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Dependence of Liquid-Crystal Behavior of a Substance on Molecular Structure

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A novel azoester homologous series of liquid crystals (LCs) consisting of 12 members has been synthesized and evaluated. All members of the series exhibit the nematic mesophase enantiotropically without the exhibition of a smectic mesophase. The textures of the nematic phase are threaded or Schlieren in type. The transition curves in the phase diagram behave in a normal manner. The N-I transition curves exhibit an odd-even effect. The analytical and spectral data support the molecular structures of the homologs. The transition temperatures and mesophase morphology were determined by an optical polarizing microscope equipped with a heating stage. The azoester compounds consist of three phenyl rings with a meta substituted –Cl group at the middle phenyl ring and –OR and –OCH₃ as terminal end groups. The average nematic thermal stability is 195°C and the nematogenic mesophase length ranges from 9°C to 186°C. The LC behaviors of the series are compared with a structurally similar series. The novel series is entirely nematogenic and of a high melting point type.

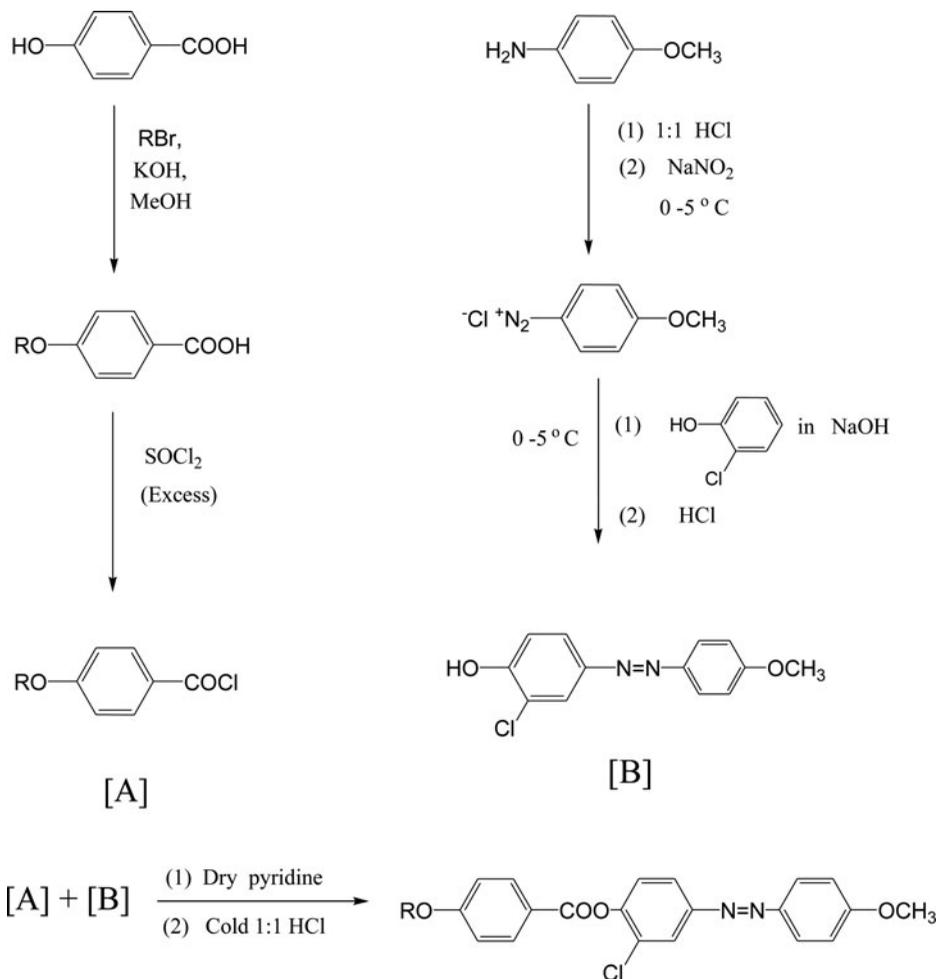
Keywords Liquid crystal; mesomorphism; nematic; odd-even effect

