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Synthesis, Characterization, and Mesomorphic Properties of New Liquid-Crystalline Compounds involving Ester-Azomethine Central Linkages, Lateral Substitution, and a Thiazole Ring

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Synthesis, Characterization, and Mesomorphic Properties of New Liquid-Crystalline Compounds involving Ester–Azomethine Central Linkages, Lateral Substitution, and a Thiazole Ring

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In continuation with our work on liquid crystals with unconventional molecular structures, two homologous series that have 1,4-disubstitution and 1,3,4-trisubstitution in the central phenyl ring, such as 2[(4-n-alkoxy-benzyloxy) phenyl azomethine]-5-methyl thiazole and 2-[(4-n-alkoxy-benzyloxy)-2-hydroxy salicyladimine]-5-methyl thiazole, have been synthesized. They have been characterized by elemental analysis, FT-IR, ^{1}HNMR, ^{13}CNMR, and mass spectrometry. The liquid-crystalline behavior of these compounds was observed by differential scanning calorimetry (DSC) and polarizing microscopy. All the compounds of the 1,4-disubstituted series show an enantiotropic nematic phase only, whereas the compounds of the 1,3,4-trisubstituted series show smectic and nematic phases. Some mesogens with a lateral hydroxy group were also synthesized to evaluate the effect of this group on melting point, transition temperatures, and mesophase morphology.

Keywords: ester; lateral group; mesophase; nematic phase; Schiff base; smectic phase; thiazole

INTRODUCTION

Conventional thermotropic liquid crystals consist of anisotropic molecules (mesogens) that are either rod shaped (calamitic) or disc shaped (discotic) [1,2]. The thermal behavior of these two types of liquid crystals is generally well understood, and therefore they have

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been recognized as materials for many practical applications, especially in liquid-crystalline display devices [3]. A considerable number of Schiff bases derived from salicyaldehyde have been reported in the past few decades because they can give rise to either thermochromism or photochromism in the solid state [4,5]. The synthesis of liquid-crystalline compounds incorporating thiazole is of considerable interest [6,7]. Thiazoles represent a very interesting class of compound because of their wide applications in pharmaceutical, phytosanitary, analytical, and industrial aspects (e.g., as antibacterial [7], fungicide [8], anti-inflammatory [9], and anti-HIV [10] substances). It is known that 2-amino thiazole is a biologically active compound with a broad range of activity that also is an intermediate in the synthesis of antibiotics and dyes.

The lateral hydroxyl substitution of the 1,4-phenylene fragment of 5,6,7,8-tetrahydroxyquinoline cyano derivatives results in increases in melting points compared to those of the corresponding unsubstituted analogues [11]. This may be due to the enhanced axial molecular polarizability resulting from delocalization of electrons caused by intramolecular hydrogen bonding, which is possibly responsible for the monomeric density wave observed from the X-ray diffraction study of the structure of the nematic phase [11]. Similar effects caused by intramolecular hydrogen bonding have been found for other laterally hydroxyl-substituted derivatives [12]. The presence of an *ortho* hydroxyl group, for instance, has been regarded as one of the important elements favoring the existence of intramolecular hydrogen bonding (O−H . . . N and O . . . H−N) and also the tautomerism that accounts for the formation of the either enol-imine or the keto-amine tautomer [12]. In our present work, series B contains an −OH group as a lateral substitution and because of the hydroxyl group, the melting point of the compounds increases. All compounds in series B show mesomorphic properties. In each case, an enantiotropic nematic mesophase is observed in the lower members, whereas the higher members of series B (10, 12, 14, 16) show an enantiotropic smectic C phase and nematic phase. In series A, there is no lateral substitution but only the nematic phase. There is a big difference in enthalpies for both the series, shown in Table 1.

