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The Dependence of Mesomorphism on the Terminal Group

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A novel azoester homologous series of liquid crystals (LCs) was synthesized and studied with a view to understanding and establishing the effect of molecular structure on LC behavior. The series consists of twelve members. All the members of the series exhibit a nematogenic mesophase. The methoxy and propyloxy derivatives are monotropic and the rest of the homologs are enantiotropic nematogenic. Smectic mesophase formation is completely absent. Transition temperatures and the textures of the nematic phase were observed and determined through an optical polarizing microscope equipped with a heating stage. Transition curves (Cr—N and N—I) of a phase diagram behave in a normal manner except for the hexadecyloxy homolog which deviates from normal behavior in the N—I transition curve. The N—I transition curve exhibits an odd-even effect. The textures of the nematic phase are threaded or Schlieren in type. The average thermal stability for the nematic phase is 158°C. The nematogenic mesophase length ranges from 27°C to 226°C. The analytical and spectral data confirms the molecular structures of the homologs. The LC properties of the presently investigated novel series are compared with a structurally similar known series. The novel azoester series is entirely nematogenic without exhibition of smectogenic character.

Keywords Azoester; enantiotropy; liquid crystal; nematic; smectic

Introduction

Liquid crystalline state (LC) of a matter in addition to well known three states of matter of solid, isotropic liquid, and gas, and has been known since 1888 [1]. Thereafter, many LC compounds [2–5] as simple monomers and dimers and polymers, etc. have been synthesized and studied with different aims objectives and views by researchers of different disciplines. We being chemists synthesize novel substances by varying molecular structure through alteration of the number of phenyl rings, central bridge or bridges, lateral, or/and terminal groups and then correlate the effect of molecular structure [6–8] on LC properties after their characterization. The present investigation is planned to synthesize and characterize novel azoester LC compounds consisting of three phenyl rings, two central bridges, two lateral

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Table 1. Elemental analysis for ethoxy, pentyloxy, octyloxy, and dodecyloxy derivatives

		Elements % found (calculated %)		
Sr. no.	Molecular formula	C	H	N
1	$C_{23}H_{20}N_2O_4Cl_2$	60.05(60.13)	4.30(4.36)	6.18(6.10)
2	$C_{26}H_{26}N_2O_4Cl_2$	62.22(62.27)	5.11(5.19)	5.51(5.59)
3	$C_{29}H_{32}N_2O_4Cl_2$	64.15(64.09)	5.80(5.89)	5.11(5.16)
4	$C_{33}H_{40}N_2O_4Cl_2$	66.18(66.11)	6.60(6.68)	4.16(4.67)

chloro groups, and two terminal end groups, with a view to understanding and establishing the relation between LC properties and the molecular structure as a consequence of molecular rigidity and flexibility [9–12]. The novel proposed azoester substances may find use in optical imaging display systems and for the study of cis-trans isomerism [13, 14].

Experimental

Synthesis

4-*n*-Alkoxy benzoic acid was alkylated by suitable alkylating agents (*R-X*) by the modified method of Dave and Vora [15]. Azodye 4-Hydroxy 3,5-dichloro phenyl azo-4′-ethoxy benzene was prepared by a usual established method (M.P is 84.0°C and Yield is 67.40%) [16]. 4-*n*-Alkoxy benzoic acids and the azodye were condensed in ice cooled pyridine to obtain a series of final azoester products [17]. The final products were individually decomposed, filtered, washed, dried, and purified until constant transition temperature were obtained.

