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Synthesis and Characterization of Liquid Crystalline Materials Incorporating the Novel 4-Amino-1,2,4-triazole and Isonicotinic Acid Hydrazone Moiety

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We report 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 viz. 4-[(4H-1,2,4-triazol-4-ylimino) methyl] phenyl 4-alkoxybenzoate and 4-(2-isonicotinoylcarbonohydrazono-nyl) phenyl 4-alkoxybenzoate. Both series have been characterized by elemental analysis, FT-IR, mass spectrometry, ^1H -NMR, and ^{13}C -NMR. Phase transition temperatures and the thermal parameters were obtained from differential scanning calorimetry (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 and the higher member of both series shows smectic phase. The use of isonicotinic acid and triazole as a terminal group has a very dramatic effect on the melting and clearing points. The mesomorphic behavior has been analyzed in terms of structural property relationship.

Keywords: ester; isonicotinic acid hydrazone; mesophase; nematic phase; smectic phase; schiff base; triazole

INTRODUCTION

Liquid crystals containing heterocyclic units are of crucial importance in the design and synthesis of novel advanced functional materials, where liquid crystalline phases, polarity, geometry, luminescence, and other properties of the molecule may be varied through the introduction of heteroatoms [1–3]. Furthermore, luminescent liquid crystals

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are of interest since their self-organizing properties can be exploited to improve device performance and to achieve linearly polarized electroluminescence [4]. Several liquid crystalline compounds containing a heterocyclic ring have been reported [4–10]. Mesogenic compounds containing thiazole have recently been reported [11]. 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 recent years, the great scientific and practical interest in liquid crystals has generated an increasing requirement for compounds with specific properties. Therefore, chemists are still searching for new structural units and structural variations in order to find compounds more capable to meet present requirements since heterocyclic compounds can be extremely useful in influencing the dielectric anisotropy, viscosity, birefringence, Smectic C (SmC) ranges positively [12].

Recently we have focussed our attention on the extent to which different heteroatoms incorporated in heterocyclic liquid crystal units influence liquid crystalline properties. Hence, we have introduced 4-amino-1,2,4-triazole and isonicotinic acid hydrazide as terminal groups and synthesized two homologues series, viz., 4-[(4*H*-1,2,4-triazol-4-ylimino) methyl] phenyl 4-alkoxybenzoate (Series A) and 4-(2-isonicotinoylcarbonohydrazonoyl) phenyl 4-alkoxybenzoate (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 an electron donor in acid amides.

EXPERIMENTAL

Reagents and Technique

The solvents were used after purification by the standard methods, described in the literature [13]. 4-Hydroxybenzoic acid, p-hydroxybenzaldehyde, and DMAP (4-dimethylaminopyridine) were obtained from Merck (Germany). 4-Amino-1,2,4-triazole, isonicotinic acid hydrazide, and dicyclohexylcarbodiimide (DCC) were purchased from Fluka Chemie (Switzerland). Elemental analyses (C, H, N) were performed at Central Drug Research Institute (CDRI), Lucknow. Infrared spectra were recorded with a Perkin-Elmer 2000 FT-IR spectrophotometer in the wave number range 4000–400 cm⁻¹ with samples embedded in

KBr discs. ^1H NMR spectra of the compounds were recorded with a Jeol-GSX-400 instrument using CDCl_3 as a solvent and TMS as an internal reference at Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai. ^{13}C NMR spectra of the compound were recorded with Bruker Avance II 400 NMR spectrometer, SAIF, Chandigarh. Mass spectra (GC-MS) of the compounds were recorded at Department of Chemistry, Saurashtra University, Rajkot (Gujarat). Thin-layer chromatography (TLC) analyses were performed using aluminium-backed silica-gel plates (Merck 60 F524) and examined under shortwave 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 shown by 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.

Synthesis

Synthesis of 4-n-Alkoxy Benzoic Acid [11]

This was prepared by the reported method.

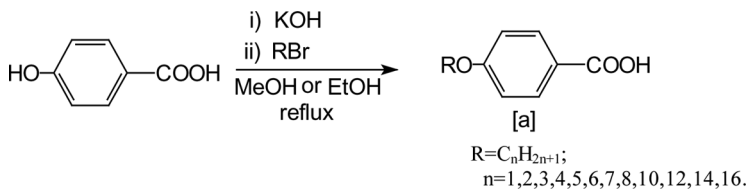
Synthesis of 4-[(4-n-Alkoxy-benzyloxy) Benzaldehyde [11]

To a mixture of 4-n-alkoxybenzoic acid (1 mmol) and p-hydroxybenzaldehyde (1 mmol) in 150 ml of distilled dichloromethane, 0.1 mmol of dimethyl aminopyridine (DMAP) was added under an argon atmosphere. The mixture was cooled in an ice-water bath, and after 10 min, 1 mmol of DCC was 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.