EXPERIMENTAL

Reagents and Technique

The solvents were used after purification using the standard methods described in the literature [13]. 4-Hydroxy benzoic acid, p-hydroxy

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TABLE 1 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_8	Cr–N	75.72 (76)	13.94	0.040
		N–I	92.03 (92)	6.59	0.018
	A_{16}	Cr–N	57.19 (57)	36.00	0.109
		N–I	81.23 (81)	6.47	0.018
B	B_{10}	Cr–N	92	14.95	0.162
		N–I	164	7.69	0.046
	B_{16}	Cr–Sm C	67	32.9	0.491
		Sm C–N	101	12.3	0.121
		N–I	160	18.6	0.116

Note. Cr, crystal; SmC, smectic C; N, nematic; I, isotropic.

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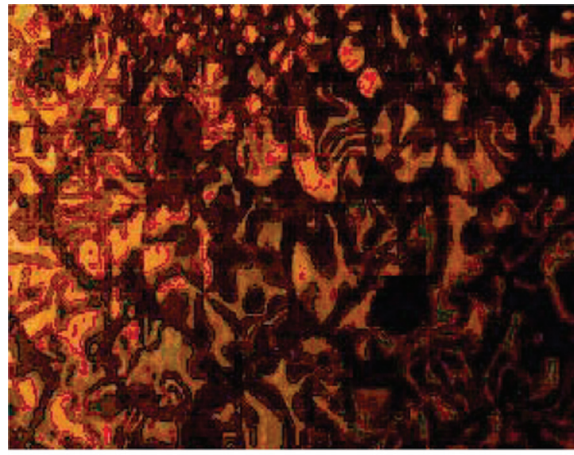
benzaldehyde, 2,4-dihydroxy benzaldehyde, and DMAP (4-dimethylaminopyridine) were obtain from Merck (Germany). 2-Amino-4-methyl thiazole and DCC (dicyclohexylcarbodiimide) were purchased from Fluka Chemie (Switzerland). Elemental analyses (C, H, N) were performed at Central Drug Research Institute (CDRI), Lucknow. Infrared spectra were recorded with a Perkin-Elmer 2000 FT-IR spectrophotometer in the frequency range 4000–400 cm^{-1} with samples embedded in KBr discs. ^{1}HNMR 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 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 Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai. 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 DSC data are shown in Table 1. 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 (Fig. 1) were observed using polarized light with crossed polarizers with the sample in a thin film sandwiched between a glass slide and cover slip.

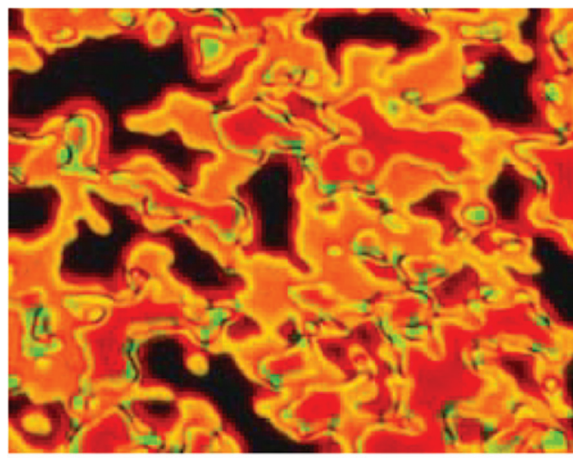
Synthesis

Synthesis of 4-n-Alkoxy Benzoic Acid [14]

This was prepared by the reported method. A mixture of 4-hydroxybenzoic acid (1 mmol) and KOH (1.5 mmol) in 250 ml of



(a)



(b)

FIGURE 1. (a) Optical photomicrograph of compound B7 exhibiting nematic Phase. (b) Optical photomicrograph of compound B14 exhibiting nematic Phase.

methanol or ethanol was stirred and heated at 70°C while 1-bromo alkane (1.02 mmol) was added slowly (1–2 h), after which the mixture was refluxed for 11–13 h. The reaction mixture was cooled to room temperature and poured into acidified crushed ice. The product obtained was filtered off and purified as reported. The molecular structures of these acids were confirmed by spectroscopic analysis and found to be in agreement with the reported data.

