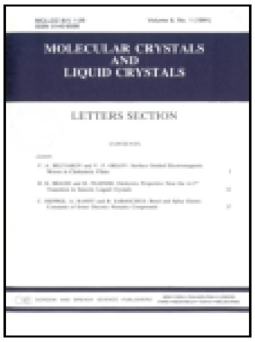

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Synthesis of novel azoester homologous series of liquid crystalline behavior and the study of mesomorphism dependence on lateral substitution of middle phenyl ring

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ABSTRACT

The titled azoester liquid crystalline homologous series consists of eleven homologues. The pentyl to tetradecyl derivatives of the series are nematogenic without exhibition of smectogenic character. Rest of the members of the series are nonliquid crystalline in nature. Textures of the nematic mesophase are schlieren or threaded type. Transition curves in the phase diagram showed normal phase behavior. Transition temperatures and liquid crystal behavior observed under an optical polarizing microscope equipped with a heating stage. An odd even effect is observed for nematic-isotropic transition curve. Analytical and spectral data confirms the structures of the molecules. Present homologous series is predominant nematogenic and partly nonmesogenic. Average thermal stability for nematic is 125.33°C and nematogenic mesophase length varies between 12°C to 48°C at tetradecyl (C_{14}) and octyl (C_8) derivatives, respectively.

KEYWORDS
Azoester; enantiotropic; liquid crystal; nematic; smectic

Introduction

An Austrian botanist Friedrich Reinitzer first observed and recognized a novel state of matter intermediate between crystalline solid and isotropic true Liquid in the year 1888 [1], which has flow property like liquid but optical properties like crystals. Such physical distinct state of a matter is called liquid crystalline (LC), mesomorphic or mesogenic state of a matter. Not all but some of the substances with suitable magnitudes of molecular rigidity and flexibility [2–5] based on molecular shape, size, and molecular structure do exhibit physically distinct state like liquid is also termed as anisotropic liquid. Thus, the presently proposed work is planned to synthesize novel liquid crystalline materials with three phenyl rings bridged through −COO− and −N=N− central bridges as rigid core and the rest of the molecular part viz., −OR, −Cl, $-OCH_3$ (terminal end group or/and lateral group) as flexible core. Thus, effect of broadening of molecular structure can be correlated with liquid crystalline behavior of the novel substances based on molecular rigidity and flexibility. Hence, present investigation is aimed to understanding and establishing the effect of molecular structure on liquid crystal properties [6–8].

