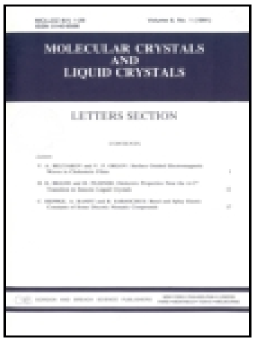

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Study of novel thermotropic liquid crystals with lateral nitro substituent

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ABSTRACT
In this article, we report synthesis and characterization of a novel thermotropic liquid crystals, namely, 4-bromo-[3′-nitro-4′(4″-n-alkoxybenzoyloxy)] phenyl azobenzenes. The first member of a homologous series is nonmesogenic in nature. The n-ethyl to n-decyl homologues exhibit enantiotropic nematic mesophases, while the n-dodecylton -hexadecyl homologues exhibit only smectic mesophases. The synthesized compounds were characterized by a combination of elemental analysis and standard spectroscopic methods. The mesogenic behavior of present series is explained by comparing each homologue of the related mesogenic series. The impact of the lateral nitro group on mesomorphism is also discussed.

KEYWORDS
Liquid crystals; mesogenic; nematic; smectic; enantiotropic

Introduction

Liquid crystals had become quintessential advanced materials in our daily life today for more than a century of studies. Its applications were developed in various areas such as advanced technological devices, prototypical self-organizing molecular materials, smart biological and pharmacological uses. Liquid crystalline materials are of great interest for material sciences as well as for life sciences. The design of novel thermotropic liquid crystals as advanced functional materials involves the suitable selection of core fragment, linking group, and terminal functionality. The mesomorphic behavior of mesogens depends upon the molecular structure of molecules and molecular forces arising, therefore, a slight change in the molecular geometry brings about considerable change in its mesomorphic properties [1–10]. Lateral substitution makes the molecule broad and hence plays an effective role in the mesogenic properties of the materials which can be used advantageously for applications. Studies on the effect of lateral substitution have been carried out by several researchers. Recently, we have also reported work on lateral methyl and aryl substituents and observed that lateral substitution in the mesogenic core of the molecules causes reduction in the mesophase thermal stabilities [11–12]. In this continuation, we have synthesized a novel homologous series containing three rings in the main core linked through ester and azo central linkages and substituted by a lateral nitro group on the central benzene ring, and investigated the influence of the lateral nitro group on mesomorphism.

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Materials and methods

4-Hydroxybenzoic acid, *n*-alkyl halides, thionyl chloride, pyridine, ethanol, potassium hydroxide, 2-nitrophenol, 4-bromoaniline, and sodium nitrite were chemically pure of lab grade. Solvents were dried and distilled prior to use. The microanalysis of the compound was performed on a Coleman carbon, hydrogen analyzer. Fourier transform infrared spectroscopy (FTIR) spectra were determined on FTIR-8400S (Shimadzu) instrument. ^{1}H NMR spectra was performed on Bruker AV III HD 300 MHz spectrometer using tetramethylsilane (TMS) as internal references substance and $CDCl_3$ as solvent and the chemical shift values recorded as (ppm units). Liquid crystalline properties were determined on a Leitz Laborlux 12 POL microscope equipped with a heating stage. Thermodynamic quantities, enthalpies (ΔH) and entropies ($\Delta S = \Delta H \backslash T$) of transition, were determined using differential scanning calorimeter (DSC) via a Mettler star SW 9.30 system and reported in J g^{-1} at a scanning rate of 5°C min^{-1}.

Synthesis of compounds

4-*n*-Alkoxy benzoic acids and 4-*n*-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora [13]. 4-Bromo-3′-nitro-4-hydroxyazobenzene (DA-1) was synthesized by known method [14].

The series, namely, 4-bromo-[3′-nitro-4′(4″-*n*-alkoxybenzoyloxy)] phenyl azobenzenes was synthesized by adding dropwise one mole solution of 4-bromo-3′-nitro-4-hydroxyazobenzene (DA-1) in dry pyridine to the respective one mole solution of 4-*n*-alkoxybenzoyl chloride at 0°C–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 representative compounds was found to be satisfactory and recorded in Table 2. The route of synthesis of series I compounds is illustrated in Scheme 1.

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

n-Alkyl, C_nH_{2n+1}, group (*n*) = Series I	Transition temperatures (°C)		
	SmC	N	I
1	–	–	180
2	–	129	165
3	–	106	172
4	–	102	162
5	–	102	140
6	–	90	135
7	–	70	130
8	–	94	125
10	–	108	128
12	88	–	115
14	71	–	102
16	61	–	90

Note. Sm – Smectic, N – Nematic, and I –Isotropic.

