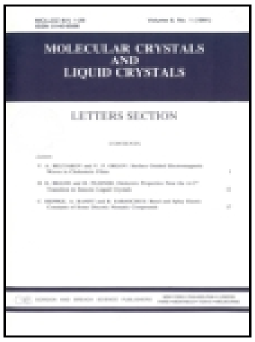

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Synthesis and Characterization of Novel Thermotropic Liquid Crystals with a Lateral Chloro Group

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Twelve novel homologues having azolinkage of the series 4-Carbethoxy-[3′chloro-4′ (4″-n-alkoxy benzoyloxy)] azobenzenes has been synthesized. The methyl to n*-hexyl homologues exhibit only a nematic mesophase, while the* n*-heptyl to* n*-dodecyl homologues exhibit both smectic and nematic mesophases. The* n*-tetradecyl and* n*-hexadecyl homologues exhibit only smectic mesophases. The plot of transition temperatures versus number of carbon atoms in alkoxy chain exhibits an odd-even effect for the nematic-isotropic transition temperatures. The mesogenic behavior of present series is explained by comparing its homologue with other homologue of related mesogenic series. The synthesized compounds were characterized by combination of elemental analysis and standard spectroscopic methods. For the exhibition of mesomorphic property the role of ester and azo linkages has been discussed. The impact of lateral chloro group on mesomorphism is also discussed.*

Keywords Liquid crystals; mesomorphic; monotropic; nematic; smectic

1. Introduction

Liquid crystalline materials are found to have an important role in new and emerging electro-optical technologies. Thermotropic liquid crystals consists of either linear or disc-like molecules like organic molecules. The general architecture for linear thermotropic liquid crystals of linearly linked ring systems and flexible chains, the permanent dipoles and polarisable moieties also being requirements. The rings may be linked to each other either directly or through some linking group (e.g. ester,olefinic, acetylenic, azo, azoxy, dimethylene or oxymethylene) that maintains the linearity of the core [1]. The flexible alkyl chains may be linked either directly with the ring or through the intervening hetero atoms such as oxygens, sulphur and nitrogens. These polar groups may also impart dielectric anisotropy to the molecules [2]. The thermal stability of the mesophase is determined by the nature of the molecule, steric, and electronic factors. It has also been reported in the literature [3–5] that the linking units capable of maintaining the rigidity and linearity of the molecule also promote mesophase stability. The aromatic esters are known for their thermal stability, easy synthesis and relative resistance to hydrolysis. Azobenzene derivatives are very effective for controlling liquid crystals by light, because the geometrical change due

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to photo-isomerisation gives a concomitant change in chemical and physical properties not only in the azobenzene residue but also in the environment around it. Such photonic control has mainly been applied in the nematic phase by means of a transmission, reflection, and light scattering mode. The photo-responsive properties of azobenzene derivatives due to photo-isomerisation have also been reported [6–12]. It is reported that the addition of chromophores such as azo groups are found the lower energy required in optical field [13]. These features have made azo compounds, promising candidates for optical applications.

Lateral substitution at the center of the mesogen increases the molar volume and hence plays an effective role in the mesogenic properties of the materials. Studies on the effect of lateral substitution have been carried out by several researchers [14–17]. Recently we have also reported a homologous series with lateral methyl substituent [18]. In this continuation, in the present paper, we report the design, synthesis, and characterization of newly designed homologous series with lateral polar chloro substituent to evaluate the effect of polar substituent on mesomorphism.

2. Experimental

2.1. Synthesis

4-Hydroxy benzoic acid, *n*-alkyl halides, thionyl chloride, pyridine, methanol, potassium hydroxide, ortho chloro phenol, ethyl 4-amino benzoate, and sodium nitrite were chemically pure of lab grade. Solvents were dried and distilled prior to use.