Introduction

The recognition of a novel physical state of a substance between the crystalline solid state and the isotropic liquid state was made in 1888 by Austrian Botanist [1] who termed this phase as the liquid crystalline (LC) state. Such a novel physical state has dual character of flow as a liquid and optical properties like a crystalline solid. Since 1888, scientists of all disciplines have shared their research interest with different aims, objects, and views according to their fields of research in specific liquid crystal area. Chemists synthesize novel substances and characterize them with analytical, spectral, and thermal data and study the effect of molecular structure on LC properties of the novel substances. Other research groups of other disciplines study the physical properties and applications using the novel substances reported by chemists [2–6]. The present proposed investigation is to synthesize novel azoester molecules with three aromatic rings bonded through –COO– and –N=N– central groups, two flexible terminal end groups –OR and –OCH₃ and one laterally substituted –Cl group at meta position with respect to –N=N– on middle phenyl ring, and to study effect of the mono substituted –Cl or –OCH₃ lateral group on

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mesomorphic behaviors of a substance or the effect of molecular structure on LC properties [7,8] in terms of molecular rigidity and/or flexibility [9–12]



Where, $\text{R} = -\text{C}_n\text{H}_{2n+1}$, $n = 1$ to $8, 10, 12, 14, \& 16$

Scheme 1. Synthetic route to series-1.

Experimental

Synthesis

2-Chlorophenol, 4-methoxyaniline, sodium nitrite, pyridine, thionyl chloride, 4-hydroxybenzoic acid, and n -alkyl halides were used directly as received. The solvents were dried and distilled before use. The synthetic route to the present series is illustrated in **Scheme 1**. The 4- n -alkoxy benzoic acid and corresponding 4- n -alkoxy benzoyl chlorides (A) were

Table 1. Elemental analysis for propyloxy, pentyloxy, octyloxy, and decyloxy derivatives

Sr. no.	Molecular formula	Elements% found (% calculated)		
		C	H	N
1	C ₂₃ H ₂₁ N ₂ O ₄ Cl	65.08(65.01)	4.99(4.95)	6.53(6.59)
2	C ₂₅ H ₂₅ N ₂ O ₄ Cl	66.36(66.30)	5.57(5.52)	6.14(6.19)
3	C ₂₈ H ₃₁ N ₂ O ₄ Cl	67.92(67.95)	6.24(6.27)	5.61(6.27)
4	C ₃₀ H ₃₅ N ₂ O ₄ Cl	68.98(68.90)	6.71(6.70)	5.39(5.36)

synthesized by the modified method of Dave and Vora [13]. 4-Hydroxy-3-chlorophenylazo-4'-methoxybenzene (B) was prepared by a known method [14a, 14b]. The 4-(4'-*n*-alkoxy benzoyloxy)-3-chlorophenylazo-4''-methoxybenzenes were synthesized by condensing the 4-*n*-alkoxy benzoyl chlorides (A) with 4-hydroxy-3-chlorophenylazo-4'-methoxybenzene (B) in pyridine [15a–15d].

Characterization

Some selected members of the series were characterized by Elemental analysis, IR spectra, ¹H-NMR spectra, mass spectra, and texture determination by a miscibility method. Micro-analysis of the representative compounds was performed on a Perkin Elmer PE 2400 CHN analyzer as shown in **Table 1**. IR spectra were performed on Perkin Elmer spectrometer and ¹H NMR spectra were performed on Bruker spectrometer using CDCl₃ as solvent. LC properties were investigated on a Leitz Laborlux 12 POL polarizing microscope equipped with a heating stage.

Spectral Data

IR in cm⁻¹ for n-Octyloxy Derivative

2920.0, 2851.6, 1467.0, 1350.1 (alkyl group), 1733.9, 1237.3 (ester group), 1602.0 (–N=N–), 1559.3 (–C=C– aromatic stre.), 1145.6 & 1166.9 (ether group), 840.9 (p-sub. benzene ring), 755.1 (tri sub. benzene ring), 720.4 (poly –CH₂- rocking bending), 1026.1 (C–Cl aromatic).