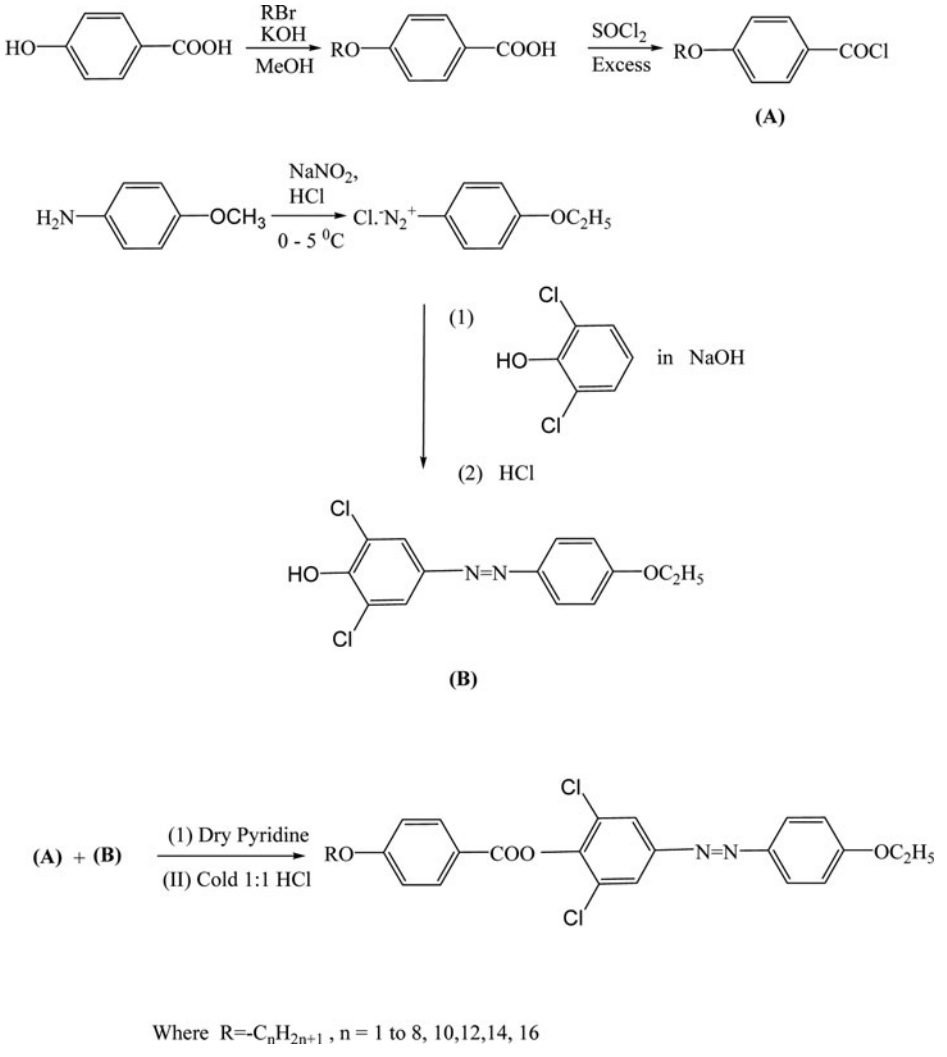
The chemicals, 4-hydroxy benzoic acid, alkyl halides [*R-X*], methanol, ethanol, KOH, thionyl chloride, pyridine, 2,6 dichloro phenol, 4-ethoxy aniline, HCl, $NaNO_2$, etc. required for synthesis were used as received excepts solvents, which were dried and distilled prior to use. The synthetic route to the series is shown in scheme 1.

Characterization

Some selected members of the novel series were characterized by elemental analysis, polarizing microscopy, mass spectra, infra red spectra, ^{1}H NMR spectra, texture determination by miscibility method. Microanalysis of the compound was performed on Perkin Elmer PE 2400 CHN analyzer as shown in Table 1. 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 in cm^{-1} for the pentyl derivative. 2924.8, 2849.6, 1451.1, 1387.7 (alkyl group), 1733.9, 1252.7 (ester group), 1596.0 (−N=N−), 1559.3 (−C=C− aromatic stre.), 1140.8 and 1163.0 (ether group), 842.8 (p-sub. benzene ring), 724.2 (poly −CH_2- rocking bending), 1041.5 (C−Cl aromatic).



Scheme 1. Synthetic route to the series.

IR in cm^{-1} for the hexyl derivative. 2934.0, 2856.0, 1442.7, 1387.7 (alkyl group), 1734.9, 1241.1 (ester group), 1588.0 (−N=N−), 1560.3 (−C=C− aromatic stre.), 1141.8 and 1164.9 (ether group), 839.0 (p-sub. benzene ring), 724.2 (poly-CH_2- rocking bending), 1043.4 (C−Cl aromatic).