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

	Element % found (compared with % calculated)		
Molecular formula	C	H	N
$C_{21}H_{16}O_5N_3Br$	52.48 (52.50)	3.36 (3.33)	8.80 (8.75)
$C_{23}H_{20}O_5N_3Br$	54.65 (54.33)	3.74 (3.93)	8.48 (8.26)
$C_{27}H_{28}O_5N_3Br$	57.70 (57.44)	5.22 (4.96)	7.7 (7.44)
$C_{29}H_{32}O_5N_3Br$	58.80 (58.78)	5.58 (5.40)	7.25 (7.09)

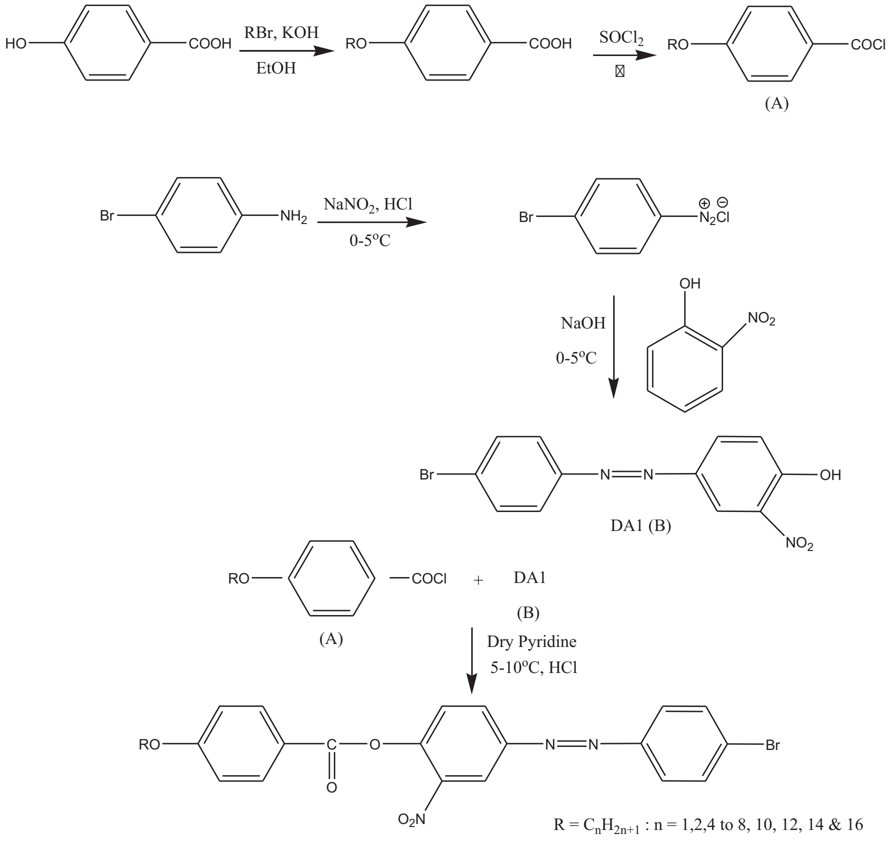
Spectral data

FTIR (KBr) spectra (cm^{-1})

n-C_6H_{13} homologue: 3000 (C–H str., aromatic), 2900 (C–H str., aliphatic), 1700 (–C=O str., ester), 1603 (–N=N– str., azo), 1340, 1270, 1165 (aryl ether), 1050, 850, and 750. n-$C_{10}H_{21}$ homologue: 3100 (C–H str., aromatic), 2925–2850 (C–H str., aliphatic), 1734 (–C=O str., ester), 1603 (–N=N– str., azo), 1380, 1285, 1155 (aryl ether), 1050, 880, and 765.

1H NMR (CDCl$_3$, 300 MHz, δ, ppm, standard TMS)

n-C_5H_{11} homologue: $\delta = 0.9$ (t, 3H, CH_3), 1.29–1.71 (m, 6H, -$(CH_2)_3$-), 3.94 (t, 2H, -Ar(OCH_2)-), and 6.91–8.93 (m, 11H, aromatic H). n-$C_{16}H_{33}$ homologue: $\delta = 0.96$ (t, 3H,



Scheme 1. The route of synthesis of series I compounds.