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Synthesis of 2-[(4-n-Alkoxy-benzyloxy)-2-X-Benzaldehyde [15,16]

To a mixture of 4-n-alkoxy benzoic acid (1 mmol) and p-hydroxy benzaldehyde (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 dicyclohexylcarbodiimide (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.

Data

Compound 10p. Yield 80%. Found: C, 75.00; H, 7.60; calc. for $C_{24}H_{30}O_4$; C, 75.39; H, 7.85%. IR (KBr): Vmax/cm^{-1} 2954, 2917, 2849 (C–H aliphatic), 1727 cm^{-1} (C=O of ester), 1701 (C=O of aldehyde).

Compound 10q. 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), 3441cm^{-1} (OH).

Synthesis of 2-[(4-n-Alkoxy-benzyloxy)-2-X-benzaldemine]-5-methyl Thiazole [15,17]

A mixture of 1 mmol of 2-[(4-n-alkoxy-benzyloxy)-2-X-benzaldehyde and 1 mmol of 2-amino 5-methyl thiazole, 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.

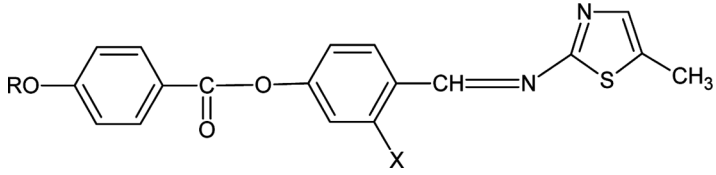
Data

Compound A_{10}. Yield 90%. mp 90°C. Found: C, 70.29; H, 7.11; N, 5.87. Calc. for $C_{28}H_{34}O_3$; N_2S; C, 70.10; H, 7.25; N, 5.55%. EI-MS m/z (rel. int. %): 478(1) $(M)^+$. IR (KBr): Vmax/cm^{-1} 2950, 2850 cm^{-1} (C–H aliphatic), 1725 cm^{-1} (C=O of ester), 1612 (CH=N), 1602 cm^{-1} (C=C aromatic), 1279 cm^{-1} (C–O), 1570 cm^{-1} (C=N, thiazole), 1034 cm^{-1} (C–S–C, thiazole).^{1}H NMR ($CDCl_3$): δ 0.90–0.93 ppm (CH_3), 1.24–1.47 ppm (CH_2), 4.03–4.07 ppm (OCH_2), 6.90–8.07 ppm (Ar-H), 9.00–9.2 ppm (CH=N), 6.89 ppm (thiazole-H). ^{13}C NMR ($CDCl_3$), 14.59 ppm (CH_3), 23.07–34.84 ppm (CH_2), 110.64–163.25 ppm (Ar-C), 164.47 ppm (C=N), 172.01 ppm (C=O ester).

Compound B_{10}. Yield 85%. mp 164°C. Found: C, 67.67; H, 7.07; N, 5.16. Calc. for $C_{28}H_{34}O_4N_2S$; C, 68.01; H, 6.88; N, 5.55%. EI-MS m/z (rel. int. %): 494(2) $(M)^+$. IR (KBr): Vmax/cm^{-1} 3434 cm^{-1} (OH),2948, 2917,2847 cm^{-1} (C−H aliphatic), 1739 cm^{-1} (C=O of ester), 1611 cm^{-1} (CH=N), 1600 cm^{-1} (C=C aromatic), 1272 cm^{-1} (C−O), 1574 cm^{-1} (C=N, thiazole), 1038 cm^{-1} (C−S−C, thiazole). $^{-1}$H NMR ($CDCl_3$): δ 0.90–0.93 ppm (CH_3), 1.31–2.60 ppm (CH_2), 4.03–4.07 ppm (OCH_2), 6.69–7.34 ppm (Ar-H), 8.50–8.90 ppm (CH=N), 6.89 ppm (thiazole-H). 12.83 ppm (OH). ^{13}C NMR ($CDCl_3$), 14.26 ppm (CH_3), 22.94–34.85 ppm (CH_2), 109.99–162.90 ppm (Ar-C), 159.96 ppm (C=N), 172.05 ppm (C=O ester).