^{1}H−NMR in $CDCl_3$, δ ppm for the butyloxy derivative. 1.00 (t, 3H, −CH_3), 1.57 (m, 2H, −CH_2-) 1.82 (m, 2H, −OCH_2-$\underline{CH_2}$-), 4.07(t, 2H, −OCH_2-), 1.46(t, 3H, −OCH_2-$\underline{CH_3}$-), 4.15 (q, 3H, −OCH_2-$\underline{CH_3}$-), 6.92–8.23 (m, 10H, Ar-H)

^{1}H−NMR in $CDCl_3$, δ ppm for the decyloxy derivative. 0.91 (t, 3H, −CH_3), 1.43–1.56 (m, 7H, 2x –CH_2-), 1.83 (m, 2H, −OCH_2-$\underline{CH_2}$-), 4.06 (t, 2H, −OCH_2-), 1.47 (t, 3H, −OCH_2-$\underline{CH_3}$-), 4.15 (q, 2H, −OCH_2-$\underline{CH_3}$-), 6.98–8.23 (m, 10H, Ar-H)

Table 2. Transition temperatures for 4-(4′-*n*-alkoxy benzoyloxy)-3,5-dichloro phenylazo-4″-ethoxy benzenes

Compound no.	*n*-Alkyl group $C_nH_{2n+1}(n)$	Transition temperatures in °C		
		Smectic (Sm)	Nematic (N)	Isotropic (I)
1	C_1	—	(195.0)	196.0
2	C_2	—	66.0	292.0
3	C_3	—	(155.0)	160.0
4	C_4	—	152.0	224.0
5	C_5	—	113.0	142.0
6	C_6	—	103.0	169.0
7	C_7	—	71.0	112.0
8	C_8	—	98.0	138.0
9	C_{10}	—	86.0	113.0
10	C_{12}	—	57.0	103.0
11	C_{14}	—	76.0	105.0
12	C_{16}	—	109.0	182.0

() indicate monotropy.

Mass Spectra(Molecular Weight) Butyloxy Homolog

Theoritical 487.
Experimental 487.

Texture Determination by Miscibility Method

Propyloxy homolog: Threaded texture
Hexyloxy homolog: Threaded texture
Hexadecyloxy homolog: Schlieren texture

Results and Discussion

The homologous series of the present investigation consists of twelve homologs and is entirely nematic in terms of mesomorphic behavior. The azodye 4-hydroxy 3,5 dichloro phenyl azo-4′-ethoxy benzene is a nonliquid crystal (NLC) (M.P. is 84°C and Yield is 67.40%) component. However on linking it with the 4-*n*-alkoxy benzoic acids through their corresponding acid chlorides in dry cold pyridine twelve homologs resulted, all with liquid crystal properties. Transition temperatures (Table 2) of the homologs are plotted versus the number of carbon atoms present in the alkoxy terminal end group. Transition curves (Cr-I or Cr—N and N—I or I—N) are obtained on linking like or related points showing phase behaviors of series in a phase diagram (Fig. 1).

The solid-isotropic or nematic (Cr—N or Cr-I) transition curve adopts a zigzag path of rising and falling values with an overall descending tendency and behaves in the usual established manner. The N—I or I—N transition curve is descended as the series is ascended up to the tetradecyloxy homolog and behaves in a normal manner. However, the hexadecyloxy homolog deviates from the descending tendency by ascending by about 82°C higher

