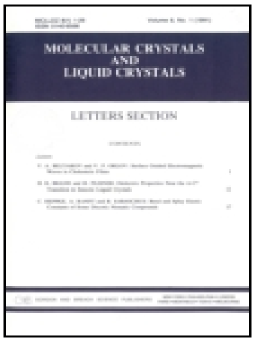

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Mesomorphism Dependence on Terminal/Lateral Substitution of Nonlinear Azoester Molecules

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A novel azo ester homologous series of liquid crystals (LCs) 2(4′-n-*alkoxy benzoyloxy) napthyl 1 azo-3″ nitrobenzenes consists of eleven members of a series with enantiotropic nematogenic mesophase formation and without exhibition of smectogenic property by all the eleven homologs. The nematogenic mesophase textures are threaded or Schlieren. Solid-nematic and nematic-isotropic transition curves of the phase diagram behave in normal manner except for the decyloxy, dodecyloxy, and tetradecyloxy homologs. Analytical and spectral data confirm the molecular structures of homologues. Thermal stability for the nematic phase is 132.6°C, and the degree of mesomorphism varies between 34°C and 79°C and the series if of a middle-ordered melting type. An odd-even effect is observed for the* N-I *transition curve with alternation of transition temperatures. The LC behavior of the series is compared with other structurally similar known homologous series to establish the relation between mesomorphism and molecular structure.*

Keywords Enantiotropic; liquid crystals; mesomorphism; nematic; smectic

Introduction

Liquid crystalline (LC) state of matter has molecular ordering between that of the ordered crystalline solid and the disordered isotropic liquid, and was discovered in 1888 [1]. The molecules of an LC state can be oriented under the influence of electric and magnetic field [2]. Many LC materials with conventional and unconventional structures and textures have been reported [3–5] due to their vital applications in various fields from manufacture of various articles to biological systems [6–8]. The science and technology oriented community of researchers have made massive contributions to thermotropic and lyotropic liquid crystals [9,10]. A chemist has to synthesize novel LC materials through binary systems and/or homologous series by changing molecular shape, size, polarity, polarizability, terminal end group, lateral group, central group, or groups etc [11,12]. The present investigation is planned to synthesize novel azoester homologous series of thermotropic type. Then it is aimed to characterize novel LC materials by elemental analysis, infrared spectra, ^{1}H NMR spectra, mass spectra, and characterization of type or types of LC state and type of texture of LC state through an optical polarization microscope equipped with a heating

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stage. Thus, the present study of LC materials is aimed with a view to understand and establish the effects of molecular structure on the LC state of the matter on the basis of molecular rigidity and flexibility [13–17] or to establish and corelate the relation between LC properties and the molecular structure.

Synthesis

4-Hydroxybenzoic acid was alkylated by suitable alkylating agents (*R*-*X*) to convert it into corresponding *n*-alkoxybenzoic acids by the usual established method of Dave and Vora [18]. Azo dye 2-Hydroxy-1-napthyl azo 3′-nitro benzene was prepared by a reported method (M.P. is 201.0°C and Yield is 78%) [19]. 4-*n*-Alkoxybenzoic acids and azo dye were individually condensed in ice-cooled pyridine to obtain a series of final azo ester products [20]. Final products were decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained.

The chemicals 4-hydroxybenzoic acid, alkyl halides [*R*-*X*], methanol, ethanol, KOH, thionyl chloride, pyridine, β–napthol, meta nitro aniline, 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 shown below in scheme 1.

Characterization

Some selected members of the novel series were characterized by elemental analysis, polarizing microscopy, mass spectra, infrared spectra, ^{1}H-NMR spectra, and texture determination by a miscibility method. Microanalysis was performed using a Perkin Elmer PE 2400 CHN analyzer, IR spectra were performed using a Perkin Elmer spectrometer, and ^{1}H-NMR spectra were performed using a Bruker spectrometer with $CDCl_3$ as solvent.

Analytical Data

IR Spectra in cm^{-1}: for Methoxy and Propyloxy derivatives:

Methoxy: 2918,2873,1447(alkyl group),1733,1684,1200(ester group),1528,1347(Ar—NO_2), 1156 (C—N Str. due to —N=N-), 668,761(m-sub.benzene) 840(p-sub benzene).