1. 4-*n*-Alkoxy benzoic acids and 4-*n*-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora [19].
2. 4-Carbethoxy-3′-chloro-4-hydroxy azobenzene (DA-1) was synthesized by known method [20].
3. The series namely 4-Carbethoxy-[3′chloro-4′(4″-*n*-alkoxy benzoyloxy)] azobenzene was synthesized by adding dropwise the solution of 4-Carbethoxy-3′-chloro-4-hydroxy azobenzene (DA-1) in dry pyridine to the respective solution of 4-*n*-alkoxy benzoyl chloride at 0–5°C. The mixture was allowed to stand overnight at room temperature. It was acidified with cold 1:1 aqueous hydrochloric acid and the separated solid was washed successively with dilute sodium hydroxide solution and water. The final product obtained was recrystallized several times from glacial acetic acid until constant transition temperatures were obtained which are recorded in Table 1. The elemental analysis of each compound was found to be satisfactory (Table 2). The route of synthesis of series 1 is illustrated in Scheme 1.

2.2. Characterization

Micro analysis of the compounds was performed on a Coleman carbon, hydrogen analyzer. FTIR spectra were determined on Nicolet impact 400 FTIR spectrometer using Nujol. ^{1}H NMR spectra was performed on Perkin-Elmer (90 MHz) spectrometer using tetramethylsilane (TMS) as internal reference and $CDCl_3$ as solvent. Liquid crystalline properties were determined on a Leitz Laborlux 12 POL microscope equipped with a heating stage. Thermodynamic quantities enthalpies (ΔH) and entropies ($\Delta S = \Delta H/T$) of transitions were determined using differential scanning calorimeter (DSC) via a Mettler TA-4000 system

Table 1. Transition temperatures (°C) of Series I

n-Alkyl CnH2n+1 Group (*n*) Series I	Transition temperatures (°C) Sm C	 N	 I
1	—	150.0	215.0
2	—	155.0	227.0
3	—	145.0	195.0
4	—	135.0	200.0
5	—	96.0	180.0
6	—	107.0	177.0
7	(73.0)*	80.0	165.0
8	70.0	109.0	160.0
10	80.0	118.0	154.0
12	95.0	132.0	147.0
14	90.0	—	143.0
16	94.0	—	137.0

()*monotropy, Sm—Smectic, N-Nematic, I-Isotropic.

and reported in Jg^{-1} at a scanning rate of 5°C min^{-1}. The calorimeter was calibrated using pure indium as standard.

2.3. *Analytical Data*

FTIR (Nujol) Spectra cm^{-1}. *n*-Butoxy Derivative : 2900 (C—H Str. Aromatic), 2900, 2850 (C—H Str.Aliphatic), 1705 (C=O Str. Ester), 1600 (N=N Str.Azo), 1370, 1270, 1160 (aryl ether), 1060, 960, 890, 760.

n-Hexadecyloxy derivative : 2950 (C—H Str. Aromatic), 2900, 2850 (C—H Str. Aliphatic), 1700 (C=O Str.Ester), 1600 (N=N Str. Azo), 1370, 1250, 1150 (aryl ether), 1050, 860, 750.

