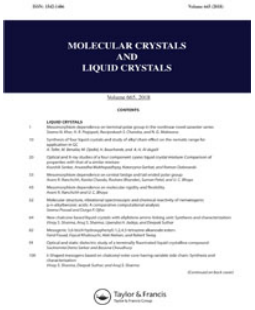

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Mesomorphism dependence on terminal polar group in the nonlinear novel azoester series

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ABSTRACT

Synthesis of a novel azoester homologous series is carried out with a view to understand and establish the effect of molecular structure on liquid crystal (LC) behaviors of a substance. Novel series consists of ten LC substances. All the homologs are enantiotropically nematogenic without exhibition of smectic property. Transition and melting temperatures, textures of LC are determined by an optical polarizing microscopy equipped with a heating stage. Textures of nematic phase are threaded or schlieren. Transition curves of a phase diagram behaved in normal manner. Nematic–isotropic transition curve exhibited odd–even effect. Analytical and spectral data supported and confirmed the structures of homologues.

KEYWORDS

Azoester; liquid crystal; mesogen; mesomorphism; nematic; smectic

Introduction

The mesomorphic state of matter intermediate to crystalline solid and isotropic liquid was discovered in 1888 [1]. Chemists design, synthesize and evaluate liquid crystal (LC) materials by carrying out changes or minor major alternations in molecular shape, size, aromaticity, terminal and/or lateral functional groups, and their positional substitution etc. On changing the above variables, the molecular rigidity and/or flexibility [2–5] changes and novel LC material are generated. The present investigation is planned with a view to understanding and establishing the relation between LC behavior of a substance and the molecular structure [6–8], as a consequence of molecular rigidity and flexibility. The novel homologous series of azoester molecules have potential applications in the photochromism and electro optical devices [9, 10].

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agents (R-X) to convert it into corresponding *n*-alkoxy benzoic acids by usual established method of Dave and Vora [11]. Azo dye 2-Hydroxy naphthyl azo 4′-bromobenzene was prepared by reported method [12]. 4-*n*-alkoxy benzoic acids and Azo dye were condensed in ice cooled pyridine to get a series of final azo ester products [13]. Final products were

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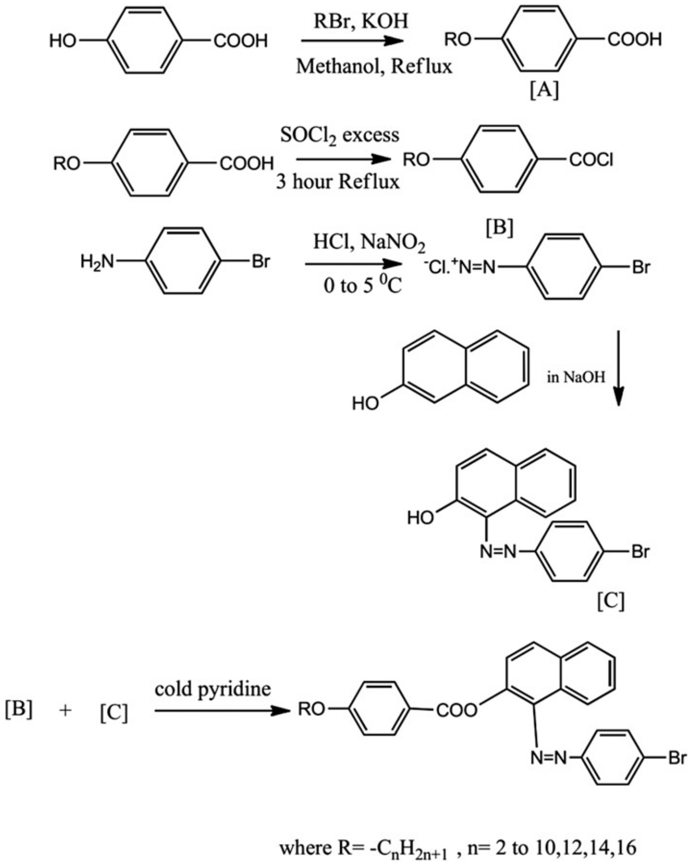

Scheme 1. Synthetic route for homologous series I.

decomposed, filtered, washed, dried, and purified till their constant transition temperature, obtained.

The chemicals 4-hydroxy benzoic acid, alkyl halides [R–X], methanol, ethanol, KOH, thionyl chloride, pyridine, *β*-naphthol, para bromoaniline, HCl, $NaNO_2$, etc. required for synthesis were used as received excepts solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below in Scheme 1.