RESULTS AND DISCUSSION

In the present study, 12 homologues from each of the two series, 2[(4-n-alkoxy-benzyloxy) phenyl azomethine]-5-methyl thiazole (series A) and 2-[(4-n-alkoxy-benzyloxy)-2-hydroxy salicylamine]-5-methyl thiazole (series B), are synthesized, and their mesomorphic properties are studied. The general molecular structure of the series is shown below.



X = H in series A,

X = OH in series B, R = C_nH_{2n+1} and n = 1–8, 10, 12, 14, 16.

As preliminary investigation, the mesophases exhibited by compounds of series A and B were examined using an optical polarizing microscope. Thin films of the samples were obtained by sandwiching them between glass slides and cover slips. All the compounds of series A and B show mesomorphism on cooling the isotropic liquid, on ordinary slides. Thread-like textures, characteristic of the nematic phase are observed for the compounds of series A. In series B compounds, on cooling the isotropic liquid, small droplets appear, which coalesce to a classical schlieren (threaded) texture characteristic of the nematic phase. On further cooling, higher members (n > 10) show the focal conic texture characteristic of the smectic C mesophase. It is consistent with the assignment of each mesophase type using the classification systems reported by Sackmann and Demus [18] and Gray and Goodby [19]. The textures of the nematic phase for compounds of series B are shown in Fig. 1. DSC is a valuable method for the

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TABLE 2 Transition Temperatures of Series B

Compounds	R = n alkoxy	Transition temperatures (°C)		
		SmC	N	I
B_1	Methyl	—	134	175
B_2	Ethyl	—	131	171
B_3	Propyl	—	124	172
B_4	Butyl	—	116	168
B_5	Pentyl	—	110	167
B_6	Hexyl	—	103	165
B_7	Heptyl	—	109	168
B_8	Octyl	—	105	170
B_{10}	Decyl	92	113	164
B_{12}	Dodecyl	86	101	162
B_{14}	Tetradecyl	84	97	154
B_{16}	Hexadecyl	67	101	160

Note. SmC, smectic C; N, nematic; I, isotropic.

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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 series B were measured by DSC. Data are recorded in Table 1. Enthalpy values of the various transitions agree well with the existing related literature values [20], which helps the further confirm the mesophase type. Inspection of the clearing temperatures also revealed a correlation between the influence of the lateral polar hydroxy group in series B. Table 2 clearly shows that compounds with the *ortho*-hydroxy group (series B) possess higher clearing temperatures than compounds without the *ortho*-hydroxy group (series A). There are also compounds in which the lateral substituents are shielded, so that they are less effective in molecular broadening [21]. The compounds of series B may give rise to shielding effects owing to the presence of intramolecular association [22], and hence the polarizability along the long axis of molecule will be larger in such compounds than in the unsubstituted analogue [23]. This results in higher clearing temperatures than in the corresponding compound without an *ortho*-hydroxy group. It can therefore be assumed that the presence of an OH group in an *ortho* position in compounds of series B confers a higher degree of stability on the mesophase, resulting from the increase in van der Waals forces, which in turn is caused by the increased anisotropy of the molecular polarizability. This information indicates that the introduction of hydroxyl group at the *ortho* position in the aldehyde fragment increases the degree of anisotropy

TABLE 3 Transition Temperatures of Series A

Compounds	R = n alkoxy	Transition Temperatures (°C)		
		Sm	N	I
A_1	Methyl	—	119	148
A_2	Ethyl	—	115	145
A_3	Propyl	—	103	132
A_4	Butyl	—	108	126
A_5	Pentyl	—	95	121
A_6	Hexyl	—	84	118
A_7	Heptyl	—	72	106
A_8	Octyl	—	76	92
A_{10}	Decyl	—	68	90
A_{12}	Dodecyl	—	63	87
A_{14}	Tetradecyl	—	61	85
A_{16}	Hexadecyl	—	57	81

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

of the molecular polarizability of the compound in series B and hence increases the degree of molecular order, causing the smectic phase to have increased stability [24].