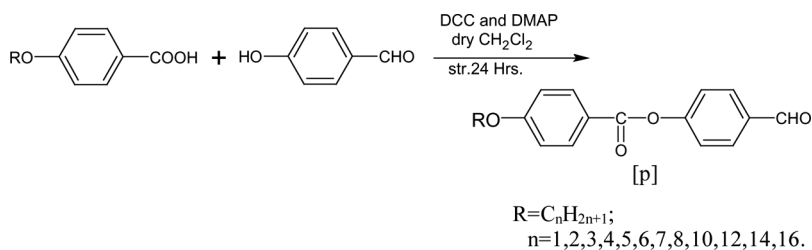
Synthesis of Compound 3A and 3B

A. *Synthesis of 4-[(4H-1,2,4-triazol-4-ylimino) methyl] Phenyl 4-alkoxybenzoate [14,15].* A mixture of 1 mmol of 4-[(4-n-alkoxybenzyloxy)benzaldehyde and 1 mmol of 4-amino-1,2,4-triazole, and three drops of acetic acid in absolute ethanol were 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.

Synthesis of 4-n-Alkoxybenzoic Acid

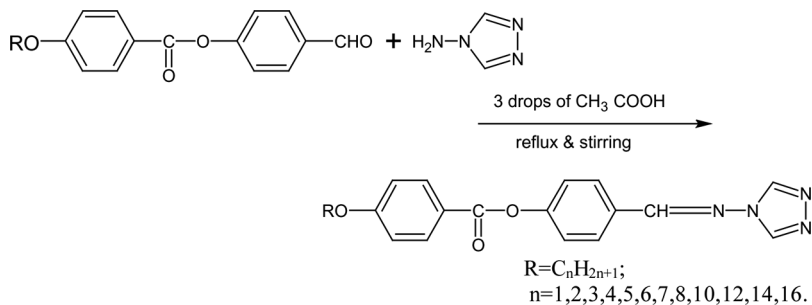


Synthesis of 4-Formylphenyl 4-Alkoxybenzoate

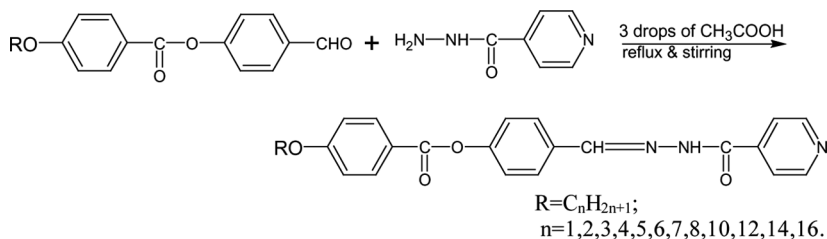


Synthesis of Compound 3A and 3B

Synthesis of 4-[(4H-1,2,4-Triazol-4-ylimino) methyl]Phenyl 4-Alkoxybenzoate(3A)



Synthesis of 4-(2-Isonicotinoylcarbonohydrazonoyl) Phenyl 4-Alkoxybenzoate(3B)



Data**Compound A₁₄:**

Yield 77%. M.P.205°C. Calc.for C₃₀H₄₀O₃N₄; C, 71.42; H, 7.93; N, 11.11%; found: C, 71.32; H, 7.83; N, 11.15. EI-MS m/z (rel.int %): 504(2) (M)⁺. IR (KBr): Vmax/cm⁻¹ 2918, 2852 cm⁻¹(C–H aliphatic), 1731 cm⁻¹(C=O of ester), 1650 cm⁻¹ (CH=N), 1585 cm⁻¹(C=C aromatic), 1281 cm⁻¹(C–O), 1589, 1601 cm⁻¹(C=N, triazole). ¹H NMR (CDCl₃): δ 0.88–0.89 ppm (s, CH₃), 1.26–1.49 ppm (m, CH₂), 4.03–4.06 ppm (t, OCH₂), 6.96–8.16 ppm (m, Ar-H), 8.79–8.90 ppm (s, CH=N), 8.23 ppm (s, triazole-H). ¹³C NMR (CDCl₃), 14.52 ppm (CH₃), 22.95–34.00 ppm (CH₂), 108.00–162.20 ppm (Ar-C), 160.15 ppm (C=N), 172.29 ppm (C=O ester), 141.00–162.00 ppm (triazole-C).