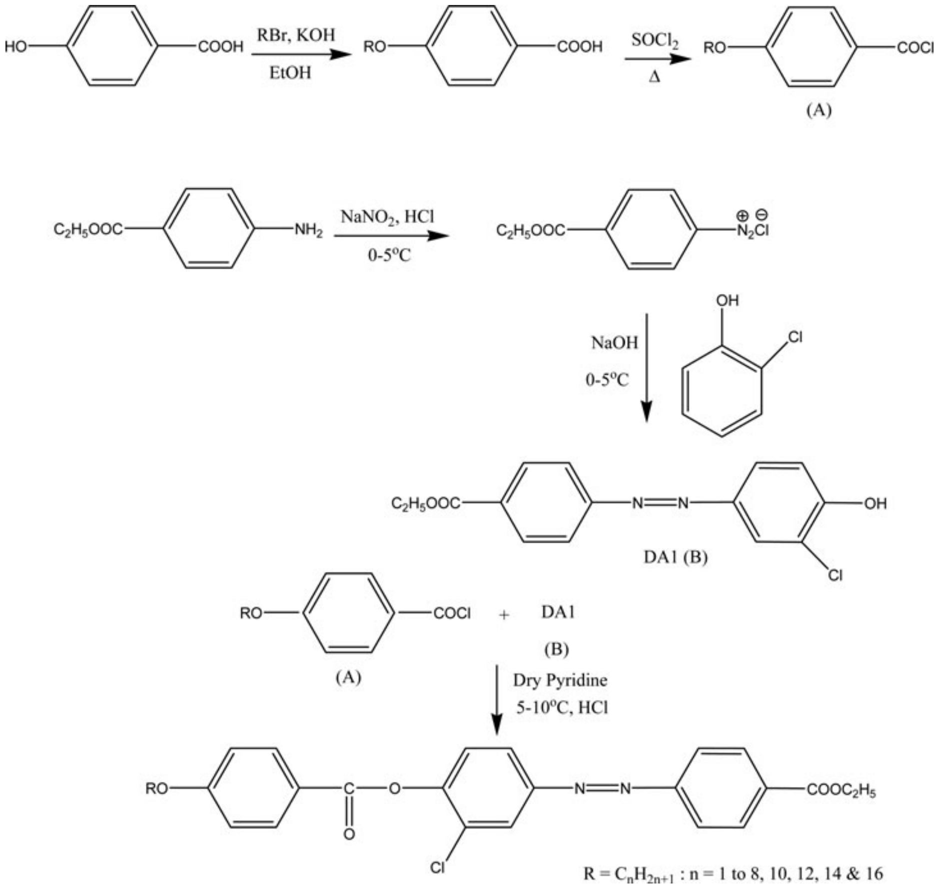
Proton NMR spectra in δ PPM (Solvent $CDCl_3$ 90 MHz, standard TMS). *n*-Butoxy Derivative: δ 1.0 (t, 3H, CH_3), 1.4 (t, 3H, CH_3), 1.8 (m, 4H, Ar-O-$(CH_{2})_{2}$-), 4.0 (t, 2H of Ar-OCH_2), 4.3 (q, 2H of Ar-$COOCH_2$), 6.9 – 8.1 (m, 11H,Ar-H).

n-Hexyloxy Derivative : δ 1.0 (t, 3H, CH_3), 1.3 (t, 3H, CH_3), 1.7 (m, 8H, Ar-O-$(CH_{2})_{4}$-), 4.1 (t, 2H of Ar-OCH_2), 4.3 (q, 2H of Ar-$COOCH_2$), 7.0 – 8.3 (m, 11H,Ar-H).

Table 2. Elemental analysis for ethyloxy, pentyloxy, octyloxy, and decyloxy derivative

Molecular formula	Element% found (compared with% calculated) C	 H	 N
$C_{24}H_{21}O_5N_2$ Cl	63.42 (63.64)	4.39 (4.64)	6.43 (6.18)
C_{27} $H_{27}O_5N_2$ Cl	65.19 (65.52)	5.01 (5.46)	6.07 (5.66)
$C_{30}H_{33}O_5N_2$ Cl	67.49 (67.10)	6.05 (6.15)	5.07 (5.21)
$C_{32}H_{37}O_5N_2$ Cl	67.82 (68.02)	6.54 (6.55)	5.25 (4.96)

The synthetic route to the series is mentioned below in Scheme 1.



Scheme 1. Synthetic route to the series I.

2.4. *Calorimetry*

Calorimetry is valuable method for the detection of phase transitions. Conclusion may be drawn concerning the nature of the phases that participate in the transition with help of calorimetric studies. In the present study, enthalpies of hexadecyl homologue of series I is determined by DSC and data is recorded in Table 3.

