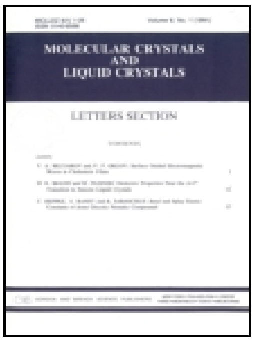

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Mesomorphism Dependence on Terminal and Lateral Polar Groups in the Nonlinear Novel Azoester Series

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The synthesis of a novel azoester homologous series was carried out with a view to understanding and establishing the effect of molecular structure on liquid crystal (LC) behavior of a substance. The novel series consists of eleven homologs, and all are enantiotropically nematogenic without exhibition of any smectic property. Transition and melting temperatures, textures of LC were determined by an optical polarizing microscope equipped with a heating stage. The textures of the nematic phase are threaded or Schlieren. Transition curves of a phase diagram behave in normal manner. The nematic-isotropic transition curve exhibits an odd-even effect. Analytical and spectral data support and confirm the structures of the homologues. Average thermal stability for the nematic is 137.2°C. The mesomorphic phase length ranges from 15°C to 50°C. LC behavior of the novel series is compared with a structurally similar known homologous series. The novel azoester homologous series is entirely nematogenic without exhibition of smectogenic character and of a middle-ordered melting type.

Keywords Liquid crystal; mesogen; mesomorphism; nematic, smectic

Introduction

The liquid crystalline state (LC) of matter intermediate to crystalline solid and isotropic liquid was discovered in 1888 [1]. Chemists, physicists, biologists, technologists, pharmacists, and engineers have shared their keen interest in the study and applications of liquid crystals [2,–5]. Various research groups of different disciplines study the LC state with different angles, views, aims and objects [6,7]. Chemists design and synthesize, and evaluate 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 [8–11] 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 [12–14], 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 [15,16]. Thus, the present study will include

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synthesis and characterization (not applications) of novel LC substances, to correlate a phenomena of mesomorphism (LC state) and the molecular structure of a substance. Further studies, including applications, will be studied by others [17,18].

Synthesis

4-Hydroxy benzoic acid was alkylated with suitable alkylating agents (*R*-*X*) to convert it into the corresponding *n*-alkoxy benzoic acids by an established method of Dave and Vora [19]. Azo dye 2-hydroxy napthyl azo 2'-nitro benzene was prepared by a reported method (M.P. is 175.0°C and Yield is 75%) [20]. 4-*n*-Alkoxy benzoic acids and the azo dye were condensed in ice cooled pyridine to obtain a series of final azo ester products [21]. Final products were decomposed, filtered, washed, dried, and purified until their constant transition temperatures were obtained.

4-Hydroxy benzoic acid, alkyl halides [*R*-*X*], methanol, ethanol, KOH, thionyl chloride, pyridine, β–naphthol, ortho nitro aniline, HCl, $NaNO_2$, etc. required for synthesis were used as received except for solvents which were dried and distilled prior to use. The synthetic route to the series is shown 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, and texture determination by miscibility method. Microanalysis of the compounds were performed on a Perkin Elmer PE 2400 CHN analyzer, IR spectra were performed on Perkin Elmer spectrometer, and ^{1}H-NMR spectra were performed on Bruker spectrometer using $CDCl_3$ as solvent.

Analytical Data

IR Spectra in cm^{-1}: for butyloxy and decyloxy derivatives:

Butyloxy: 2919, 2852(alkyl group),1733,1684,1204(ester group),1559,1360(Ar-NO_2), 1163(C-N Str. due to $-N{=}N-$), 758(o-sub.benzene) 848(p-sub benzene).