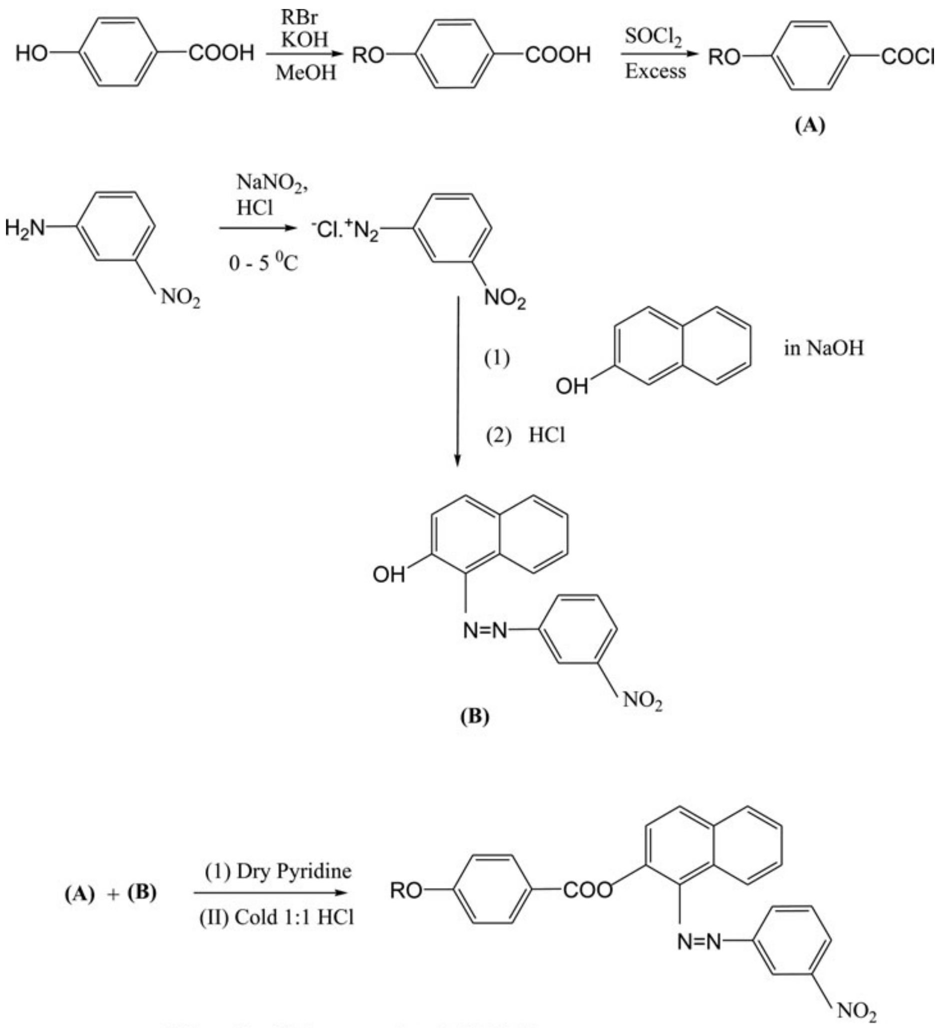
Propyloxy: 2966, 2848,1457(alkyl group),1733(ester group), 1528,1350 (Ar—NO_2), 1167 (C—N Str. due to —N=N—), 642,773 (m-sub. benzene), 848 (p-sub benzene).

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

Butyloxy: 0.98(t, 3H —CH_3),1.25(m,4H,—CH_2),4.052 (t, 2H,—OCH_2),7.0–8.40(m,14H, Ar—H).

Octyloxy:0.89(t, 3H,-CH_3),1.80(m,12H,—CH_2),4.01(t,2H,—OCH_2),6.90-8.36(m,14H, Ar—H).