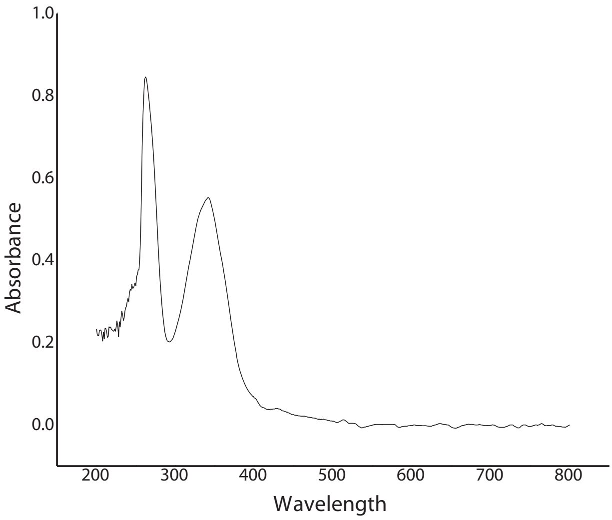


Figure 1. UV-visible spectra of C_{10} homologue in chloroform.

CH_3), 1.29–1.71 (m, 28H, -$(CH_2)_{14}$-), 3.94 (t, 2H, -Ar(OCH_2)-), and 6.92–8.93 (m, 11H, aromatic H).

UV study of azo compounds

The presence of an azobenzene group leads to the possibilities of photoisomerization and photochromic behavior. Therefore, permeability studies of photophysical properties were carried out in chloroform solution of concentration $C = 2.5 \times 10^{-3}$ g dm^{-3} for *n*-decyl homologue and shown in Fig. 1. The compounds displayed primarily two absorptions with maximum absorbance at about 250 and 342 nm.

The azo compound in the trans form shows a strong band in ultraviolet region 342 nm which is attributed to the trans-to-cis (π-π^*) transition. The trans form is much more stable than the cis form but each isomer can be converted into the other by light irradiation of the appropriate wavelength.

Calorimetry

Calorimetry is valuable method for the detection of phase transitions. Conclusion may bedrawn concerning the nature of the phases that participate in the transition with help ofcalorimetric studies. In the present study, enthalpies of decyl homologue is determined by DSC and data are recorded in Table 3.

Table 3. DSC data.

Series	Member	Transition	Peak temperature (microscopic reading)	Δ(H/J g^{-1})	Δ(S/J g^{-1} K^{-1})
I	Decyl	Cr-N	100 (108)	9.02	0.0241
		N-Iso	120 (128)	28.06	0.071

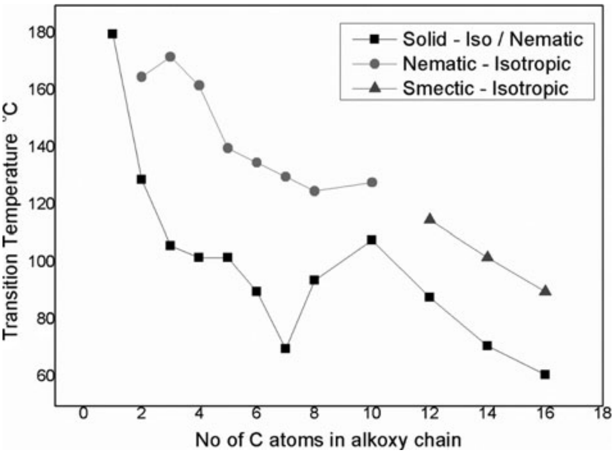


Figure 2. The phase behavior of series.

Results and discussion

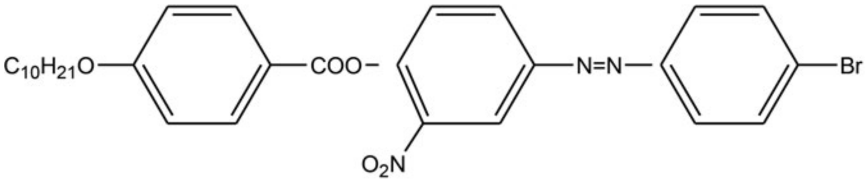
In the present study, 12 homologues of the series 4-bromo-[3′nitro-4′(4″-*n*-alkoxy benzoyloxy)] phenyl azobenzenes were synthesized and their mesomorphic properties were studied. All members except the first member of the series exhibit mesomorphism. The *n*-ethyloxy to *n*-decyloxy homologues exhibit enantiotropic nematic mesophases. The *n*-dodecyloxy to *n*-hexadecyloxy members exhibit only smectic mesophases. The transition temperatures are plotted versus number of carbon atoms in alkoxy chain and shown in Table 1. The phase diagram showing phase behavior is depicted in Fig. 2. Both nematic-isotropic transition and smectic-isotropic transition curves show falling tendency as series is ascended. The nematic phase length vary from 20°C to 66°C and smectic phase length vary from 27°C to 31°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 3 shows the transition temperatures and molecular structures of the *n*-decyloxy derivative of the present series I and the structurally related compounds A [9] and B [15] reported in literature.