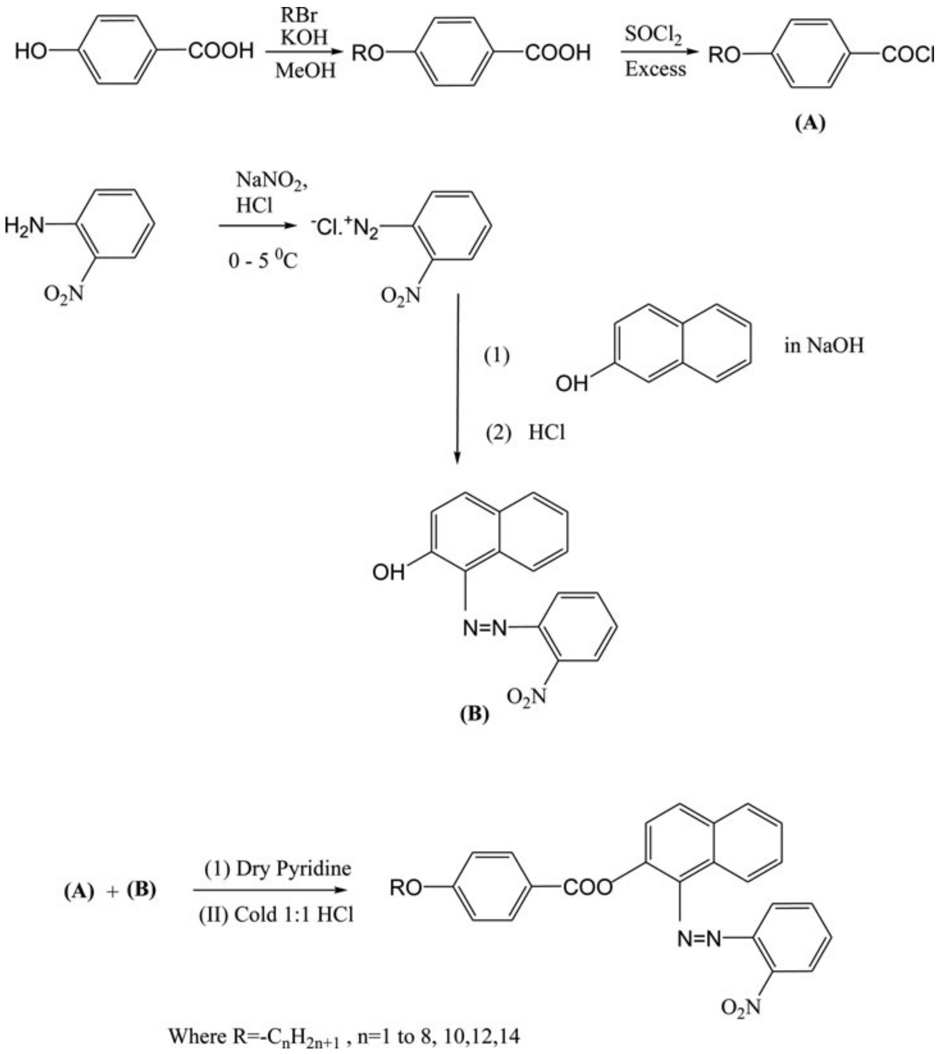
Decyloxy: 2920,2849(alkyl group),1652,1733(ester group), 1559,1300 (Ar-NO_2), 1169 (C-N Str. due to $-N{=}N{=}$), 740 (o-sub. benzene), 844 (p-sub benzene).

^{1}H- NMR Spectra in $CDCl_3$ in δ ppm: for methoxy and tetradecyloxy derivatives

Methoxy:3.91 (t, 3H, $-OCH_3$) 7.02–8.80 (m, 14H, Ar-H)

Tetradecyloxy: 0.88 (t,3H, $-CH_3$)1.25 (m, 24H, $-CH_2$) 4.053 (t, 2H, $-OCH_2$) 6.66–8.45 (m, 14H, Ar-H)

Mass spectra (molecular weight) ethoxy homolog:
Calculated-441
Experimental-441
Textures by miscibility method
Nematic:
Propyloxy homolog—threaded texture
Heptyloxy homolog—threaded texture
Decyloxy homolog—Schlieren texture



Where R=-C_nH_{2n+1} , n=1 to 8, 10,12,14

Scheme 1. Synthetic route to the series.