Mass spectra (molecular weight) propyloxy homolog:
Calculated-455
Experimental-455
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

Transition and melting temperatures of the novel homologues (Table 2) were plotted versus the number of carbon atoms present in the *n*-alkoxy terminal end group. Like or related points are linked to draw the solid-nematic and nematic-isotropic transition curves forming a phase diagram (Fig. 1) showing phase the behavior of the series.

The solid-nematic transition curve adopts a zigzag path of rising and falling values with an overall descending nature and behaves in a normal manner. The *N-I* transition curve for odd members (C_1–C_7) initially rises and then descends and for even members of the series it descends up to the octyloxy homolog and then it ascends to the dodecyloxy homolog through the decyloxy homologue derivative and finally descends to the tetradecyloxy homologue. Thus, the *N-I* transition curve behaves in a normal manner up to the octyloxy homologue, but it deviates from normal behavior by about 5°C–10°C from and beyond the

Table 1. Elemental analysis for propyloxy, pentyloxy, heptyloxy, and dodecyloxy derivatives

		Elements% found (calculated%)		
Sr. no.	Molecular formula	C	H	N
1	$C_{26}H_{21}N_3O_5$	68.67(68.57)	4.51(4.61)	9.23(9.33)
2	$C_{28}H_{25}N_3O_5$	68.90(69.56)	5.01(5.17)	8.59(8.69)
3	$C_{30}H_{29}N_3O_5$	70.35(70.45)	5.49(5.67)	8.10(8.21)
4	$C_{35}H_{39}N_3O_5$	72.18(72.28)	6.51(6.71)	7.10(7.22)

octyloxy homolog. An odd-even effect is exhibited by the $N-I$ transition curve. The $N-I$ transition curves for odd and even members merges into each other between the octyloxy and the nonyloxy derivatives of the series and the $N-I$ curve propagates as a single curve. Smectogenic property is totally absent against the nematogenic property, which is totally present for all the members of the series. LC behavior of the series varies from homolog to homolog. The average thermal stability for nematic is 132.6°C. The mesomorphic phase length varies from a minimum of 34°C at the propyloxy homolog to a maximum of 79°C at the dodecyloxy homolog. The isotropic temperatures range from 125°C to 146°C. Thermal data confirmed on an optical polarizing microscope. Analytical and spectral data confirms the molecular structures of novel homologs. Thus novel homologous series is entirely nematogenic with a rich degree of mesomorphism.

The odd-even effect observed for the $N-I$ transition curve is due to the sequentially added methylene unit to the *n*-alkyl chain. Exhibition of LC state by the members of the series is attributed to the misalignment of the molecules at an angle of less than 90° with the plane of a surface resisting against the exposed thermal vibrations for some temperatures

Table 2. Transition temperatures in °C for 2(4′-*n*-alkoxy benzoyloxy)-napthyl-1-azo-3″-nitro Benzenes

		Transition temperatures in °C		
Compound no.	*n*-alkyl group $C_n H_{2n+1}$ (*n*)	Sm	*N*	Isotropic
1	1	—	94.0	129.0
2	2	—	109.0	140.0
3	3	—	99.0	133.0
4	4	—	94.0	132.0
5	5	—	89.0	125.0
6	6	—	86.0	128.0
7	7	—	81.0	125.0
8	8	—	72.0	128.0
9	10	—	83.0	133.0
10	12	—	67.0	146.0
11	14	—	69.0	140.0

Sm, smectic; N, nematic.