IR in cm⁻¹ for n-Tetradecyloxy Derivative

2916.2, 2849.6, 1478.0, 1381.9 (alkyl group), 1734.9, 1237.3 (ester group), 1600.0 (–N=N–), 1559.3 (–C=C– aromatic stre.), 1141.8 & 1167.8 (ether group), 833.2 (p-sub. benzene ring), 758.0 (tri sub. benzene ring), 716.5 (poly-CH₂- rocking bending), 1033.8 (C–Cl aromatic).

¹H-NMR in CDCl₃, δppm for n-Pentyloxy Derivative

0.95 (t, 3H, –CH₃), 1.41-1.46 (m, 4H, 2x–CH₂-), 1.83 (m, 2H, –OCH₂-CH₂-), 4.05 (t, 2H, –OCH₂-), 3.9 (s, 3H, –OCH₃), 6.90-8.21 (m, 11H, Ar-H).

¹H-NMR in CDCl₃, δppm for *n*-Hexyloxy Derivative

0.92 (t, 3H, -CH₃), 1.35-1.47 (m, 6H, 3 × -CH₂-), 1.83 (m, 2H, -OCH₂-CH₂-), 3.90 (s, 3H, -OCH₃), 4.05 (t, 2H, -OCH₂-), 6.90-8.21 (m, 11H, Ar-H).

Mass Spectra for Heptyloxy Homolog

Calculated value = 480.5

Experimental value = 480.5

Textures of Nematic Phase by Miscibility Method

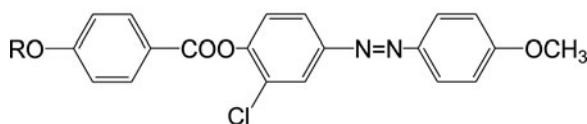
Pentyloxy homolog = Threaded nematic

Heptyloxy homolog = Schlieren nematic

Decyloxy homolog = Schlieren nematic

Results and Discussion

4-Hydroxy-3-chlorophenylazo-4'-methoxy benzene (m.p. 111°C, yield 68.5%) is a non-LC component, but on linking it with dimeric 4-*n*-alkoxy benzoic acids through their corresponding acid chlorides in pyridine an entirely nematogenic novel azoester homologous series is generated with a 9-186°C LC mesophase length in an enantiotropic manner. Smectogenic mesomorphism is absent throughout the series. Dimerization of 4-*n*-alkoxy benzoic acids disappears on esterification. Transition temperatures [Table 2] as determined by an optical polarizing microscopy equipped with a heating stage were plotted versus the number of carbon atoms present in *n*-alkyl chain, bonded to phenyl ring through oxygen atom. Like or related points are linked to form solid-nematic and nematic-isotropic transition curves showing phase behaviors of a novel azoester series in a phase diagram [Fig. 1]. Solid-nematic transition curve adopt a zigzag path of rising and falling values as the series is ascended with an overall descending tendency. The nematic-isotropic transition curve descended as series is ascended with the exhibition of an odd-even effect. Thus, both transition curves of a phase diagram behaved in a normal manner. The textures of the nematic phase are threaded or Schlieren, and characterization data supports the molecular structures of the novel homologs. The odd-even effect diminishes as the series is ascended. Curves for odd and even members match with each other near the heptyloxy homolog and then continue for higher homologs as a single curve. The average thermal stability for the nematic phase is 195°C. Thus, the entire series is nematogenic without the exhibition of a smectic mesophase with a mesophase length from 9°C to 186°C.

Homologous Series: 4-(4'-*n*-Alkoxy Benzoyloxy) -3-Chloro phenylazo-4''-Methoxy Benzenes

A long molecular length in the final azodyes is generated through esterification of 4-*n*-alkoxy benzoic acids through their corresponding acid chlorides with the azodye phenols. The long molecular length, lateral and terminal end to end attractions, molecular