Characterization

Some selected members of a novel series were characterized by elemental analysis, polarizing microscopy, mass spectra, infrared spectra, ^{1}H-NMR spectra, texture determination by miscibility method and DSC scan. Microanalysis of the compound was performed on Perkin Elmer PE 2400 CHN analyzer, IR spectra were performed on Perkin Elmer spectrum, and ^{1}H-NMR spectra were performed on Bruker spectrometer using $CDCl_3$ as solvent. Transition temperatures of synthesized homologous series are recorded in Table 1. Elemental analysis and IR spectra analysis are shown in Tables 2 and 3, respectively.

Table 1. Transition temperatures in °C for 2-(4′-*n*-alkoxy benzoyloxy) naphthyl -1-azo-4″-bromobenzenes.

	Transition temperatures in °C	
Number of carbon atoms in *n*-alkyl chain	Nematic	Isotropic
2	78.7	94.9
3	69.4	114.0
4	82.4	130.5
5	109.2	125.5
6	57.5	100.0
7	63.9	93.0
8	74.5	96.2
10	47.2	72.8
12	51.1	74.6
14	–	113.7

^{1}H NMR of 2-(4′-*n*-hexyloxy benzoyloxy)-naphthyl-1-azo-4″-bromobenzene in CDCl3, δ ppm.
0.927 (t, 3H, $-CH_3$)
1.251-1.356 (m, 8H, $-CH_2$)
4.004 (t, 2H, $-OCH_2$)
6.846–8.529 (m, 14H, Ar–H)
NMR confirms the above structure.
^{1}H NMR of 2-(4′-*n*-heptyloxy benzoyloxy)-naphthyl-1-azo-4″-bromobenzene in $CDCl_3$, δ ppm.
0.88 (t, 3H, $-CH_3$)
1.256–1.315 (m, 10H, $-CH_2$)
3.428 (t, 2H, $-OCH_2$)
7.266–8.383 (m, 14H, Ar–H)
NMR confirms the above structure.

Mass spectra (molecular weight) octyloxy homolog (gram/mole)

Calculated-559
Experimental-559

Textures by miscibility method

Nematic

Propyloxy homolog – threaded texture
Heptyloxy homolog – threaded texture
Decyloxy homolog – schlieren texture

Results and discussion

Novel homologous series 2-(4′-*n*-alkoxy benzoyloxy) naphthyl azo -4″-bromobenzenes consisted of ten homologs. All the members are enantiotropically nematogenic without exhibition of any smectogenic property. Transition and melting points of homologs as determined by an optical polarizing microscopy, equipped with a heating stage

Table 2. Elemental analysis for ethyloxy, hexyloxy, octyloxy and dodecyloxy derivatives.

		Elements % found (calculated %)		
Sr. No.	Molecular formula	C	H	N
1	$C_{25}H_{19}N_2O_3Br$	63.25(63.15)	4.22(4.00)	5.99 (5.89)
2	$C_{29}H_{27}\ N_2O_3Br$	65.83(65.53)	5.58(5.08)	5.39 (5.27)
3	$C_{31}H_{31}\ N_2O_3Br$	66.69 (66.54)	5.69(5.54)	5.28 (5.00)
4	$C_{35}H_{39}\ N_2O_3Br$	68.53(68.29)	6.64(6.34)	4.73 (4.55)

Table 3. IR absorptions of 2-(4′-*n*-heptyloxy benzoyloxy)-naphthyl-1-azo-4″-bromobenzene.

759 cm^{-1}	Ortho substituted benzene ring
886 cm^{-1}	Para substituted benzene ring
1010 cm^{-1}	–C = O bend
1155 cm^{-1}	C–N str. Due to –N = N–
1202 cm^{-1}	C–O str.(ester)
1260 cm^{-1}	C–O str. (ether)
1471 cm^{-1}	Aromatic –C = C–
1503 cm^{-1}	
1600 cm^{-1}	
1736 cm^{-1}	C = O str.(ester)
2854 cm^{-1}	Sat. C–H str.
2924 cm^{-1}	
1052 cm^{-1}	Ar–Br
IR confirms the above structure	

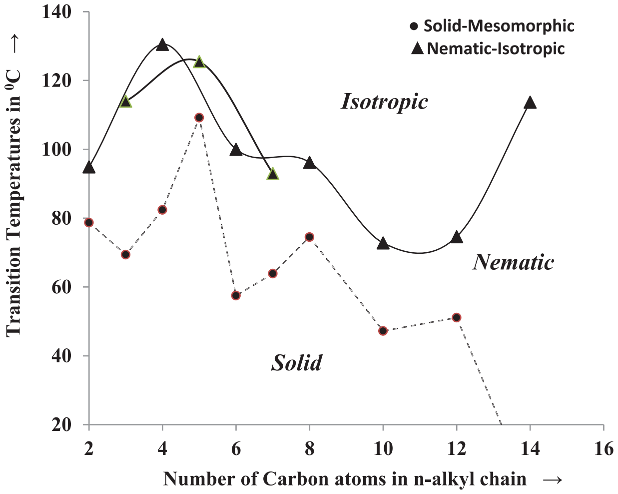

Figure 1. Phase behaviour of Series.