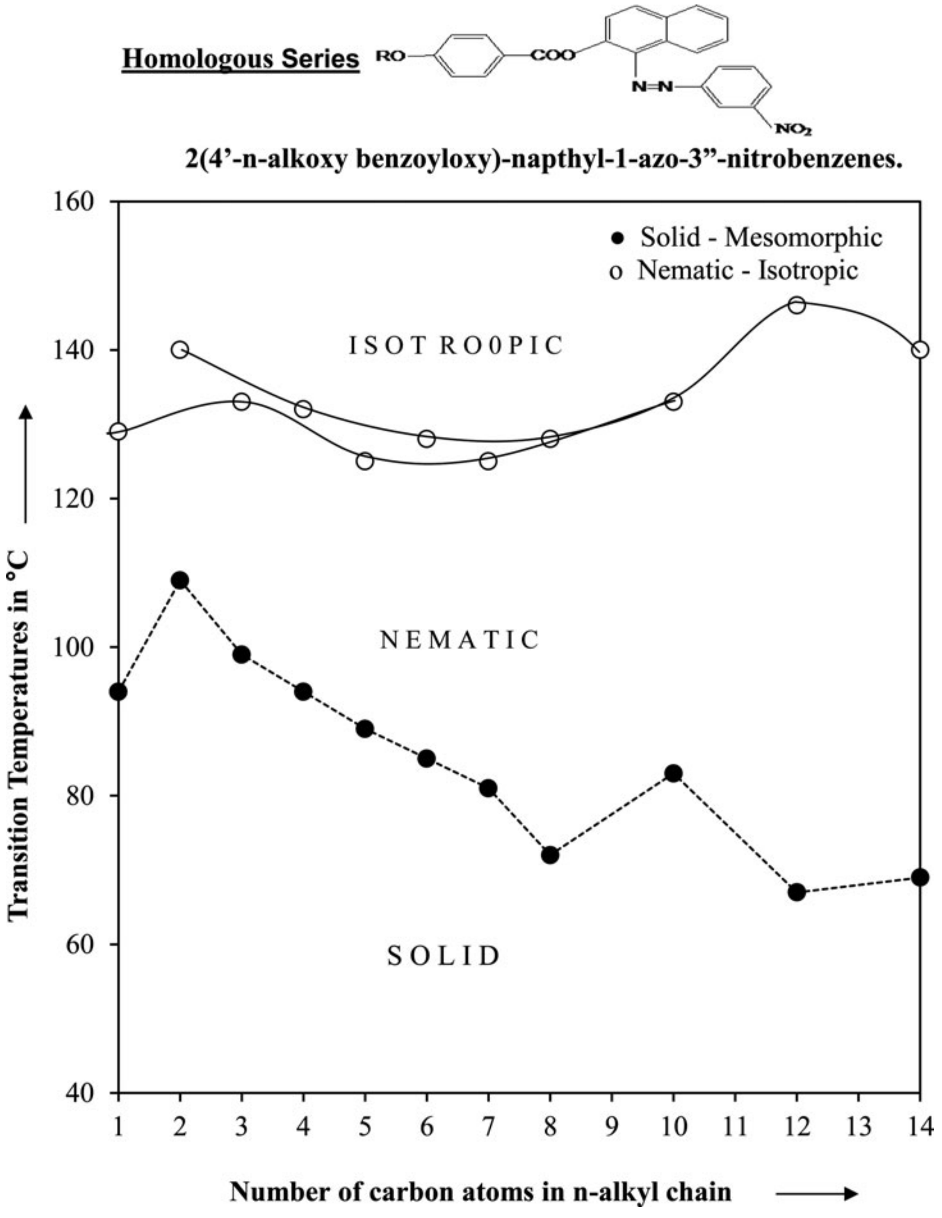


Figure 1. Phase behaviours of series.

limit; beyond which withstanding of exposed thermal vibrations ceases to resist. The net magnitude of intermolecular attractions actually generated is sufficient to maintain statistically parallel orientational order of molecules to facilitate nematic mesophase formation only. But it is insufficient to maintain two- or three-dimensional molecular network in a floating condition to slide out the layers of molecules on the surface, causing elimination of the smectic mesophase for all the novel homologs of presently investigated series. The normal behavior of the $N-I$ transition curve is attributed to normal status of n-alkyl chain