Results and Discussion

Azo dye 2-hydroxy napthyl azo 2′-nitrobenzene is nonmesomorphic (m.p. = 175.0 °C). However on linking it with the 4-*n*-alkoxy benzoic acids through their acid chlorides novel nematogenic azoester derivatives are generated. Transition temperatures and melting temperatures of homologs (Table 2) were plotted versus the number of carbon atoms in *n*-alkoxy terminal end group. Like or related points are linked to form solid-nematic and *N-I* transition curves to represent the phase behavior of the novel series in a phase diagram (Fig. 1).

The solid-nematic transition curve follows a zigzag path of rising and falling values with an overall descending tendency in a normal manner. The *N-I* transition curve is descended as the series is ascended except for the last tetradecyloxy homolog, which shows a negligible deviation of about 5° from a normal behavior with the exhibition of odd-even

Table 1. Elemental Analysis for Ethyloxy, Hexyloxy, Octyloxy, and Dodecyloxy Derivatives

Sr. no.	Molecular formula	Elements% found (calculated%)		
		C	H	N
1	$C_{25}H_{19}N_3O_5$	68.09(68.02)	4.00(4.30)	9.50(9.50)
2	$C_{29}H_{27}N_3O_5$	70.05(70.02)	5.35(5.43)	8.37(8.45)
3	$C_{31}H_{31}N_3O_5$	70.55(70.85)	5.80(5.90)	7.88(8.00)
4	$C_{35}H_{39}N_3O_5$	72.00(72.28)	6.59(6.71)	7.13(7.22)

effect. Thus, both the transition curves of the phase diagram behave in normal manner. The *N-I* transition curves for the odd and even homologs merge into each other at the octyloxy homolog and from the tetradecyloxy derivative a single transition curve results. The LC behavior varies from homolog to homolog in the present novel series. The average thermal stability for nematic is 137.2°C and mesophase length varies between 15°C and 50°C. Thus, the entire novel series is fully nematogenic and of a middle-ordered melting type.

The induction of LC property in first (C_1) and second azoester derivatives is due to the linking of the 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 molecules of all the members of the novel azoester series, under the influence of externally exposed thermal vibrations, misalign at an angle less than 90° and resist

Table 2. Transition Temperatures in °C for 2(4'-*n*-alkoxy benzoyloxy)-napthyl -1-azo-2''-nitro Benzenes

Compound no.	*n*-alkyl group $C_n H_{2n+1}$ (*n*)	Transition temperatures in °C		
		Sm	*N*	Isotropic
1	1	—	94.0	127.0
2	2	—	135.0	170.0
3	3	—	134.0	149.0
4	4	—	130.0	163.0
5	5	—	95.0	123.0
6	6	—	99.0	147.0
7	7	—	103.0	121.0
8	8	—	114.0	136.0
9	10	—	89.0	126.0
10	12	—	71.0	121.0
11	14	—	99.0	127.0

Sm, smectic; *N*, nematic.