(Table 1) were plotted *versus* the number of carbon atoms present in *n*-alkyl chain of left *n*-alkoxy terminal end group of the molecules of each homolog (Fig. 1). Some selected members of a novel series were characterized by elemental analysis, DSC (Fig. 2a–b), polarizing microscopy, IR spectra, texture determination by miscibility method. Textures observed by optical polarizing microscope (POM) are shown in Figure 3. Present investigation is planned to synthesize novel azoester homologous series consisting of naphthyl unit linking a phenyl ring through –COO– and other phenyl ring through –N = N– central bridges to which –OR *n*-alkoxy terminal end group and at the other end para substituted –Br with respect to –N = N– group to be synthesized

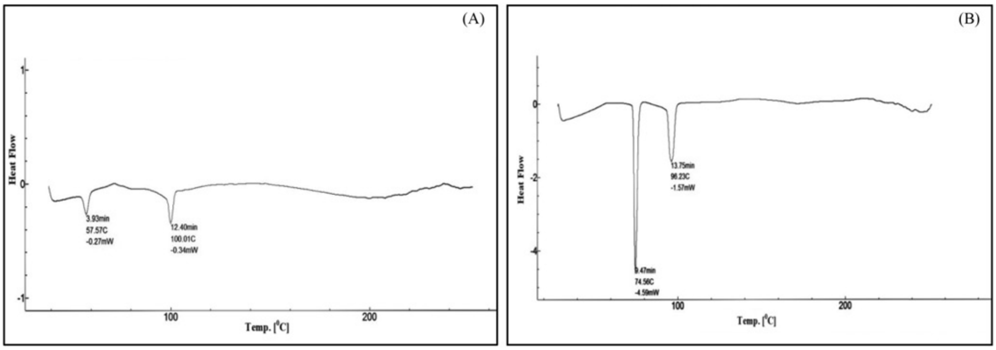

Figure 2. (a) 2-(4′-*n*-hexyloxy benzoyloxy)-naphthyl-1-azo-4″-bromobenzene. (b) 2-(4′-*n*-octyloxy benzoyloxy)-naphthyl-1-azo-4″-bromobenzene.

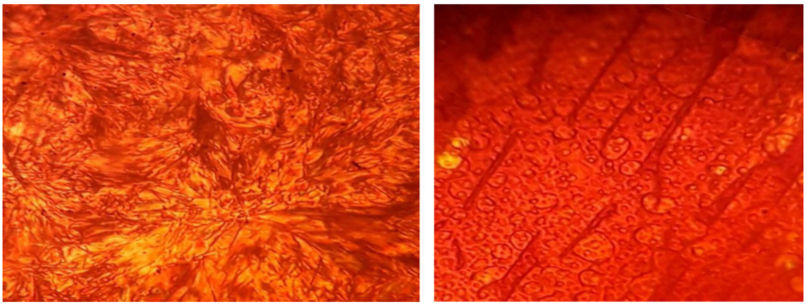

Figure 3. Textures observed by POM.

and characterized by analytical data. Thus, study is aimed to understand and establish the effect of molecular structure on mesomorphism as a consequence of molecular rigidity and flexibility [2–5].

The present investigation has been inspired with the desire to search for new LCs or nonamphiphile which may be endowed with specific characteristics. The synthesis had been undertaken after giving due consideration to the molecular geometry enhancing the potential probability of the new compounds to exhibit mesomorphism preferably in the lower range of temperature. The generalization concerning mesophase get strengthened from the present investigation, as the results obtained supports the generally accepted criteria and some new trends of transition curves and characteristics. The following homologous series have been synthesized and their characteristics have been determined.

LC characteristics of individual series

Homologous series: 2-(4′-n-alkoxy benzoyloxy)-naphthyl-1-azo-4″-bromobenzenes

Ten compounds have been synthesized and their mesogenic properties are determined. The phase transition temperatures of these compounds are recorded in Table 1. All the members exhibit mesomorphic character, except last member of present homologous series. Because mesomorphism is displayed by all the members of the series except last homolog of this series enantiotropically with nematic phase. Appearance of nematic mesophase comes from the second member of the series and continues up to the twelfth member of the series. This series is purely nematogenic. No smectic mesophase occurs *i.e.* smectic mesophase is absent in all members of this homologous series. Odd–even effect is clearly observed. Transition temperatures are plotted *versus* the number of carbon atoms in *n*-alkyl chain of left alkoxy group of the homologs as given in Figure 1. Smooth curves are drawn through the points for like or related transitions.