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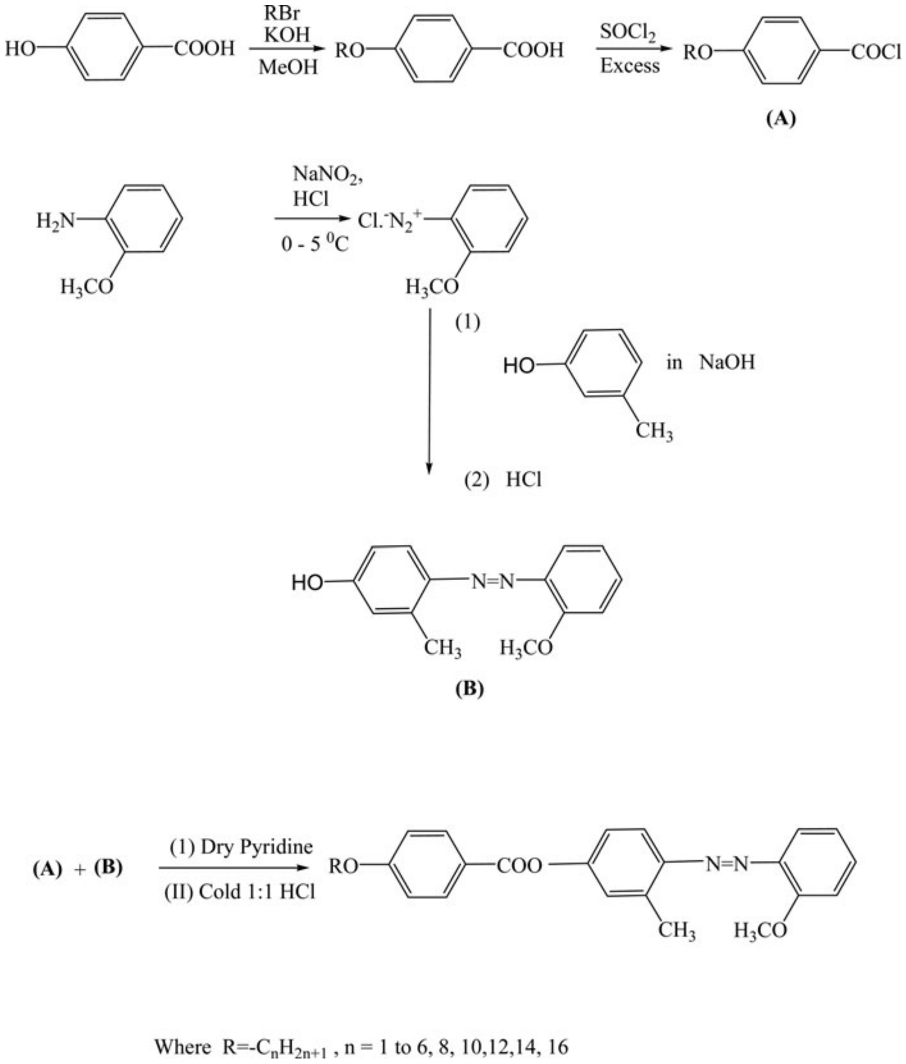
Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable corresponding alkyl halides [R-X] and converted to corresponding 4-n-alkoxy benzoyl chlorides (X) using thionyl chloride by the modified method of Dave and Vora [9]. 2-Methyl -4- hydroxyphenyl azo -2′- methoxy benzene (Y) was prepared by a known method [10]. Component (X) acid chloride and (Y) azo dye were condensed in dry cold pyridine to give the final azoester homologues [11]. 4-Hydroxy benzoic acid, alkyl halides, thionyl chloride, pyridine, KOH, methanol, O-anisidine, m-methyl phenol etc., required for synthesis were used as received except solvents which were dried and distilled prior to use. Synthetic route to the series is shown below as Scheme 1.



Scheme 1. Synthetic route to the series.

Characterization

Some selected members of the series were characterized by elemental analysis, infra red spectra (IR), and ^{1}H NMR spectra. Microanalysis was performed on Perkin-Elmer PE C, H, N analyzer (Table 1). IR spectra were recorded on Perkin–Elmer spectrum GX and ^{1}H NMR spectra were recorded on Bruker using $CDCl_3$ solvent. Liquid crystal properties were determined using an optical polarizing microscopy equipped with a heating stage. Textures of the nematic phase determined by miscibility method.

Analytical data

IR spectra in Cm^{-1} for C_8 and C_{14} homologues

Octyl

2920.0, 2850.6, 1370.6 (alkyl group), 1685.5, 1126.4 (ester group), 1257.5, 1168.8 (ether group), 1431.1(–N=N–), 844.8(p-sub benzene), 771.5 (o-sub. benzene).

Tetradecyloxy

2920.0, 2850.6, 1396.4(alkyl group), 1685.7, 1114.8, 1064.6(ester group), 1164.9, 1257.5(ether group), 1431.1(–N=N–), 844.8(p-sub benzene), 767.6 (o-sub. benzene).

^{1}H- NMR Spectra in $CDCl_3$ in δ ppm for Octyloxy ($C_{8)}$ & Dodecyloxy ($C_{10)}$ homologues:

Octyl

0.889(-CH_3 of -C_8H_{17}), 1.306(-CH_2 of -C_8H_{17}),1.806(-CH_2CH_2O of -C_8H_{17}), 2.742(-OCH_3, -C_8H_{17}) 4.035(-OCH_2CH_{2-}-), 6.905 & 6.934(p-sub Benzene), 7.253(o-sub Benzene).