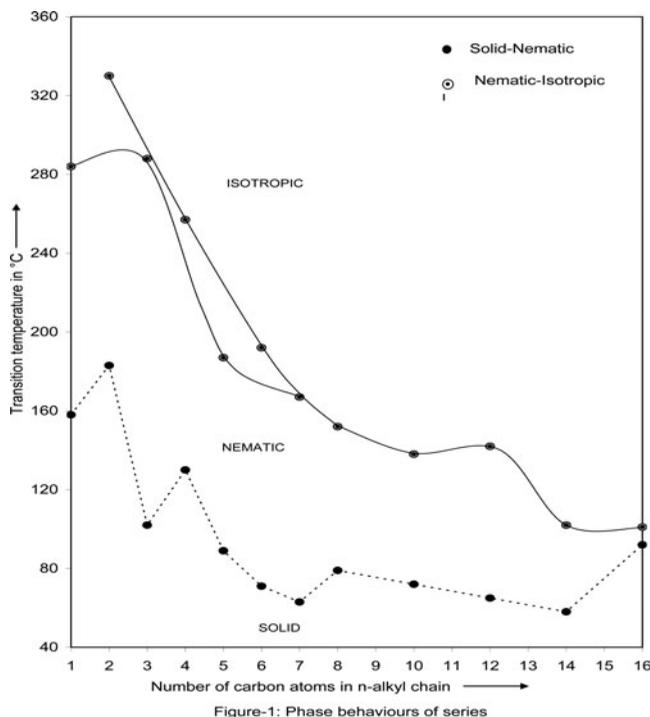


Figure 1. Phase behaviours of series.

polarity, and polarizability induce LC properties in all the twelve homologues of the novel series. The molecules of each homolog under the influence of exposed thermal vibrations are floated with a statistically parallel orientational order as a consequence of favorable molecular rigidity and flexibility to cause nematic mesophase formation in an enantiotropic manner with mesomorphism ranging from 9°C to 186°C without the exhibition of a smectic mesophase. The absence of smectogenic character indicates the absence of lamellar packing of molecules in their crystal lattices and unsuitable extent of molecular planarity, which hinders the formation of three dimensional molecular networks to cause sliding layered molecular arrangement in floating condition. An odd-even effect is observed due to the progressively and sequentially added methylene group to the *n*-alkoxy terminal end group. The disappearance of the odd-even effect beyond the heptyloxy (C₇) homolog is attributed to the coiling or bending or flexing or coupling of *n*-alkyl chain with the major axis of the core structure of a molecule. The changing trend in LC behaviors from homolog to homolog in the same series is also attributed to the changing number of methylene units and hence the changing magnitudes of molecular flexibility responsible for mesomorphism. The LC behaviors of presently investigated homologous series-1 are compared with structurally similar other known homologous series-X [16] and Y [17] as shown below in Fig. 2.

The novel homologous series-1 [Fig. 2] and series-X selected for comparison is structurally isomeric and similar, but their laterally and terminally substituted -Cl and -OCH₃ groups are exchanged with each other. Therefore, their molecular rigidity and molecular flexibility will differ. The novel homologous series-1 and series-Y only differ in respect of one terminal group as seen in Fig. 2. Thus, variations in mesomorphic behaviors and the

Table 2. Transition temperatures in °C for 4-(4'-*n*-alkoxy benzoyloxy)-3-chloro phenylazo-4''-methoxybenzenes

Compound no.	<i>n</i> -Alkyl group-C _n H _{2n+1} (<i>n</i>)	<i>Sm</i>	<i>N</i>	Isotropic
1	1	—	158.0	284.0
2	2	—	183.0	330.0
3	3	—	102.0	288.0
4	4	—	130.0	257.0
5	5	—	89.0	187.0
6	6	—	71.0	192.0
7	7	—	63.0	167.0
8	8	—	79.0	152.0
9	10	—	72.0	138.0
10	12	—	65.0	142.0
11	14	—	58.0	102.0
12	16	—	92.0	101.0

Sm, smectic; *N*, nematic.

degree of mesomorphism will depend upon changing trend of molecular rigidity and/or flexibility from homolog to homolog and series to series as a consequence of even minor variations in a molecular structure. Table 3 shows the comparison of LC behavior, thermal stability, commencement of mesophase, mesophase length for the novel series-1 and the series-X and series-Y chosen for comparison.