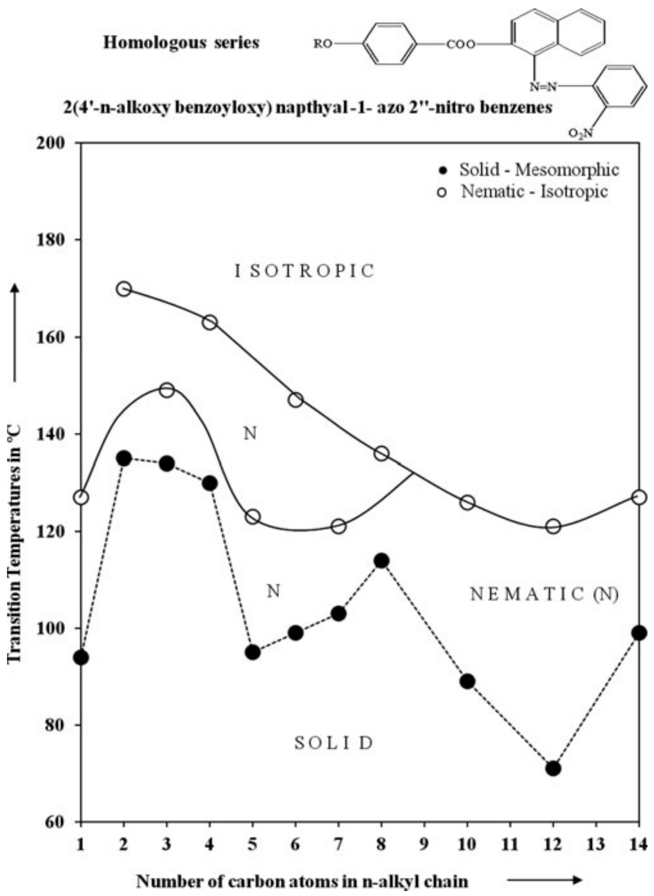


Figure 1. Phase behaviors of A series.

exposed thermal vibrations for some temperature difference called the degree of mesomorphism and then the molecules of a sample under microscopic examination cease to appear from and beyond isotropic temperature. The molecules of C_1–C_{14} adopt a statistically parallel orientational molecular order within a definite range of temperature prior to the isotropic temperature. However, the 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 the nematic mesophase reversibly below the isotopic temperature on cooling the melt under microscopic observation. The absence of a smectic phase is attributed to the absence of lamellar packing of molecules in their crystal lattices and unfavorable extent of noncoplanarity of the azoester molecules due to the nonlinear shape and size. The odd-even effect observed for *N-I* transition curve is attributed to the sequentially added methylene unit to the *n*-alkoxy chain bonded to phenyl ring. The odd-even effect for the *N-I* transition curve diminishes for higher homologs as the series is ascended because the *n*-alkoxy end group may coil or bend or flex or couple to lie with the major axis of the core structure. Variations in mesomorphic behavior from homolog to homolog in the same series are attributed to the changing length

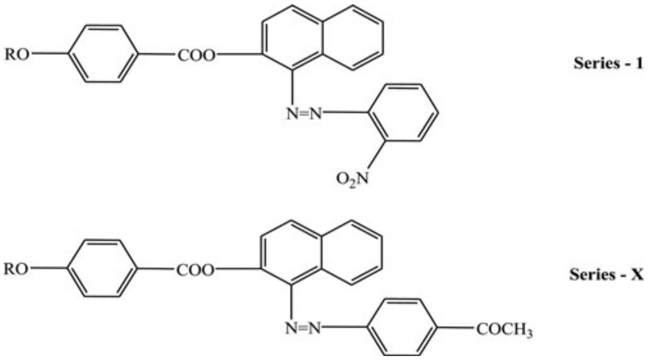


Figure 2. Structurally similar series.

of *n*-alkyl chain, and hence the changing molecular length, molecular polarity and polarizability, etc. Some mesomorphic properties of presently investigated homologous series 1 are compared with the structurally similar known homologous series X [22] as shown in Fig. 2.

Homologous series 1 and X are structurally similar and identical with respect to one napthyl and two phenyl rings bonded through –COO- and –N = N- central bridges as well as left *n*-alkoxy terminal end group for the same homolog from series to series. But they differ from each other with respect to right handed terminal or lateral end groups ortho $-NO_2$ or para $-COCH_3$ for the same series 1 and X, respectively. Therefore, the variations in mesomorphic properties and the degree of mesomorphism depend upon varying lateral or terminal end group for the same homolog from series to series and from homolog to homolog in the same series. Table 3 shows the average thermal stability, commencement of mesophase, phase length for the present series 1 and a series X chosen for comparison.

