibit mesomorphism. The plot of transition temperature against the number of carbon atom in the alkoxy chain (Fig. 2) shows a smooth falling tendency for nematic-isotropic transition temperatures throughout the series. Series-B also exhibit falling tendency of Sm-N

TABLE 3 DSC Data for Series–A and B Compounds

Series	Compound	Transition	Peak Temp. (Microscopic temp.) °C	ΔH Jg^{-1}	ΔS $Jg^{-1}K^{-1}$
A	A_{10}	Cr-N	147	32.04	0.076
		N-I	173	83.88	0.188
	A_{16}	Cr–Sm C	72	6.82	0.019
		Sm C-N	124.92	11.85	0.029
		N-I	147	13.94	0.033
B	B_{10}	Cr–Sm A	99	47.83	0.128
		Sm A-N	139	67.15	0.162
		N-I	183.59	88.41	0.193
	B_{14}	Cr–Sm A	77	37.33	0.106
		Sm A–N	83	40.24	0.113
		N–I	178.01	86.30	0.191

Note: Cr, crystal; SmA, smactic A; SmC, smectic C; N, nematic; I, isotropic.

TABLE 4 Different Transition Temperatures and Range of Mesophases Observed in Series A and B

Series	Compound	SmC	N	I	Sm-N mesophase range (°C)	N-I mesophase range (°C)
A	n = 14	86	132	160	46	28
B	n = 14	77	83	178.01	6	104.01

transition temperatures for higher homologous. Table 3 shows the phase transition temperatures, associated enthalpy (ΔH) and molar entropy (ΔS) for compound of series-A (A_{10}, A_{16}) and series-B (B_{10},B_{14}). Enthalpy values of the various transitions agree well with the existing related literature values [33].

Table 4 shows the comparison of Sm-N and N-I transition temperature of compound n = 14, series A, and structurally related compounds n = 14, series B. The Sm-N mesophase range of compound n = 14 (series A) is higher by 40°C, respectively, when compared with compound n = 14 (series B). The N-I transition temperature of compound, series-B, is lower by 76.01°C, respectively, when compared with compound 14 (n = 14, series B). The two series differs by terminal heterocyclic ring (series-A contain 1,2,4-triazole and series-B contain pyridyl ring) as well as linking group. Ester linkage is common in both the series but another linkage is different (series -A contain Schiff base linkage and series -B contain hydrazone linkage). The thermal stability of series-B is lower than of series -A due to hydrazone linkage and terminal pyridyl ring.

4. CONCLUSION

In this article we have presented the synthesis and characterization of two new mesogenic homologous series of ester-azomethine derivatives containing 1,2,4-triazole and isonicotinic acid hydrazide heterocyclic ring as terminal group and -OH group as lateral substitution. Ester derivatives are more stable compound to Schiff's base derivatives. Compound of series -A shows Sm C mesophase along with nematic phase as it is a short two phenyl rings system, where as series-B exhibit nematic as well as Sm C and Sm A mesophases due to the presence of –CH=N–NH–CO– linkage and terminal pyridyl ring. From the study of transition temperature of both the series we can assume that the introduction of hydroxy group at the *ortho* position in the aldehyde fragment increases the degree of anisotropy of the molecular polarizability of compounds in both the series. The compound exhibit mesomorphic properties with good thermal stabilities if properly designed.

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