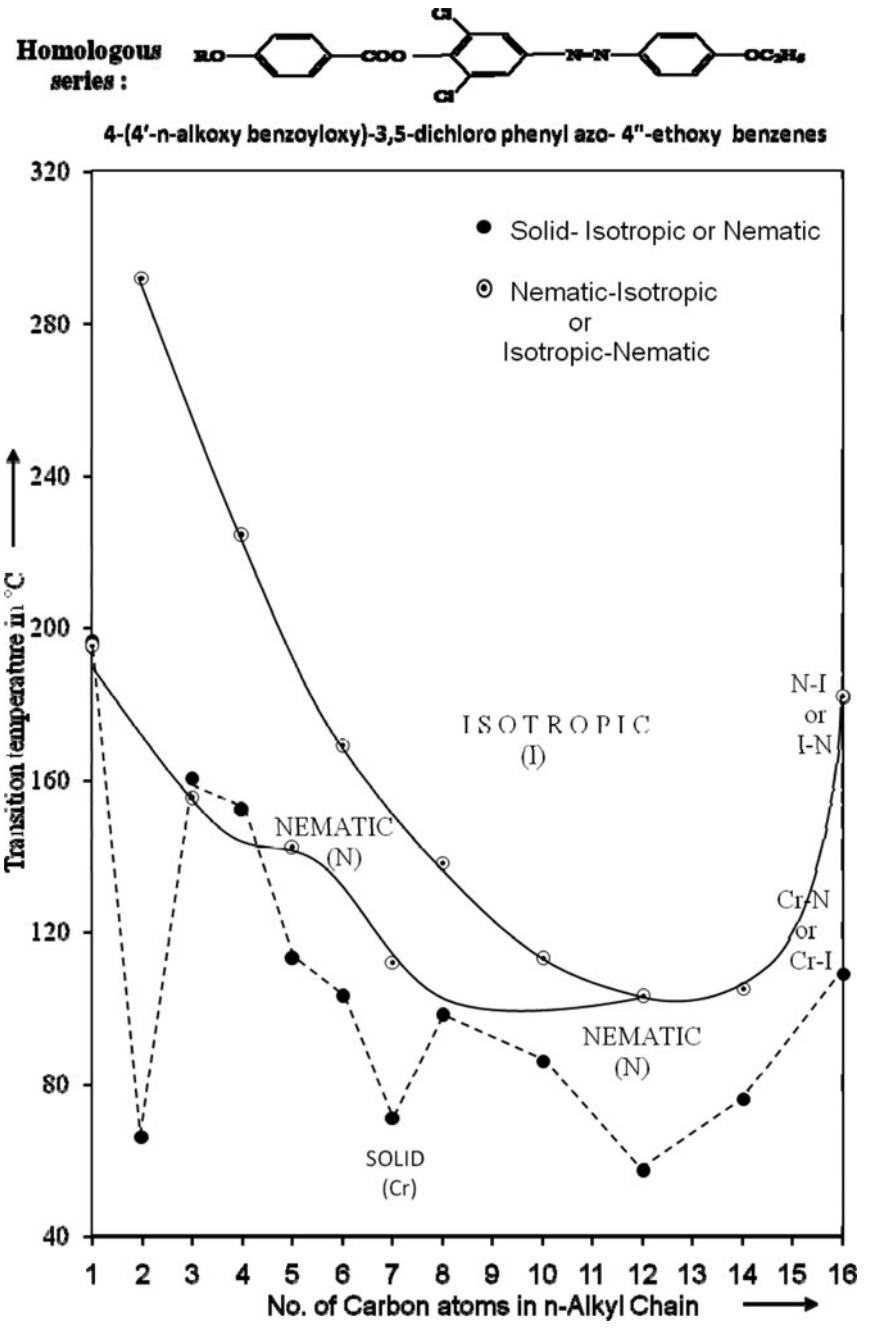


Figure 1. Phase behaviors of series.

than the expected normal behavior. The N—I Transition curve for the odd members (C_1–C_7) of the series lie below the transition curve for the even members and both transition curves (for odd and even members) merge into each other at the dodecyloxy (C_{12}) homolog and then continue as a single N—I curve. The mesomorphic (LC) properties vary from homolog