Dodecyl

0.880(-CH_3 of -$C_{10}H_{23}$), 4.035(-OCH_2CH_2 of -$C_{12}H_{23}$), 1.264 (-CH_2CH_2 of -$C_{12}H_{23}$), 2.742(-OCH_3)

Textures by miscibility method

Nematic

Octyloxy homologue—Threaded texture
Dodedecyloxy homologue—Schlieren texture

Results and discussion

n-Alkoxy benzoic acids are dimeric. Their dimerization disappears on esterification by linking with azo dye (Y) due to breaking of hydrogen bonding. Methyl to butyl and hexadecyl derivatives of the series are nonliquid crystalline. The rest of the derivatives of the series are liquid crystalline with enantiotropically nematogenic character and absences of smectogenic character. Plot of the transition temperatures (Table 2) versus the number of carbon atoms in *n*-alkyl chain of the left *n*-alkoxy terminal end group shows phase behavior (Fig. 1) of the series.

The solid–isotropic or nematic transition curve continuously falls from methyl (C_1) to hexyl (C_6) derivative and then rises by 14°C at octyloxy homologue and again rises in minor magnitudes and fall by very few degrees of temperature. Nematic–isotropic transition curve

Table 1. Elemental analysis for propyloxy, hexyloxy, decyloxy derivatives.

		Elements% found (Calculated%)		
Sr. No.	Molecular Formula	C	H	N
1	$C_{24}H_{24}N_2O_4$	71.20 (71.28)	5.85 (5.94)	6.75 (6.93)
2	$C_{27}H_{30}N_2O_4$	72.64 (66.88)	6.70 (6.72)	6.21 (6.27)
3	$C_{31}H_{38}N_2O_4$	74.30 (74.11)	7.40 (7.56)	5.50 (5.57)

Table 2. Transition temperatures of the homologous series.

		Transition Temperatures in °C		
Compound No.	*n*-alkyl group C_nH_{2n+1} (n)	Smectic (Sm)	Nematic (N)	Isotropic (I)
1	C_1	–	–	180.0
2	C_2	–	–	148.0
3	C_3	–	–	138.0
4	C_4	–	–	134.0
5	C_5	–	123.0	140.0
6	C_6	–	83.0	125.0
7	C_8	–	97.0	145.0
8	C_{10}	–	89.0	128.0
9	C_{12}	–	82.0	114.0
10	C_{14}	–	88.0	100.0
11	C_{16}	–	–	90.0

4(4′-*n*-alkoxy benzoyloxy) -2- methyl phenyl azo-2″ -methoxy benzenes.