Table 3 indicates that

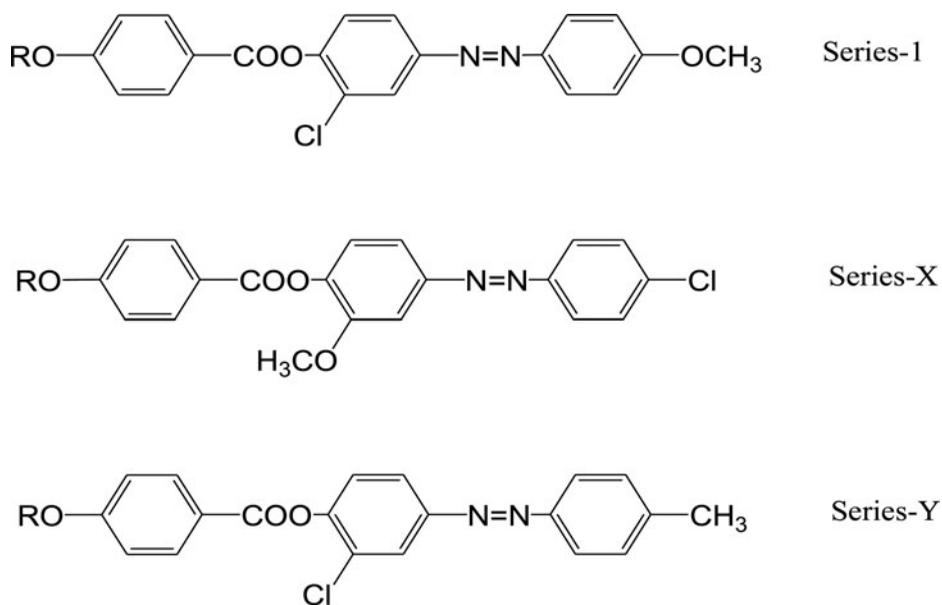
**Figure 2.** Structurally similar homologous series.

Table 3. Average thermal stability in °C

Series	1	X	Y
Smectic-nematic or smectic-isotropic commencement of Smectic phase	—	87.55 (C ₄ –C ₁₀) C ₄	—
Nematic-isotropic commencement of nematic phase	195.0 (C ₁ –C ₁₆) C ₁	125.60 (C ₃ –C ₁₆) C ₃	175.75 (C ₁ –C ₁₆) C ₁
Mesophase length range in °c	9–186 = 177	28–64 = 36	66–129 = 63

Homologous series-1 and series-Y are only nematogenic without exhibition of smectogenic character, but a homologous series-X is nematogenic with exhibition of smectogenic property.

Nematogenic property commences from very first (C₁) member of series-1 and series-Y, but it commences from third (C₃) member of a series-X. Smectic mesophase commences early from fourth (C₄) member of a series-X.

Nematic thermal stability of present series-1 is the highest (195) and that of the series-X is the lowest (125.60) among the homologous series-1, series-X, and series-Y under comparative study.

Smectogenic mesophase is stabilized from C₄ to C₁₆ homologs of series-X while, it destabilized in case of series-1 and series-Y.

Smectic and/or nematic phase length range is in the order of

Series-1 (177°C) > Series-Y (63°C) > Series-X (36°C)

Molecules of homologous series-1 and series-Y under comparison bear commonly lateral –Cl group at meta position to –N=N– central bridge and changing –OCH₃ or –CH₃ group as end group while –OCH₃ group is substituted at the same identical meta position in series-X, with –Cl as end group. The –Cl or –OCH₃ polar functional group substituted at meta position to –N=N– central bridge almost equally increases molecular width and reduces intermolecular attractions, but at the same time the same laterally substituted groups increases intermolecular attractions through molecular polarizability in unequal manner due to their different group polarity. The changing molecular polarity and/or polarizability increases intermolecular end to end attractions for the same homologue from series to series more or less depending upon group polarity of –OCH₃, –Cl and –CH₃. Thus, by exchanging the positions of polar groups –OCH₃ and –Cl for isomeric series-1 and series-X. The suitable magnitudes of anisotropic forces of intermolecular end to end attractions of series-1 exceeds to series-X, due to highly polar end group –OCH₃ in comparison with weakly polar –Cl group for inducing and stabilizing nematic phase. However, the lamellar packing of molecules in the crystal lattices of the homologs belonging to series-1 are hindered, but, the same are not hindered in case of the molecules of series-X, due to stronger interlocking of molecules by highly polar –OCH₃ lateral group as compared to weaker interlocking of laterally substituted –Cl group of series-1. Thus, smectogenic character is favorably induced in the molecules of series-X, but it is hindered to stabilize and facilitate smectic mesophase formation in case of the molecules of series-1. The early