The comparison of *n*-decyloxy derivative (compound 1) of the present series with the structurally related compound A shows that compound 1 exhibits only nematic mesophase with phase length of 20°C, whereas compound A exhibits both smectic and nematic mesophases with phase lengths of 21°C and 32°C, respectively. The absence of smectic phase and lowering of nematic phase length by 12°C in compound 1 can be explained on the basis of difference in the molecular geometries possessed by these compounds. The compound 1 have three phenyl rings joined through ester and azo central linkages with an alkoxy and bromine as terminal groups and a lateral nitro group at the second phenyl ring. The compound A differs, firstly in the type of one terminal group which is fluorine in place of bromine, and secondly, it do not possess any lateral group. The presence of lateral nitro group in compound 1, forces apart the molecular axes of the molecules, causes breadth increasing effect and changes molecular conformation which results in depression of transition temperatures and thermal stabilities and also to the absence of smectic mesophase as compared to compound A.

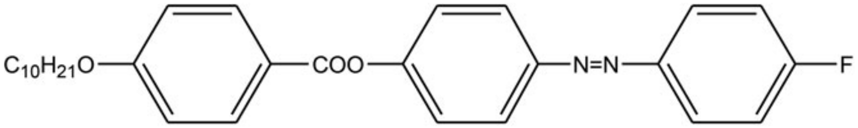
Comparing compound 1 with compound B, it is clear that compound 1 has nematic phase length of 20°C whereas compound B has nematic phase length of 36°C. The lowering of nematic phase length by 16°C in compound 1 as compared to compound B can be explained on the basis of their structures. The molecular structure of compound 1 differs from the

Compound 1



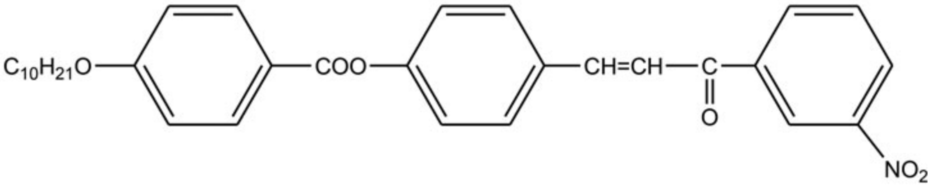
Cr 108°C N128°C I

Compound A



Cr 89 °C SmC170 °C N 200 °C I

Compound B



Cr 111°C SmC 120 °C N156° C

Figure 3. Comparative molecular geometries of compounds 1, A, and B.

molecule of compound B in terminal as well as in the central linkage. The molecule of compound 1 has -Br group at one terminal and –N=N– central linkage, whereas molecules of compound B do not have any terminal group and –CH=CH–CO– central linkage. Lateral $-NO_2$ group is common feature in both the compounds. The compound B have longer length due to presence of longer –CH=CH–CO– linkage as compared to short –N=N– linkage in compound 1. Increased molecular length of compound B interact with one another and stabilizes the molecular packing required for nematic phase. Gray [1] has also explained that increased length and polarizability enhances both mesogenic properties and thermal stabilities. Hence, nematic thermal stability of compound B should be higher than that of compound 1, which is the case.

In the present series, SmC (Schlieren texture) and nematic (marble structure) are inferred from the textures observed under a polarizing microscope and are shown in Figs. 4 and 5, respectively.

Figure 4. Optical micrograph Schlieren texture of smectic C mesophase of C_{14} homologue on cooling at 80°C.

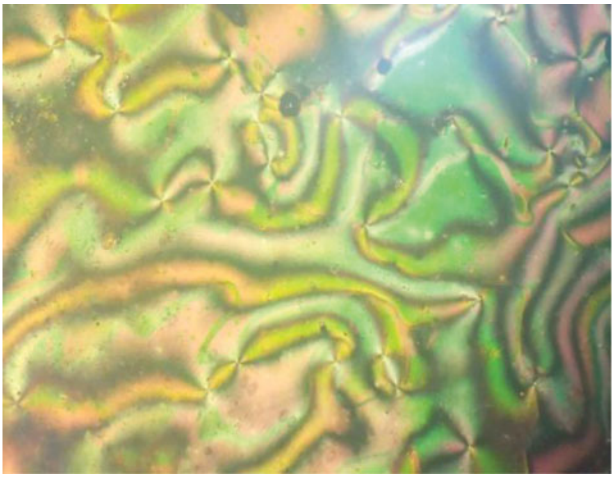


Figure 5. Optical micrograph of threaded texture of nematic mesophase of C_7 homologueobtained on cooling at 85°C.

5. Conclusion

In this article, we have presented the synthesis and characterization of a homologous series with central ester and azo linkages and a lateral nitro substituent. Compounds of the present series exhibited nematic mesophases along with the smectic C mesophases. The study revealed that introduction of lateral nitro group increases the breadth of molecule and decreases thermal stabilities of nematic mesophase.

Acknowledgment

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