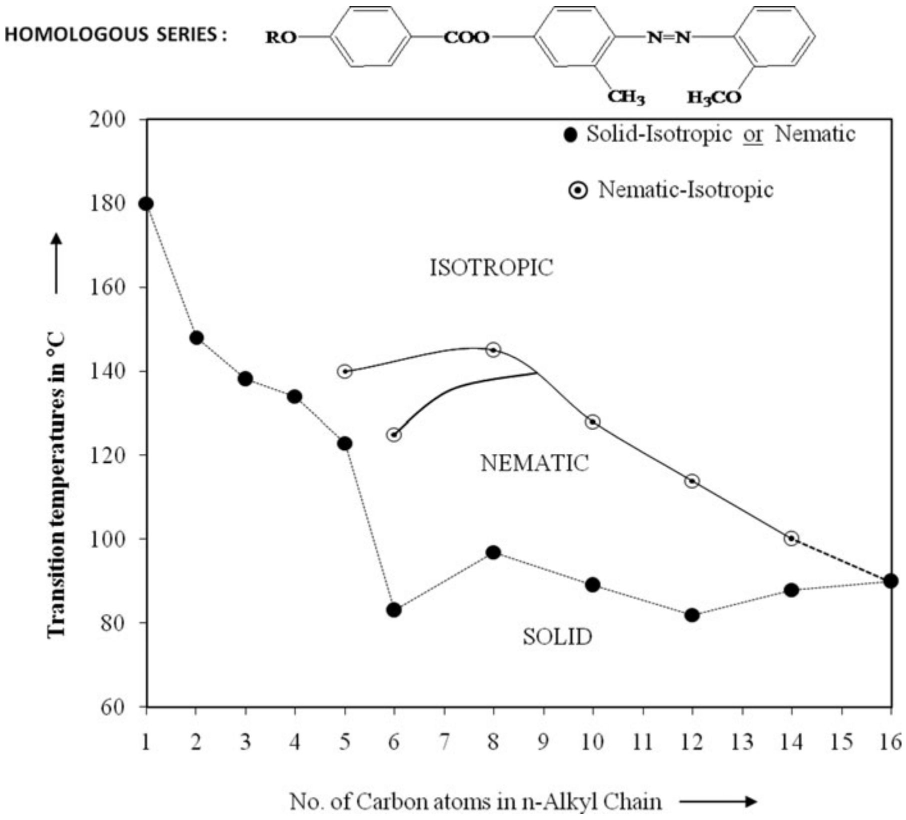


Figure 1. Phase behaviors of series.

showed descending tendency as series is ascended in usual expected manner with exhibition of odd-even effect. Nematic–isotropic transition curve is extrapolated [12–14] to the nonliquid crystalline hexadecyloxy homologue to predict latent transition temperature [LTT] for nematic. LTT merges or coincide into the solid-isotropic point of hexadecyl derivative of the series i.e. 90°C. This indicates that nematogenic phase length of hexadecyloxy homologue must be 90–90 = 0 i.e. nematic phase cannot occur and actually or practically does not occur is very well proved from the phase diagram. Nematic–isotropic transition temperature vary between 100°C to 145°C with nematogenic mesophase length varying minimum of 12°C at the tetradecyloxy derivative to the maximum of 48°C at the octyloxy derivative of the series. Thus, presently investigated homologous series is predominantly nematogenic and partly nonmesogenic without exhibition of smectogenic character. Nonmesogenic property showed by methyl to butyl derivatives of the series is attributed to their high crystallizing tendency arising from stronger intermolecular attractions due to relatively shorter n-alkyl chain length of left *n*-alkoxy terminal end group. The energy associated to stabilize and facilitate mesophase formation is insufficient to arrange statistically parallel orientations order of molecule in floating condition by unsuitable and unfavorable magnitudes of molecular rigidity and flexibility. Therefore, methyl to butyl derivatives sharply passes into isotropic state directly, without showing liquid crystal state at their relatively higher melting point. The nonmesogenic behavior of hexadecyl derivative of the series is attributed to its amorphous nature due to longer *n*-alkyl chain of left *n*-alkoxy end group. Thus hexadecyl homologue molecules are unable to resist thermal vibrations exposed upon them. Thus, unsuitable magnitudes of anisotropic forces of intermolecular end to end attractions of C_1 to C_4 and C_{16} homologues are unable to resist exposed thermal vibrations to exhibit mesomorphic state of either type or the mesophase formation is missing. Hence, it melts sharply at its melting point relatively at lower temperature without passing through liquid crystal state due to lower intermolecular attractions or heat content (ΔH). Thus, reasons for inability, to resist thermal vibrations for methyl to butyl group of homologues and hexadecyloxy homologue are different. Pentyl to tetradecyl derivatives of the series showed ability to withstand or resist thermal vibrations exposed upon them from thermodynamic surroundings. Therefore a thermodynamic system of molecules under examination disalign at an angle less than ninety degree from the plane of the surface within definite range of temperature and arrange themselves to maintain, statistically parallel orientational order of two dimensional array of restricted randomness or entropy ($\Delta S = \Delta H/T$) in floating condition, which maintain suitable magnitudes of intermolecular anisotropic forces of end to end attractions. Thus, nematogenic mesophase formation stabilizes within different range of temperature for different homologues of the same series and or the same homologue from series to series. Absence of smectogenic mesophase is attributed to absence of lamellar molecular packing in the crystal lattices of mesomorphic homologues. Thus, absence of lamellar packing in the crystal lattices hinders the smectogenic mesophase formation. Nematogenic mesophase disappears from and beyond isotropic temperature because, the limit of withstanding power (ΔH) against exposed thermal vibrations of a sample substance ceases and its molecules randomly orient in all possible directions without any sort of regularity of molecular order or one can say a high order of disorder of molecules or entropy (($\Delta S = \Delta H/T$) occur in destabilized state or floating condition. Such situation of a physical state of a matter is called the isotropic state. The mesomorphic properties including thermal stability of any homologue in same series and for the same homologue from series to series vary due to terminal end group and/or lateral group or a flexible part of molecules. The odd even effect and variations in mesomorphic properties from homologue to homologue in the same series is attributed to the sequentially added methylene unit at left *n*-alkyl chain of