3. Results and Discussion

The homologous series 4-Carbethoxy [3′chloro-4′-(4″-n-alkoxybenzoyloxy)] azobenzenes consisting of twelve mesomorphic homologues. The methyl to *n*-hexyl derivatives exhibit enantiotropic nematic mesophases. The smectic mesophase commences in the monotropic form, from the *n*-heptyl derivative which becomes enantiotropic from the next member i.e. *n*-octyl derivative. The *n*-octyl to *n*-dodecyl derivatives are enantiotropically smectics and nematics. The *n*-tetradecyl and *n*-hexadecyl derivatives exhibit only enantiotropic smectic mesophases. The transition temperatures (Table 1) are plotted versus the number of carbon

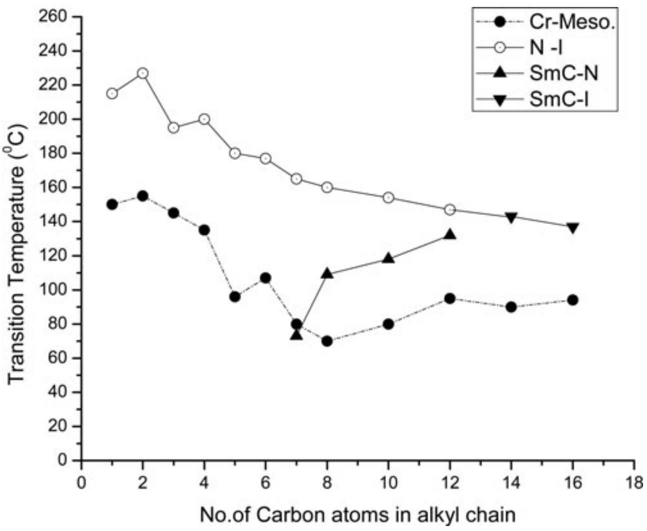


Figure 1. The phase behavior of series 1.

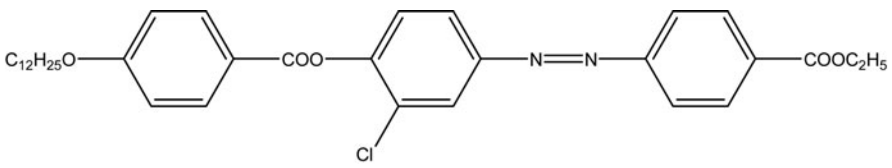
atoms in alkyl chain of *n*-alkoxy terminal end group. The phase diagram showing phase behavior is depicted in Figure 1. The smectic–nematic transition curve shows rising tendency. The nematic-isotropic transition curve shows falling tendency as series is ascended with exhibition of odd–even effect. The nematic phase lengths vary from 15° to 84°C and the smectic phase lengths vary from 39 ° to 53°C.

There is close relationship between mesomorphism and molecular constitution of organic compounds. Hence thermal stability, a measure of mesomorphism, can be correlated with the molecular constitution of the compounds. Figure 2 shows the transition temperatures and molecular structures of the *n*-dodecyloxy derivative (compound 10) of the present series I and the structurally related compound A [21], B [22], and C [23] reported in literature.

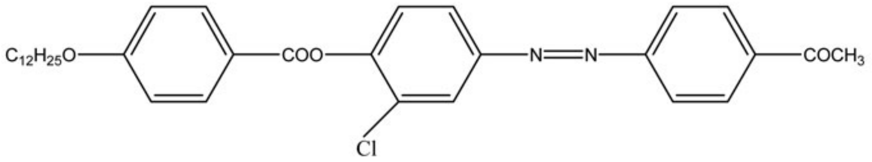
Reference to Figure 2 indicates that the compounds 10, A and B consists of three phenyl rings, two central groups $-COO^-$ and $-N{=}N^-$, one *n*-alkoxy terminal end group and laterally substituted chloro $-Cl$ group as common identical features. The only one terminal end groups of compounds 10, A and B viz. $-COOC_2H_5$, $-COCH_3$, and $-F$ are uncommon features. Figure 2 indicates that the compound 10 exhibits smectic and nematic mesophases whereas compound A exhibits only nematic mesophase. Both the compounds under comparison possess laterally substituted chloro groups at the middle phenyl rings