The common molecular part as described above for the same homolog from series to series and from homolog to homolog in the same series contributes almost equal molecular rigidity except for the induced effect of the lateral or terminal end groups of $-NO_2$ or $-COCH_3$, respectively. The changing parts are the *n*-alkyl chain for the same series and the lateral or terminal group for the same homolog from series to series, which contributes to the molecular flexibility. Thus, the combined effects due to molecular rigidity and flexibility are responsible for inducing mesomorphism in a substance, and vary from homolog to homolog in the same series and from series to series for the same homolog.

Table 3. Average Thermal Stabilities in °C

Series →	1	X
Smectic-nematic or smectic-isotropic commencement of Smectic mesophase	–	–
Nematic-isotropic commencement of nematic phase	137.2 (C_1–C_{14}) C_1	144.0 (C_6–C_{14}) C_6
Mesophase range	15°C–50°C C_3 C_{12}	47°C–60°C C_8 C_{12}

Table-3 indicates that

Both azoester homologous series under comparison are nematogenic only without exhibition of any smectogenic character.

A nematogenic mesophase formation commences from very first member (C_1) of a presently investigated novel series 1 but it commences late from sixth (C_6) member of a series X, chosen for comparison.

Average thermal stability of series 1 is (137.2°C) lower than a series X (144.0°C).

The mesophase length ranges from 15°C to 50°C for a series 1, while it ranges from 47°C to 60°C, i.e., phase length ranges for $50 - 15 = 35$°C and the same is appearing for $60 - 47 = 13$°C for series 1 and X, respectively.

Nematogenic mesophase induced from C_1 to C_{14} in present novel series, while the same is induced from C_6 to C_{14}.

The absence of smectogenic property in both the series under comparison is attributed to the absence of lamellar packing of molecules in their crystal lattices due to unsuitable magnitudes of anisotropic forces of intermolecular attractions required to build up three-dimensional molecular network in crystalline state or two dimensional sliding layered molecular ordered network in floating condition.

The unfavorable extent of noncoplanarity of molecules also hinders the formation of smectic phase till the last member of the series 1 and X. Lateral substitution of flexible group and a part of nonlinearity of molecules of both series 1 and X increases molecular width. Increased molecular width reduces intermolecular attractions on one hand and on the other hand it enhances the intermolecular attractions due to increased molecular polarizability. Thus, two opposing effects are operated at a time for the same (width) reason. The resultant net effect of intermolecular attractions depends upon the dominant factors operating at a same time for the same reason. Looking to the thermal stability values 137.2 and 144.0 of series 1 and X, they are nearer to each other with a difference of 8.8 more of series X. This difference of series X destabilizes and hinders even formation of nematic phase in methoxy to pentyloxy homologues of series X due to para substitution of highly polar $-COCH_3$ group. The presence of highly polar $-NO_2$ lateral group (ortho substituted) causes such a suitable magnitudes of anisotropic forces of intermolecular end to end attractions that, nematic mesophase induces from the very first member of a seris 1, i.e., the nematic mesophase is stabilized and facilitated for homologues of entire series at enthalpy value(ΔH) corresponding to 137.2°C thermal stability. Thus, nematogenic mesophase formation facilitated earlier for present series 1 as compared to series X. Hence, the mesomorphic behaviors for the same homolog from series to series vary mainly with the changing molecular flexibility by ortho $-NO_2$ and para $-COCH_3$ group from series 1 to series X.

Conclusions

Azoester novel homologous series of 11 homologs is entirely nematic with absence of smectic phase.

The group efficiency order derived for nematic on the basis of (i) thermal stability and (ii) early commencement of mesophase is as under.

Nematic: para $-COCH_3 >$ ortho $-NO_2$

Nematic: ortho $-NO_2 >$ para $-COCH_3$

LC with napthyl 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 phenomena of mesomorphism depends upon the molecular structure of a substance concerned, i.e., molecular shape, size, molecular polarity and polarizability, dispersion forces, and aromaticity constituting the molecular rigidity and flexibility.

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