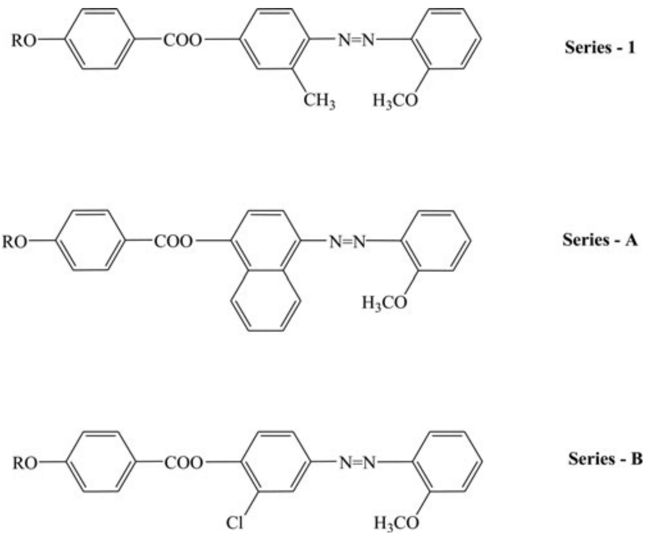


Figure 2. Structurally similar series.

n-alkoxy terminal end groups. The odd–even effect diminishes as series is ascended because longer n-alkyl chain of left *n*-alkoxy group may coil, bend or flex or couple to lie with the line of a major axis of the core. The mesomorphic properties of the presently investigated series-1 are compared with structurally similar homologous series A [15] and B [16] as mentioned below in Fig. 2.

Homologous series 1, A and B consisted of identically three phenyl rings bridged through −COO− and −N=N− as rigid core. Left *n*-alkoxy terminal end group for the same homologue and $-OCH_3$ lateral groups are commonly present at the left phenyl ring and right sided phenyl ring at ortho position to −N=N− central group. The only uncommon features are at the middle phenyl ring, which involves $-CH_3$, fused phenyl ring (naphthyl) and −Cl group as laterally substituted varying flexible core. Therefore, overall flexibility and rigidity vary for the same homologue from series to series and homologue to homologue in the same series. Table 3 represents the average thermal stability of all the three series under comparison and commencement of nematogenic mesophase formation.

Table 3 indicates that average thermal stability of series 1 is less than the series A [containing fused phenyl ring] and more than series B [containing −Cl]. All the three series under comparison are equally lengthened but they differ with respect to the ortho or meta-substituted lateral groups at the middle phenyl ring, whose, polarities are different. Moreover, all the three series 1, A, and B are broadened by $-CH_3$, fused phenyl ring and −Cl group, respectively, in addition to the commonly present ortho-substituted $-OCH_3$ group to −N=N− at the third phenyl ring. These two variations causes variations in length to breadth ratio, ratio

Table 3. Relative thermal stabilities in °C.