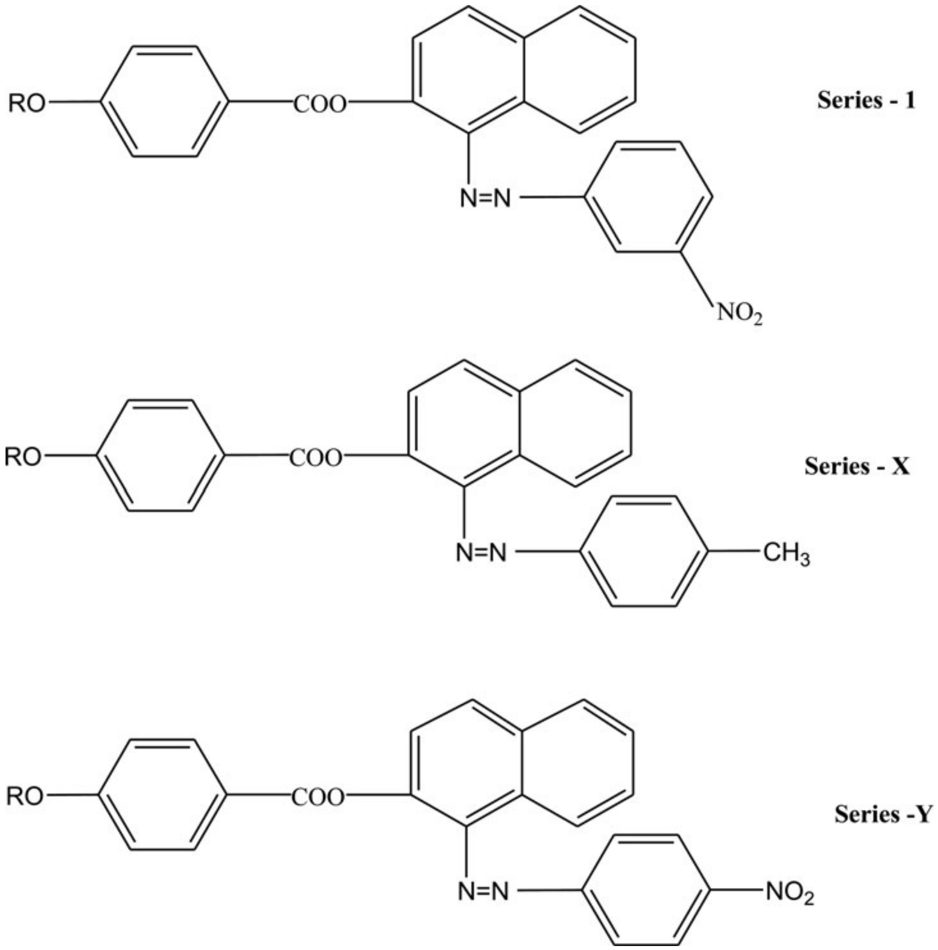


Figure 2. Structurally similar series.

ineffective to molecular rigidity and flexibility. The diminishing of the odd-even effect in the N—I transition curve from and beyond the seventh or eighth homolog of the series is due to coiling or bending or flexing or coupling of *n*-alkyl chain with the major axis of a core structure of the homolog molecules. The variations in mesomorphic properties from homolog to homolog in the same series is due to the changing number of carbon atoms present in *n*-alkyl chain of left *n*-alkoxy terminal end group; which causes gradual variations in molecular flexibility in combination of molecular rigidity. The low melting (67°C–109°C) is due to the nonlinear shape of the molecules, which widens the homologue molecules to increase the intermolecular closeness avoiding effect of polarizability factor. However, molecular rigidity and flexibility responsible to induce a rich mesomorphism (34°C–79°C) is enough for nematogenic mesophase but it is not favorable to fulfill the requirements to induce and stabilize smectic mesophase. The mesomorphic (LC) behaviors of the presently investigated novel homologous series 1 are compared with the structurally similar known homologous series X [21] and Y [22] as shown in Fig. 2.

The presently investigated azoester homologous series 1 and the structurally similar known homologous series X and Y chosen for comparison are identical with respect to

Table 3. Average Thermal Stabilities in °C

Series →	1	X	Y
Smectic-nematic or Smectic-isotropic commencement of smectic mesophase	—	—	—
Nematic-isotropic commencement of nematic phase	132.6 (C_1–C_{14}) C_1	127.27 (C_1–C_{14}) C_1	162.90 (C_1–C_{14}) C_1
Degree of mesomorphism from t_1 to t_2°C	34°C–79°C	10°C–41°C	29°C–93°C