The solid-mesomorphic curve follows a zigzag path of rising and falling nature., *i.e.* falling from second to third homolog and then continuously rise up to fifth member and again falls at the sixth member of the series; with rises up to eighth homolog and then falls at the tenth homolog and small rising of 3.9 °C for twelfth homolog of series. All the members of the homologous series are enantiotropic nematic and smoothly transform into isotropic liquid at definite temperature.

The usual odd–even effect is observed in nematic–isotropic transition curves with alternation of transition temperatures. The nematic–isotropic transition curve for even member follows smooth zigzag path of rising and falling nature up to the twelfth homolog and for the odd members it rises from the third homolog to the fifth and falls at the seventh. The usual odd–even effect is observed in the nematic–isotropic transition curve with alternation of transition temperatures.

Thus, the present homologous series under discussion can be considered as middle ordered melting type series. Thus, present series under discussion is purely enantiotropic nematic. Thus, smectic mesophase is totally absent. The nematic phase has threaded texture as judged directly by visualizing the field of view in the hot stage POM. The series under discussion is purely nematogenic with middle ordered melting type.

Homologous series with above core structure reported is known to show mesomorphic characteristics. It is interesting to note that all the homologous series display mesomorphism from the second homolog of the homologous series in the enantiotropic condition. Mesomorphic characteristics exhibited by the molecules are directly related with the intermolecular or intramolecular forces arising out of the design of the molecular structure which is nothing but its molecular geometry. Polarity of the attached substituent groups, polarizability, length to breadth ratio, rigidity and linearity of molecule, steric hindrance caused by certain groups attached to the phenyl rings of the molecule, planner and non-planner nature, electron–electron interaction or charge transfer, π-electron density are considered important factors responsible for mesogenic characteristics of the molecules.

The basic length due to the two phenyl rings and one Napthyl ring and central linking units *viz.* –COO– and –N = N–, aromaticity of the molecule etc. are the constant unchanging feature and display of mesomorphism due to the molecular forces arising on account of these will remain the same for the homologous series (1). The left terminal is the *n*-alkyl (–R) chain of the alkoxy group in which progressively increases the number of carbon atom. Thus, the number of carbon atoms increases in the case of the various homologs of the present homologous series, keeping the other core structure intact. The right terminal is bromo functional group for series (1) along with the progressive increase in the number of carbon atoms of the *n*-alkyl chain at the left terminal for present homologous series.

2-Hydroxy-napthyl azo-4′-bromo-benzene is non- mesomorphic in nature. However, addition of napthyl ring linked through carboxylate –COO– central bridge and Para substituted *n*-alkoxy terminal increases the length and aromaticity of the molecule. Increased length and aromaticity of the molecule increases molecular polarity, molecular polarizability and length to breadth ratio, causing induction of liquid crystallinity in the molecule. Thus, added linking units to the different azo dyes induces mesomorphism enantiotropically optically especially nematic type mesophase of presently reported homologous series up to fourteenth homolog. This results in the exhibition of mesomorphism in the molecules of the present homologous series. The molecules exhibiting only nematic property is due to the capability of molecule to resist the strong thermal vibrations at high temperature to yield oriented anisotropic liquid. The molecules set themselves parallel to each other in a flowing condition giving rise to a threaded texture of nematic mesophase enantiotropically for ten homologs under present discussion.

Intermolecular Hydrogen Bonding and Mesomorphism: *p*-*n*-alkoxy benzoic acids are mesomorphic in behavior with relatively high transitions, their mesogenic properties are due to the dimerization of the acid molecules through hydrogen bonding. The elimination of hydrogen bonding through esterification should yield mesomorphism with relatively lower transitions. However, coupling of unit to the napthyl ring linked through –COO– bridge increases the transition temperatures of the "azo ester" molecules in case of linear molecule. But in present study, homologous series is nonlinear so transitions are relatively lower. Thus, the view that, the elimination of hydrogen bonding lowers the transitions of mesomorphism is further supported by the present investigation.