In series A, 12 compounds have been synthesized, and their mesogenic properties are evaluated. All the compounds synthesized exhibit an enantiotropic nematic mesophase. For series A, transition temperatures are recorded in Table 3, and a plot of transition tempera-

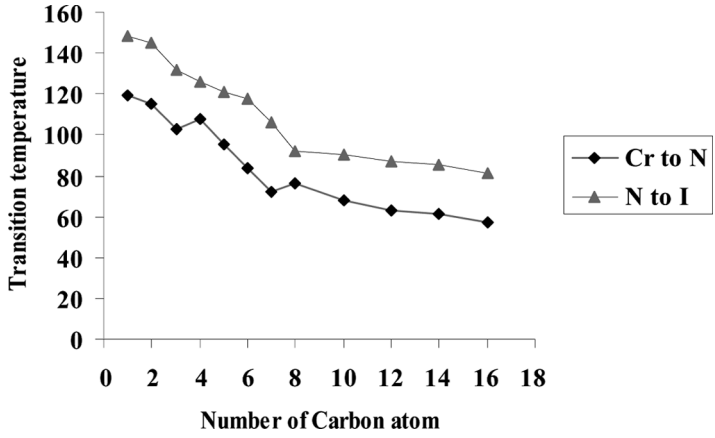

FIGURE 2 Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain for series-A.

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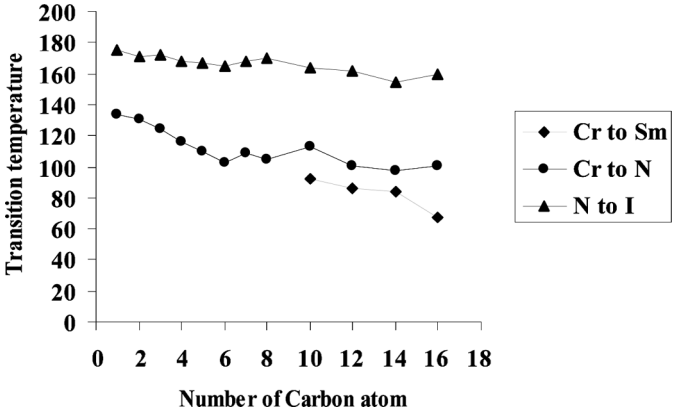

FIGURE 3 Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain for series-B.

tures against the number of carbon atoms in the alkoxy chain (Fig. 2) shows a steady fall in N–I transitions.

In series B, all 12 members synthesized exhibit an enantiotropic nematic mesophase. The smectic C mesophase appears from the n-dodecyloxy derivative as an enantiotropic phase and remains up to the n-hexadecyloxy derivative. The transition temperatures are recorded in Table 2. The entire homologous series B exhibits mesomorphism. The plot of transition temperature against the number of carbon atoms in the alkoxy chain (Fig. 3) shows a smooth falling tendency for nematic–isotropic transition temperatures throughout the series. Series B also exhibits a falling tendency of smectic–nematic transition temperatures for higher homologues.

The enthalpies of the n-hexadecyloxy derivatives of each of the series were measured by DSC, which is recorded in Table 1. The enantiotropic nematic phase of series B is shown in Fig. 1.

CONCLUSION

In this article, we have presented the synthesis and characterization of two new mesogenic homologous series of ester-azomethine derivatives containing a thiazole ring as a terminal group and an −OH group as a lateral substitution. Ester derivatives are more stable compounds than Schiff base derivatives. Series A is purely nematogenic, as it is a short (two-phenyl-ring) system, whereas compounds of series B exhibit the nematic as well as the smectic C mesophases because of the presence of an additional phenyl ring along with an ester linkage.

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