B. Synthesis of 4-(2-Isonicotinoylcarbonohydrazonoyl) Phenyl 4-alkoxybenzoate [14,15]. A mixture of 1 mmol of 4-[(4-n-alkoxybenzyloxy)benzaldehyde and 1 mmol of isonicotinic acid hydrazide, and three drops of acetic acid in absolute ethanol were refluxed 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 B₁₄:**

Yield 76%. M.P.157°C. Calc.for C₃₄H₄₃O₄N₃; C, 73.24; H, 7.71; N, 7.54%; found: C, 73.20; H, 7.69; N, 7.68. EI-MS m/z (rel.int %): 557(1) (M)⁺. IR (KBr): Vmax/cm⁻¹ 2918,2850 cm⁻¹(C-H aliphatic), 1730 cm⁻¹ (C=O of ester), 1652 cm⁻¹(CH=N), 1605 cm⁻¹ (C=C aromatic), 1272 cm⁻¹ (C–O), 1665 cm⁻¹ (C=O of hydrazone linkage), 3176–3270 cm⁻¹ (NH) 1566,1570 cm⁻¹ (C=N, pyridyl ring). ¹H NMR (CDCl₃): δ 0.86–0.89 ppm (s, CH₃), 1.32–1.84 ppm (m, CH₂), 4.04–4.07 ppm (t, OCH₂), 6.96–8.07 ppm (m, Ar-H), 8.49–8.77 ppm (s, CH=N), 11.74 ppm (s, NH), 8.76–8.77 ppm (s, pyridyl-H). ¹³C NMR (CDCl₃), 14.32 ppm (CH₃), 23.00–34.70 ppm (CH₂), 111.00–163.00 ppm (Ar-C), 159.00 ppm (C=N), 172 ppm (C=O ester), 154.00–167.00 ppm (–C=O–NH–), 150.00 ppm (pyridyl-C).

RESULTS AND DISCUSSION

The elemental analyses of series A and B compounds synthesized above are shown in Tables 1 and 2. The observed values are in well agreement with theoretical values indicating structure of respective compounds. The representative compounds are subjected for ¹H-NMR study. The ¹H-NMR data are given in Tables 3 and 4.

TABLE 1 Data Table of the Elemental Analysis for the Series A

Compound	Molecular formula	Molecular weight g/mol	M.P. (°C)	% yield	Color	Analysis % found (calcd.)		
						C	H	N
1	C ₁₇ H ₁₄ N ₄ O ₃	322	243	80	Off white	63.24 (63.35)	4.39 (4.34)	17.28 (17.39)
2	C ₁₈ H ₁₆ N ₄ O ₃	336	239	78	Off white	64.23 (64.28)	4.55 (4.76)	16.62 (16.66)
3	C ₁₉ H ₁₈ N ₄ O ₃	350	238	81	Off white	65.01 (65.14)	5.17 (5.14)	15.89 (16.00)
4	C ₂₀ H ₂₀ N ₄ O ₃	364	232	85	Off white	65.85 (65.93)	5.41 (5.49)	15.10 (15.17)
5	C ₂₁ H ₂₂ N ₄ O ₃	378	229	76	Off white	66.59 (66.66)	5.74 (5.82)	14.69 (14.81)
6	C ₂₂ H ₂₄ N ₄ O ₃	392	226	74	Off white	67.26 (67.34)	6.01 (6.12)	14.22 (14.28)
7	C ₂₃ H ₂₆ N ₄ O ₃	406	219	79	Off white	67.91 (67.98)	6.32 (6.40)	13.71 (13.79)
8	C ₂₄ H ₂₈ N ₄ O ₃	420	215	83	Off white	68.50 (68.57)	6.59 (6.66)	13.20 (13.33)
10	C ₂₆ H ₃₂ N ₄ O ₃	448	208	82	Off white	69.50 (69.64)	7.03 (7.14)	12.57 (12.50)
12	C ₂₈ H ₃₆ N ₄ O ₃	476	207	82	Off white	70.52 (70.58)	7.51 (7.56)	11.72 (11.76)
14	C ₃₀ H ₄₀ N ₄ O ₃	504	205	77	Off white	71.32 (71.42)	7.83 (7.93)	11.15 (11.11)
16	C ₃₂ H ₄₄ N ₄ O ₃	532	191	79	Off white	72.11 (72.18)	8.20 (8.27)	10.45 (10.52)