Alternation in transition temperature due to odd–even effect is exhibited in present homologous series in nematic–isotropic curve. The alternation of transition temperatures for odd and even members of the series is due to the difference in the length and linearity of *n*-alkyl group of left alkoxy group. It is directly related to magnitude of cohesive forces arising out of length and linearity of *n*-alkyl chain. Generally odd number *n*-alkyl chain causes weaker cohesion as compared to even number *n*-alkyl chain. Role of oxygen in *n*-alkoxy terminal should be considered. However overall intermolecular cohesive forces of attraction are affected by odd and even members of the homologous series; and hence the normal behavior of nematic–isotropic transition curves is also affected as series is ascended. It is seen that nematic–isotropic transition curve shows alternation of transition temperatures up to seventh homolog but alternation diminishes as series is ascended. This is because in case of longer *n*-alkyl chain, it coils and behaves as shorter chain and hence the cohesive forces are also altered.

Showing of alternations of transition temperatures for odd and even members of the series up to seventh homolog is understandable because alkyl chain of alkoxy group at the left alternates in number of $–CH_2–$ group. Generally odd homologs are loosely packed as compared to even homologs up to fifth member of the series but thereafter longer *n*-alkyl chain is coiled and does not maintain linearity. Hence transition temperatures of homologs beyond fifth are less affected or rather irregular change of transition temperatures is observed or normal behavior is observed for nematic–isotropic (or vice versa) transition curve.

Dimerization of *n*-alkoxy benzoic acids, nonmesomorphicity of tetradecyloxy (C_{14}) derivative and smectogenic property of ethyloxy to tetradecyloxy (C_2–C_{14}) derivatives disappears on esterification of *n*-alkoxy benzoic acids through their corresponding acid chlorides. Azo dye 2-hydroxy naphthyl azo 4′-bromobenzene is nonmesomorphic. However, on linking it with 4-*n*-alkoxy benzoic acids through their acid chlorides yielded nematogenic novel azoester homolog derivatives. Transition temperatures and melting temperatures of homologs (Table 1) are plotted *versus* the number of carbon atoms in *n*-alkyl chain of the left *n*-alkoxy terminal end group. Like or related points are linked to form solid-nematic and N–I transition curves to represent the phase behaviors of a novel series in a phase diagrams (Fig. 1).

The relative lowering of transition temperatures of azoester molecules and the disappearance of dimerization of *n*-alkoxy benzoic acids are due to the breaking of hydrogen bonding between two molecules of 4-*n*-alkoxy benzoic acid on esterification process. The induction of LC property in azoester homolog derivatives is due to the linking of azo dye to *n*-alkoxy benzoic acid molecules which increases molecular length and width and acquires the suitable magnitudes of anisotropic forces of end to end intermolecular attractions as a consequence of appropriate molecular rigidity and flexibility. The disappearance of smectogenic behavior of ethyloxy to tetra decyloxy (C_2–C_{14}) *n*-alkoxy acids is due to the nonlinear geometrical shape of corresponding novel azoester molecules, which hinders lamellar packing of molecules in their crystal lattices as required for smectic mesophase formation. The molecules of all the members of a presently investigated azoester series under the influence of externally exposed thermal vibrations disalign at an angle less than ninety degree and resisting exposed thermal vibrations for some temperature difference called as degree of mesomorphism and then the molecules of a sample under microscopic examination ceases to appear from and beyond isotropic temperature. The molecules of C_2–C_{14} adopt a statistically parallel orientational molecular order within definite range of temperature prior to isotropic temperature in floating condition. However same molecules are randomly oriented in all possible directions with high order of disorder or high entropy ($\Delta S = \Delta H/T$) from and beyond isotropic temperature. The same molecules show nematic mesophase reversibly below isotopic temperature on cooling the melt under microscopic observation. Absence of smectic phase is attributed to the absence of lamellar packing of molecules in their crystal lattices and unfavorable extent of noncoplanarity of azoester molecules due to its odd fitting of intermolecular nonlinear shape and size.

Conclusions

In conclusion, this work presents a successful approach to the synthesis of azoester molecules exhibiting liquid crystalline phases. To the best of our knowledge, as stated at the beginning, these may help to improve the technology of reflective LC devices. The formation of the low temperature nematic phase in these azo esters may also be useful in the area of ferroelectric LC displays. Azoester novel homologous series of ten homologs is entirely nematic with absence of smectic phase.

- LC with naphthyl derivatives are generally nematogenic.
- Suitable magnitudes of anisotropic forces of intermolecular end to end attractions occur as a consequence of favorable rigidity and flexibility.

- Molecular rigidity and flexibility are sensitive and susceptible to molecular structure.
- A phenomenon of mesomorphism depends upon the molecular structure of a substance concerned *i.e.* molecular shape, size, molecular polarity and polarizability, dispersion forces, aromaticity constituting the molecular rigidity and flexibility.

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