	Average thermal stabilities in °C		
Series	Series – (1)	Series – (A)	Series – (B)
Smectic-Isotropic	–	–	–
Commencement of smectic phase	–	–	–
Nematic-Isotropic	125.33 (C_5 - C_{14})	149.2 (C_6 - C_{14})	105.4 (C_6 - C_{14})
Commencement of Nematic phase	C_5	C_6	C_6

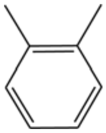
of the molecular polarity to polarizability, molecular aromaticity, electron–electron interactions, inductive effect, magnitude of steric hindrance etc. Hence, the overall molecular rigidity and flexibility [1–4] as a consequence of changing permanent dipole moment across the long molecular axis and dipole–dipole interactions and dispersion forces, affects LC properties of the substance depending upon molecular structure. The broadening or increased width of the molecule increases intermolecular distance and hence decreases intermolecular attractions on one hand and at the same time it increases molecular polarizability for which increases intermolecular attractions, on other hand. Thus, two opposing effects [7,8] are operating at a time for the same reason i.e. due to broadening of a molecule for all the three series 1, A, and B. The resultant net effect will be the predominating effect out of two opposing effects. All the three series [1,A,B] are only nematogenic without exhibition of smectogenic character. This observation substantiates relatively lower magnitudes of intermolecular attractions due to which absence of lamellar packing and hence absence of smectic mesophase formation of sliding layered molecular arrangement fails to appear, and lowering of nematogenic thermal stability resulted. Thus, polarizability factor does not predominate but declining of intermolecular attractions by increased molecular width factor predominates and raises its effectiveness to maintain only statistically parallel orientational order of molecule in floating condition, which enables only nematic mesophase formation. The highest value of nematic thermal stability of series A is attributed to the fused phenyl ring which raises molecular aromaticity or molecular rigidity at the cost of molecular flexibility in comparison with series 1 and B. Lowest value of nematic thermal stability of series B is attributed to the difference of steric hindrance caused by monoatomic –Cl group and tetra atomic -CH_3 group or fused phenyl ring. The unfavorable extent of noncoplanarity restricted to commence smectic mesophase till the last hexadecyloxy homologue of series-1, A, and B. Nematogenic mesophase commences from fifth, sixth and sixth members of the series 1, A, and B, respectively, due to difference of magnitudes of end to end attractions which causes present series 1 is as predominantly nematogenic and partly nonmesomorphic. Thus, variations in mesomorphic properties for the same homologue from series to series is attributed to molecular structure and especially the laterally substituted –CH_3, fused phenyl ring and –Cl group of series 1, A, and B of fixed polarity respectively.

Conclusions

1) Broadening of molecular width may increase or decrease the intermolecular attractions.
2) Homologous series with naphthyl moiety are generally nematogenic.
3) A Homologous series without right terminal (-H) end group and with laterally substituted functional group or groups hinders lamellar packing of molecules and are missing smectogenic character with exhibition of only a nematogenic mesophase formation.
4) Laterally substituted groups considerably affects the molecular rigidity and flexibility which are directly related to the magnitudes of anisotropic forces of intermolecular end to end attractions, and the lamellar packing of molecules.

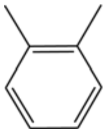
I) The group efficiency order derived for nematic on the basis of (i) thermal stability and the (ii) early commencement of mesophase with reference to functions group attached to middle phenyl ring at ortho or meta position to the central group is as below.

II) **Group efficiency** Fused Phenyl ring > $-CH_3$ > $-Cl$



order for nematic :

III) **Nematic:** $-CH_3$ > $-Cl$ = Fused Phenyl ring



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