TABLE 2 Data Table of the Elemental Analysis for the Series B

Compound	Molecular formula	Molecular weight g/mol	M.P. (°C)	% yield	Color	Analysis % found (calcd.)		
						C	H	N
1	C ₂₁ H ₁₇ N ₃ O ₄	375	201	71	Off white	67.11 (67.20)	4.45 (4.53)	11.19 (11.20)
2	C ₂₂ H ₁₉ N ₃ O ₄	389	195	70	Off white	67.75 (67.86)	4.50 (4.58)	10.60 (10.79)
3	C ₂₃ H ₂₁ N ₃ O ₄	403	192	74	Off white	68.40 (68.48)	5.25 (5.21)	10.31 (10.42)
4	C ₂₄ H ₂₃ N ₃ O ₄	417	190	76	Off white	69.13 (69.06)	5.48 (5.51)	10.00 (10.07)
5	C ₂₅ H ₂₅ N ₃ O ₄	431	184	71	Off white	69.50 (69.60)	5.78 (5.80)	9.67 (9.74)
6	C ₂₆ H ₂₇ N ₃ O ₄	445	177	80	Off white	70.01 (70.11)	5.95 (6.06)	9.59 (9.65)
7	C ₂₇ H ₂₉ N ₃ O ₄	459	176	81	Off white	70.47 (70.58)	6.22 (6.31)	9.50 (9.53)
8	C ₂₈ H ₃₁ N ₃ O ₄	473	169	76	Off white	71.08 (71.03)	6.50 (6.55)	8.86 (8.87)
10	C ₃₀ H ₃₅ N ₃ O ₄	501	167	83	Off white	71.79 (71.85)	6.90 (6.98)	8.30 (8.38)
12	C ₃₂ H ₃₉ N ₃ O ₄	529	161	75	Off white	72.48 (72.58)	7.37 (7.37)	7.98 (7.93)
14	C ₃₄ H ₄₃ N ₃ O ₄	557	157	74	Off white	73.29 (73.24)	7.69 (7.71)	7.68 (7.54)
16	C ₃₆ H ₄₇ N ₃ O ₄	585	152	70	Off white	73.76 (73.84)	8.01 (8.03)	7.06 (7.17)

TABLE 3 ^1H -NMR Spectral Data for the Series A

Sr. No.	Compound	$-\text{CH}_3$ proton of <i>n</i> -alkyl chain	$-\text{CH}_2$ proton of <i>n</i> -alkyl chain	$-\text{CH}_2\text{O}$ proton of alkoxy	Phenyl multiplate	CH=N	Remarks
1	A ₄	0.90 (t)	1.23–1.49 (m)	4.02–4.06 (t)	6.98–8.16 (m)	9.02 (s)	8.26 (Triazole-H)
2	A ₈	0.91 (t)	1.23–1.48 (m)	4.02–4.06 (t)	7.00–8.17 (m)	9.02 (s)	8.25 (Triazole-H)
3	A ₁₂	0.91 (t)	1.23–1.49 (m)	4.02–4.06 (t)	7.00–8.17 (m)	9.02 (s)	8.26 (Triazole-H)
4	A ₁₄	0.88 (t)	1.26–1.49 (m)	4.03–4.06 (t)	6.96–8.16 (m)	8.90 (s)	8.23 (Triazole-H)

In continuation with our earlier work on heterocyclic liquid crystals with unconventional molecular structures, two homologous series that have 1,2,4-triazole and pyridyl heterocyclic ring as terminal group, such as 4-[(4*H*-1,2,4-triazol-4-ylimino)methyl] phenyl 4-alkoxybenzoate and 4-(2-isonicotinoylcarbonohydrazonoyl) phenyl 4-alkoxybenzoate, have been synthesized. Conventional thermotropic liquid crystals consist of anisotropic molecules (mesogens) that are either rod-shaped (calamitic) or disc-shaped (discotic). The thermal behavior of these two types of liquid crystals is generally well understood and therefore they have been recognized as materials for many practical applications, especially in liquid crystal display devices. The common structural features of the compounds are that they consist

TABLE 4 ^1H -NMR Spectral Data for the Series B

Sr. No.	Compound	$-\text{CH}_3$ proton of <i>n</i> -alkyl chain	$-\text{CH}_2$ proton of <i>n</i> -alkyl chain	$-\text{CH}_2\text{O}$ proton of alkoxy	Phenyl multiplate	CH=N	–NH–	Remarks
1	B ₄	0.86 (t)	1.32–1.84 (m)	4.03–4.07 (t)	7.00–8.13 (m)	8.49 (s)	11.70	8.76–8.77 (pyridyl-H)
2	B ₅	0.86 (t)	1.33–1.83 (m)	4.03–4.07 (t)	7.00–8.13 (m)	8.49 (s)	11.73	8.76–8.77 (pyridyl-H)
3	B ₁₀	0.87 (t)	1.33–1.84 (m)	4.03–4.07 (t)	6.99–8.13 (m)	8.49 (s)	11.76	8.70–8.75 (pyridyl-H)
4	B ₁₂	0.87 (t)	1.31–1.83 (m)	4.03–4.07 (t)	6.96–8.10 (m)	8.49 (s)	11.70	8.76–8.77 (pyridyl-H)
5	B ₁₄	0.86 (t)	1.32–1.84 (m)	4.04–4.07 (t)	6.96–8.07 (m)	8.49 (s)	11.74	8.76–8.77 (pyridyl-H)

of two phenyl rings 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. Table 5 shows the phase transition temperatures and associated enthalpy (ΔH) for compound of series A (A_{14} , A_{16}) and series B (B_{10} , B_{14}). Enthalpy values of the various transitions agree well with the existing related literature values [16].