Table 3. DSC Data

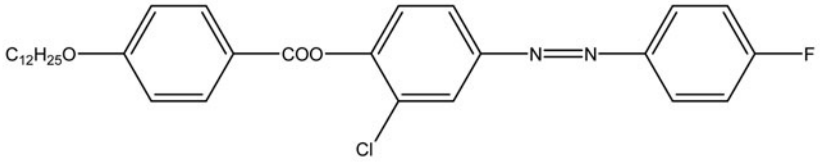
Series	Member	Transition	Peak temperature (microscopic reading)	Δ (H/Jg$^{-1)}$	Δ (S/Jg^{-1} K$^{-1)}$
I	Hexadecyl	Cr−Sm	88.3 (94)	43.33	0.119
		Sm-Iso	132.4 (137)	0.689	0.001699



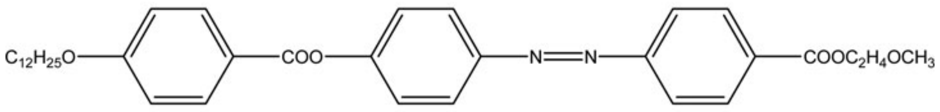
Compound **10** :Cr 80 °C SmC 118 ° C N 154 °C Iso



Compound **A:** Cr 80 °C N 125 °C Iso



Compound **B:** Cr 83 °CSmC 93 °C N 113 °C Iso



Compound **C:** Cr 97 °C SmA 159 °C N 226° C Iso

Figure 2. The Comparative molecular structures of compounds 10, A, B, and C.

which will affect the length to breadth ratio and polarizability to a different extent for compounds 10 and A due to the presence of different end groups $-COOC_2H_5$ and $-COCH_3$. The molecules of compound 10 are longer due to the presence of longer $-COOC_2H_5$ terminal group at one end, as compared to shorter $-COCH_3$ group in compound A at that position. The longer terminal$-COOC_2H_5$ group aids the formation of smectic mesophase due to enhanced lateral attraction as compared to terminal attraction which facilitates lamellar packing required for smectic mesophase [26]. Thus compound 10 exhibits smectics mesophase along with nematic phase. The nematic phase length of compound A is marginally higher (9°C) than that of compound 10 can be understandable because of the difference in terminal attraction arising due to different terminal groups. Further both smectic and nematic phase lengths and thermal stabilities of compound 10 are greater than that of compound B. The molecules of compound 10 and compound B differ only in the right terminal end groups, other structural features are being the same. The compound 10 posses long and more polarisable —$COOC_2H_5$ group at one end whereas compound B has short —F group at that end. The presence of long and polarisable —$COOC_2H_5$ group of compound 10 increases length of the molecules, as a result of its polarizability, increases the intermolecular cohesive forces responsible for wider mesophase length and higher thermal stabilities of compound 10 in comparision to compound B with short terminal —F group.

The comparison of the compound 10 and compound C shows that the smectic and nematic thermal stabilities of compound 10 are lower by 17°C and 72°C, respectively, than those of compound C. This can be explained on the basis of their structural variations. The molecular structure of compound 10 differs from the molecules of compound C in the terminal as well as in the central part of the benzene ring. The molecules of the compound 10 has —$COOC_2H_5$ group at the one terminal and —Cl lateral group at the central benzene ring, whereas, molecules of compound C has —$COOC_2H_4OCH_3$ group at the same terminal position without any lateral substituent. The presence of lateral chloro group increases the breadth of the molecules of compound 10 and the length is also shorter than the molecules of compound C because of absence of additional −OCH3 unit. Gray [24] has explained that increase in breadth of molecules reduces both nematic and smectic thermal stabilities. Thus, both reduced length and enhanced breadth factors resulted in lower smectic and nematic thermal stabilities of compound 10 reported in present investigation.

In the present series SmC (schlieren texture) and nematic (marble texture) are inferred from textures observed under a polarizing microscope.

4. Conclusion

In this paper, we have presented the synthesis and characterization of a homologous series with central ester and azo linkages and lateral chloro substituent. Compounds of the present series exhibited nematic mesophases along with the SmC mesophases. The study revealed that enhanced length of the molecules of the present series due to the presence of long –$COOC_2H_5$ terminal substituent favored formation of smectics mesophase while increased breadth due to the presence of the lateral chloro group lowered its mesophase thermal stabilities.

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