or late mesophase formation depends upon magnitudes of suitability of anisotropic forces of intermolecular closeness and end to end or/and lateral attractions as a consequence of favorable molecular rigidity and/or flexibility as well as the extent of noncoplanarity among the molecules under comparative study. The extent of molecular noncoplanarity, end to end lateral attractions, molecular polarizability, dispersion forces, etc. changes with the laterally substituted penta atomic $-\text{OCH}_3$ and mono atomic $-\text{Cl}$ groups. Therefore series-1 and series-Y which are laterally substituted by $-\text{Cl}$ group on identical position to $-\text{N}=\text{N}-$ showed commencement of LC state from very first member (C_1) of the series-1 and Y, but the commencement of LC state takes place a little bit late from third (C_3) member of a series to which $-\text{Cl}$ and $-\text{OCH}_3$ groups are exchanged on identical positions. The mesophase length varies from series to series due to varying molecular resistivity against exposed thermal vibrations as reflected through the values of average thermal stabilities mentioned in Table 3. Thermal stabilities of the series under comparison are associated with energy stored of every substance due to its mass and characteristics (ΔH). Thus, highest and the lowest resistivity against exposed thermal vibrations are associated with the molecules of series-1 (177) and series-X (36), respectively. Thus, LC behaviors from homolog to homolog in the same series are associated with changing number of methylene unit or units keeping right terminal end group unchanged. However, changing trend of LC behaviors for the same homolog from series to series is attributed to the changing functional end groups $-\text{OCH}_3$, $-\text{Cl}$, or $-\text{CH}_3$. The difference of LC behaviors between series-1 and series-Y depends upon the difference of only one oxygen atom, i.e., between terminal end group $-\text{OCH}_3$ and $-\text{CH}_3$ for the same homolog, keeping rest of the molecular part unchanged.

Conclusions

Novel azoester series of twelve members with three phenyl rings, two central bridges, one meta-substituted lateral group $-\text{Cl}$ and two para-substituted terminal end groups is entirely nematogenic without exhibition of smectogenic character as a consequence of molecular rigidity and flexibility of suitable magnitudes to induce nematic mesophase depending upon molecular structure.

LC mesophase formation is very sensitive and susceptible to a molecular structure.

LC behaviors of isomeric substances with exchange of same polar functional groups at the same position and phenyl rings can have unequal LC behaviors.

The group efficiency order derives for smectic and/or nematic mesophase formation on the basis of (i) thermal stability, (ii) early commencement of mesophase, and (iii) mesophase length range are as under.

- (i) Nematic: $-\text{OCH}_3 > -\text{CH}_3 > -\text{Cl}$ —Smectic: $-\text{Cl} > -\text{OCH}_3 = -\text{CH}_3$
- (ii) Nematic: $-\text{OCH}_3 = -\text{CH}_3 > -\text{Cl}$ —Smectic: $-\text{Cl} > -\text{OCH}_3 = -\text{CH}_3$
- (iii) Smectic + nematic: $-\text{OCH}_3 > -\text{CH}_3 > -\text{Cl}$

Variations in LC behaviors from homolog to homolog in the same series depend upon changing sequentially or progressively molecular part, (methylene unit) keeping rest of the molecular part unchanged.

Variations in LC behaviors from series to series for the same homolog depends upon varying only lateral or only terminal end group keeping rest of the molecular part intact.

Molecular LC behaviors are the function of molecular rigidity and/or flexibility as a consequence of molecular structure.

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