All the compounds of series A and B (except B_1 , B_2 , and B_3) exhibit enantiotropic mesomorphism, on ordinary slides. The melting peaks are sharp. In series A, the lower members show nematic phase whereas the higher member of the series shows SmC phase along with nematic phase. Only A_{16} shows SmC mesophase at very low temperature. On cooling the isotropic liquid, small droplets appear which coalesce to a classical schlieren texture characteristic of the nematic phase. It is consistent with the assignment of each mesophase type using the classification systems reported by Gray and Goodby [17]. The textures of the SmC phase for compounds of series A is shown in Figure 1. Transition temperatures are recorded in Table 6 and plot of transition temperatures against the number of carbon atom in the alkoxy chain (Fig. 2) shows steady fall in N-I and Sm-N transitions. In series B, n-methoxy to n-propyloxy does not show mesomorphism. First, three compounds in series B have sharp melting point due to short alkoxy chain. B_4 to B_{16} exhibit an enantiotropic nematic mesophase. A smectic mesophase appears from the n-dodecyloxy derivative,

TABLE 5 DSC Data for Series A and B Compounds

Series	Compound	Transition	Peak temp. (Microscopic temp.) °C	ΔH Jg ⁻¹
A	A_{14}	Cr-SmC	62.82 (63)	52.34
		SmC-N	142 (143)	59.00
		N-I	205 (205)	54.50
	A_{16}	Cr-SmC	30 (32)	48.27
		SmC-N	128 (129)	50.83
		N-I	191 (192)	51.37
B	B_{10}	Cr-SmC	129 (131)	49.65
		SmC -N	159 (159)	39.00
		N-I	167 (166)	33.54
	B_{14}	Cr-SmC	100.81 (101)	46.30
		SmC-N	143.84 (144)	37.82
		N-I	157.06 (157)	32.52

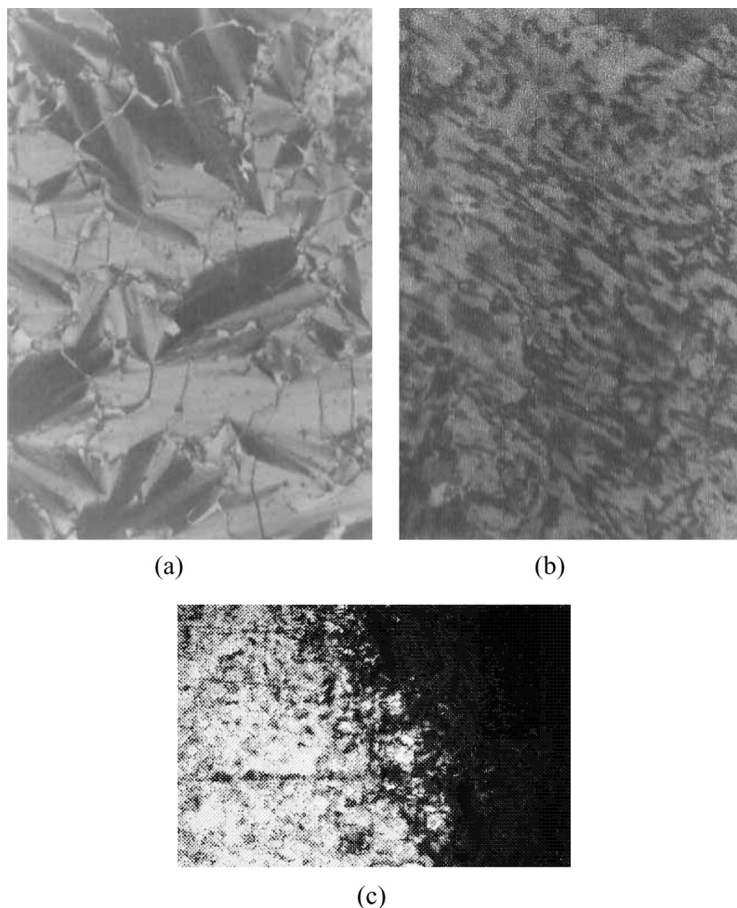


FIGURE 1 (a) Fan texture of the SmC phase of A₁₆ at 30°C; (b) optical photomicrograph of compound B₁₄ exhibiting Nematic Phase; (c) SmC Phase of C₁₀ at 131°C.