two phenyl and one napthyl ring, —COO— and —N=N— central bridges and an *n*-alkoxy $–OC_nH_{2n+1}$ terminal end group for the same homolog from series to series, but it differs with respect to changing meta $–NO_2$, para $–CH_3$ and para $–NO_2$ from series 1 to X to Y, respectively. Therefore, variation in liquid crystal or mesomorphic property for the same homolog from series to series and the degree of mesomorphism, average thermal stability, commencement of mesophase, and other physical properties vary according to changing molecular flexibility in combination with the molecular rigidity from series to series for the same homolog. The variations in liquid-crystal properties from homologue to homologue in the same series depend upon the changing molecular flexibility due to changing number of methylene unit or units of the *n*-alkoxy terminal for all the homologs of the same series. Table 3 represents changing trend of average thermal stability, commencement of mesophase, and degree of mesomorphism as shown below.

Homologous series 1 and Y are isomeric except positions of the $—NO_2$ group substituted at the meta or para position of the same phenyl ring. Homologous series Y is identical in all respects to series 1 except for the $—CH_3$ group substituted in para position of a phenyl ring bonded to the —N=N— central bridge. Therefore, variations arising in LC behaviors will depend only on the changing molecular part; viz., meta $—NO_2$, para $—CH_3$ and para $—NO_2$ terminal or laterally substituted group of each series under comparison. Table 3 indicates that

All the three azoester homologous series (1,X,Y) under comparison are entirely nematogenic without exhibition of smectogenic mesophase.

Nematogenic mesophase commences from the very first member of all the three series and continued up to the last tetra decyloxy homologue with more or less thermal stabilities and the degree of mesomorphism.

Nematic thermal stability of presently investigated series 1 is more than a series X and less than a series Y under comparison.

The degree of mesomorphism of present series 1 is more ($79 – 34 = 45$) than a series X ($41 – 10 = 31$) and less than ($93 – 29 = 64$) a series Y.

All the three series contains a napthyl unit and two phenyl ring as well as two central bridges viz., —COO— and —N=N— as common identical part which contributed to molecular rigidity almost in equal proportion but molecular flexibility due to laterally and terminally substituted groups vary from homolog to homolog in the same series and for the same homologue from series to series (1 to X to Y). The absence of smectogenic mesophase formation indicates that the combine effects of molecular rigidity and flexibility emerging unequal anisotropic forces of intermolecular attractions of almost equally spaced nonlinear molecules and of unequal molecular polarity and polarizability of series 1, X, and Y under comparison, hinders the lamellar packing of molecules in their crystal lattices to form three-dimensional layered molecular network ordered arrangement which can result into sliding layered ordered arrangement while floating on the surface. Thus, smectic mesophase formation is hindered and only nematogenic mesophase formation is favored by suitable net magnitudes of anisotropic forces of intermolecular end to end attractions in series 1, X, and Y. The suitable magnitudes of anisotropic forces of intermolecular end to end attractions as a consequence of favorable molecular flexibility and rigidity facilitate and maintain the statistically parallel orientational order of molecules only from very first member to last member of all the series under comparison in floating condition; but it is efficient to hinder sliding layered arrangement of molecules until the last tetra decyloxy homolog, eliminating formation of smectic phase. The changing magnitudes of molecular flexibility in combination with their corresponding rigidity vary for the same homolog from series to series due to the variations of individual polar nature of less polar $-CH_3$ and highly polar $-NO_2$ groups and their varying positional (-ortho, -meta, and -para) status.

Conclusions

Presently investigated novel azoester homologous series consisting of 11 nematogenic homologues is an entirely nematogenic with absence of smectogenic character.

Nonlinearly shaped azoester series containing napthyl unit are generally nematogenic.

Group efficiency order for nematic derived on the basis of (i) thermal stability and (ii) the early commencement of nematic are as under.

Nematic:

para $-NO_{2}$- > meta $-NO_{2}$- > para $-CH_3$

Nematic: meta $-NO_{2}$-=para $-NO_{2}$-=para $-CH_3$

Group efficiency of same polar group depends upon its position of substitution.

The phenomena of mesomorphism is sensitive and susceptible to rigidity and flexibility of a molecular structure.

Degree of mesomorphism and mesomorphic behaviors of a substance are sensitive to molecular structure.

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