as enantiotropic behavior and remains up to the n-hexadecyloxy derivative. The texture of the nematic phase for compounds of series B is shown in Figure 1. The transition temperatures are recorded in Table 7. The plot of transition temperature against the number of carbon atom in the alkoxy chain (Fig. 3) shows a smooth falling tendency for nematic-isotropic transition temperatures throughout the series. Series B also exhibit falling tendency of Sm-N transition temperatures for the higher homologous. From the plot of transition temperatures against the number of carbon atoms (Figs. 2 and 3), it can be noticed

TABLE 6 Transition Temperature of Series A

Compound	R = <i>n</i> -alkoxy	Cr		SmC		N		I
1	1	•	—	•	226	•	243	•
2	2	•	—	•	213	•	239	•
3	3	•	—	•	209	•	238	•
4	4	•	—	•	204	•	232	•
5	5	•	—	•	196	•	229	•
6	6	•	—	•	189	•	226	•
7	7	•	—	•	177	•	219	•
8	8	•	—	•	162	•	215	•
9	10	•	—	•	164	•	208	•
10	12	•	76	•	166	•	207	•
11	14	•	63	•	142	•	205	•
12	16	•	30	•	128	•	191	•

Note: SmC - Smectic C; N - nematic; I - isotropic.

that Cr-M transition temperature decreases with increase in the length of terminal alkoxy chain. However, the odd-even effect of this series is not so pronounced. This is in agreement with the data reported earlier for such homologous series [18].

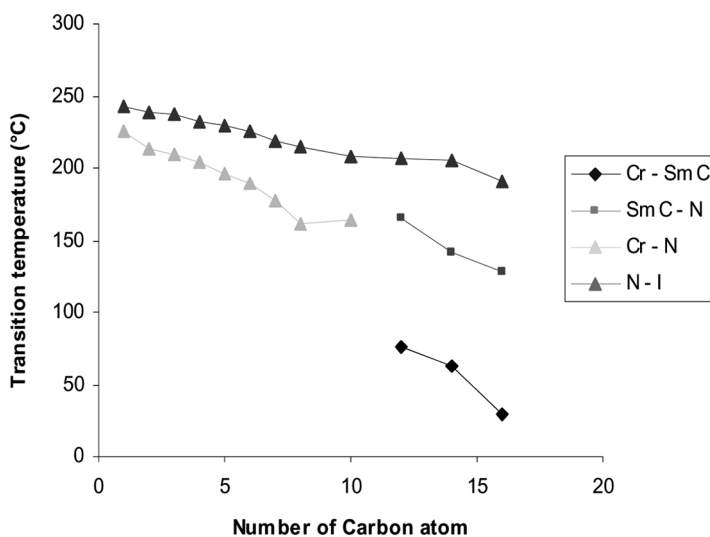


FIGURE 2 Mesomorphic behavior as a function of the number of carbon atoms (*n*) in the terminal alkoxy chain for series A.

TABLE 7 Transition Temperature of Series B

Compound	R = <i>n</i> -alkoxy	Cr		SmC		N		I
1	1	•	–	•	–	•	201	•
2	2	•	–	•	–	•	195	•
3	3	•	–	•	–	•	192	•
4	4	•	–	•	82	•	190	•
5	5	•	–	•	98	•	184	•
6	6	•	–	•	121	•	177	•
7	7	•	–	•	129	•	176	•
8	8	•	–	•	142	•	169	•
9	10	•	129	•	159	•	167	•
10	12	•	113	•	132	•	161	•
11	14	•	101	•	144	•	157	•
12	16	•	87	•	139	•	152	•

Note: SmC - Smectic; N - nematic; I - isotropic.

DSC is a valuable method for the detection of phase transition. It yields quantitative results; therefore, we may draw conclusions concerning the nature of the phases that occur during the transition. In the present study, enthalpies of two derivatives of series A and

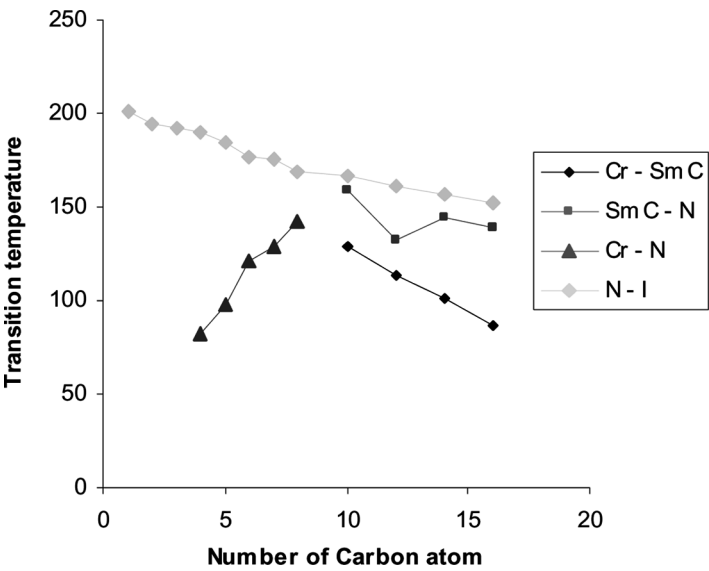


FIGURE 3 Mesomorphic behavior as a function of the number of carbon atoms (*n*) in the terminal alkoxy chain for series B.

series B were measured by DSC. Enthalpy values of the various transitions agree well with the existing related literature values [19] which helps to further confirm the mesophase type. There have been a variety of compounds reported with liquid crystalline properties, but heterocyclic moieties [20, 21] 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 [22]. In our present study we introduced two new heterocyclic moieties, one is 1,2,4-triazole and the second is isonocotinic acid hydrazide. Isotropic temperature of compound in series A is higher than the compound of series B which is due to hydrozone linkage. Hydrazone linkage is less stable than azomethine linkage. Conjugation in compound of series A has also affected the transition temperature. In the past, many compounds contain ester-Schiff's base central linkage shows mesomorphism [11,23]. Table 8 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 SmC-N mesophase range of compound $n = 14$ (series A) is higher by 36°C , when compared with compound $n = 14$ (series B). The N-I transition temperature of compound of, series B, is lower by 50°C , when compared with compound 14 ($n = 14$, series B). The two series differ by terminal heterocyclic ring (series A contains 1,2,4-triazole and series B contains pyridyl ring) as well as linking group. Ester linkage is common in both the series but another linkage is different (series A contains Schiff base linkage and series B contains hydrazone linkage).

Thermal Study

Thermal properties of both series were investigated by POM and DSC. The polarized microphotographs and the typical DSC thermogram for the compounds under study are shown in chart Figures 1, 4, and 5, respectively. In order to aid an analysis of their mesomorphic

TABLE 8 Different Transition Temperatures and Range Mesophases Observed in Series A and B

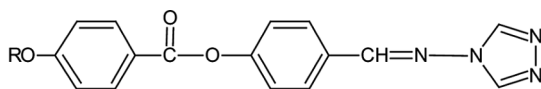
Series	Compound	SmC	N	I	Sm-N mesophase range ($^{\circ}\text{C}$)	N-I mesophase range ($^{\circ}\text{C}$)
A	N = 14	63	142	205	79	63
B	N = 14	101	144	157	43	13

Note: SmC - Smectic C; N - nematic; I - isotropic.

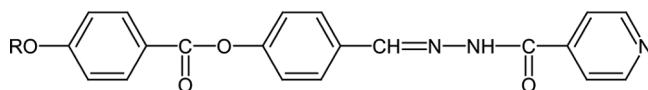
behavior, the target compounds were grouped into two sets, series A and B; for compounds where the [1,2,4]-triazole heterocycle was placed at the end of the rigid core (series A). The DSC thermograms for this compound (A_{14}) are shown in Figure 4. On heating, the compound melts to the SmC phase at 62.82°C and goes to the nematic phase at 142°C just below the clearing point at 205°C , at a rate of $10^\circ\text{C}/\text{min}$. The enthalpy value of A_{14} is mentioned in Table 5. A typical thermogram obtained for compound B_{14} by DSC analysis is presented in Figure 5. On heating, the compound melts at 100.81°C to the SmC phase and goes to nematic phase at 143.84°C and at the last an isotropic liquid at 157.06°C . The same pattern is observed on cooling in both cases. Compounds of both series are enantiotropic in nature. DSC studies further reported the appearance of an enantiotropic nematic phase in all the compounds studied.

The present series A and B are compared with other structurally related compounds to evaluate the effect of terminally situated cyclohexyl ring and naphthalene ring.

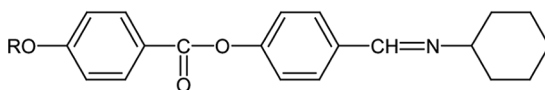
The present homologues series A and B are compared with structurally related series.



SERIES A

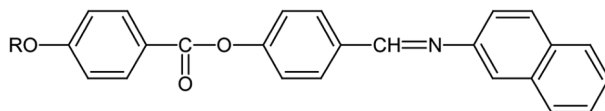


SERIES B



SERIES C

R = C_4 to C_{16}



SERIES D

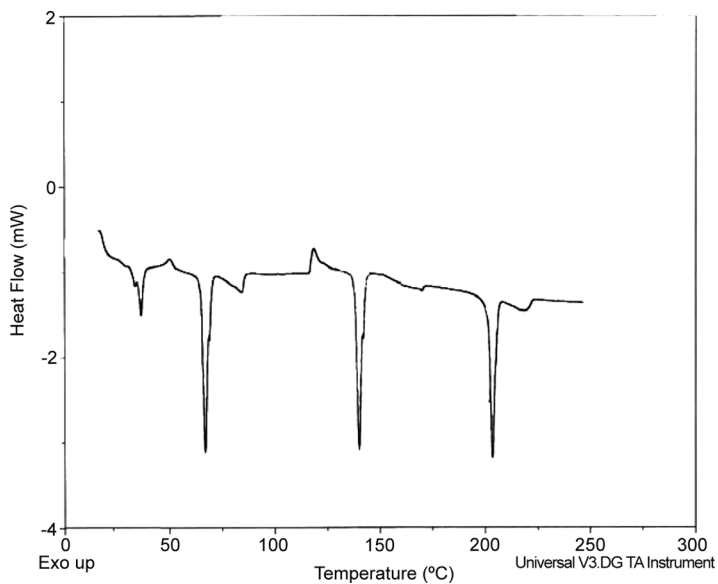


FIGURE 4 DSC thermogram for the compounds A₁₄.

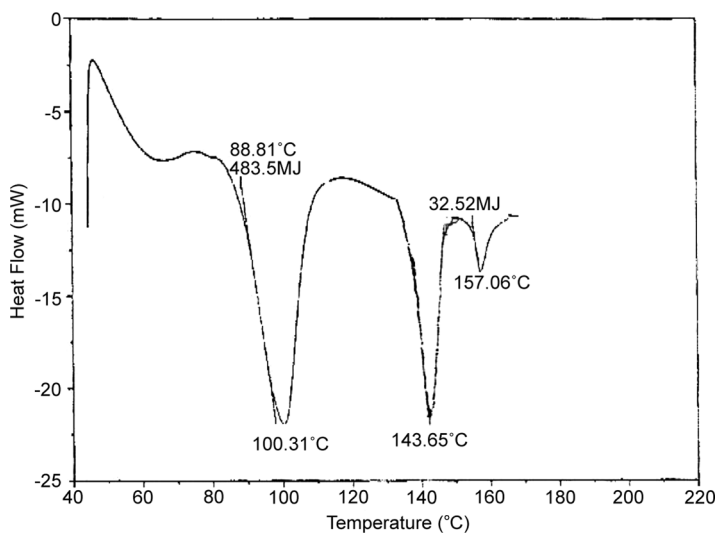


FIGURE 5 DSC thermogram for the compounds B₁₄.

TABLE 9 Melting Points of Series C

<i>n</i> -alkoxy	M.P.
Butyl	140
Hexyl	140
Heptyl	142
Octyl	136
Decyl	133
Tetradecyl	127
Hexadecyl	115

Comparison of series A and series B with series C, respectively, give 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 B are mesogenic (Tables 6 and 3) whereas series C is nonmesogenic (Table 9) in nature [24]. This is because of cyclohexane moieties nonconductive for mesomorphism and saturated nonheterocyclic ring. Series A and series B are compared with related series D. All the members of series D exhibit an enantiotropic nematic phase. The SmC mesophase commences from the *n*-heptyloxy and *n*-octyloxy derivative as a monotropic phase. *n*-Decyloxy to *n*-hexadecyloxy members exhibit an enantiotropic SmC phase [25], whereas in series A *n*-dodecyloxy to *n*-hexadecyloxy exhibit SmC phase along with enantiotropic nematic phase. Thermal stabilities of the compounds of series D is greater than compounds of

TABLE 10 Transition Temperature of Series D

Compounds	R = <i>n</i> -alkoxy	Cr		SmC		N		I
1	1	•	–	•	142	•	270	•
2	2	•	–	•	137	•	167	•
3	3	•	–	•	129	•	254	•
4	4	•	–	•	133	•	249	•
5	5	•	–	•	128	•	239	•
6	6	•	–	•	116	•	235	•
7	7	•	(85)	•	120	•	225	•
8	8	•	(94)	•	115	•	220	•
9	10	•	109	•	141	•	209	•
10	12	•	106	•	157	•	198	•
11	14	•	101	•	162	•	194	•
12	16	•	95	•	155	•	187	•

Note: Values in parantheses indicate monotropy.

series A and B; this is because the naphtha ring is more conducive for mesomorphism and highly resonating in nature (Table 10).

CONCLUSION

We have described the synthesis of new heterocyclic ring based liquid crystalline compounds which exhibit enantiotropic mesomorphism. We have noticed that the molecules generated as highly ordered molecular aggregations by introduction of the terminal heterocyclic ring. The comparison of both our series with nonheterocyclic ring, the heterocyclic ring propose mesomorphism that of nonheterocyclic ring which does not have any conjugation. Thermal stabilities of series A is also high compared with series B due to triazole ring.

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