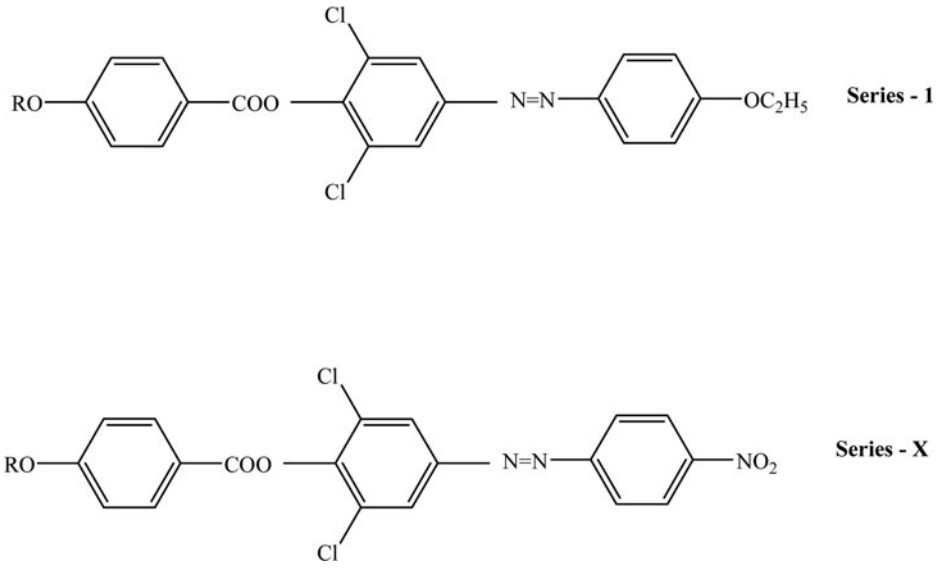


Figure 2. Structurally similar series.

to homolog in the present novel series. The average thermal stability for the nematic phase is 158°C and their mesomorphic mesophase length ranges from a maximum of 226°C at the C_2 homolog to a minimum of 27°C at the C_{10} homolog. Thus, homologous series under discussion is entirely nematogenic without exhibition of smectic mesophase formation.

Linking of 4-*n*-alkoxy benzoic acids with a NLC component Azodye, increases the length of molecules and hence the molecular rigidity and flexibilities are also enhanced as a consequence of the resulted permanent dipole moment acting across the long molecular axis, dipole–dipole interactions, dispersion forces, etc., which generate suitable magnitudes of anisotropic forces of end to end intermolecular attractions caused by molecular polarizability and other cohesive forces. Hence, the molecules of all the homologs (C_1–C_{16}) exhibit only a statistically parallel orientational order; either in reversible or irreversible manner, resisting exposed thermal vibrations for definite range of temperature depending upon the degree of resistivity toward heat and the angle of molecular disalignment. Thus, only nematogenic mesophase formation is facilitated. The diminishing of the odd-even effect from and beyond the dodecyloxy (C_{12}) homolog is attributed to the coiling or flexing or bending or coupling of *n*-alkyl chain with the major axis of the core structure of a molecule. The variations in mesomorphic properties from homolog to homolog in the present series is attributed to the sequentially added methylene unit in the *n*-alkyl chain, keeping the right handed terminal end group $-OC_2H_5$ unchanged. Thus, present novel series is nematogenic, and of middle ordered melting type, whose mesogenic phase length is wide, without exhibition of smectogenic property. The mesomorphic (LC) property of a present novel series is compared with a structurally similar homologous series X [18] as mentioned below in Fig. 2.

Novel homologous series 1 and a homologous series chosen for comparison X as shown in Fig. 2 are identical with respect to three phenyl rings, central bridges −COO− and −N=N−, two laterally substituted chloro groups at the middle phenyl ring and left *n*-alkoxy (−OR) terminal end group for the same homolog from series to series. However, they differ with respect to right side terminal end groups $-OC_2H_5$ (series 1) and $-NO_2$

Table 3. Relative thermal stabilizes in °C

Series →	1	X
Smectic-isotropic or Smectic-nematic Commencement of smectic phase	—	—
Nematic-isotropic	158.0	113.25
Commencement of *N* phase	(C_1–C_{16}) C_1	(C_4–C_{12}) C_2
Mesophase length range in °C	27–226	21–35

(series X). Therefore, the contribution of identical parts of the series under comparison for the same homolog toward molecular rigidity, flexibility, polarity, and polarizability, etc. related to suitable magnitudes of anisotropic forces of intermolecular end to end attractions are equivalent. However, the flexibility contribution by the $-OC_2H_5$ and $-NO_2$ terminal end groups differs in considerable magnitudes due to variation in permanent dipole moment across the long molecular axis, dipole–dipole interactions, dispersion forces, group polarities of individual terminal end groups $-OC_2H_5$ and $-NO_2$ for phenyl ring $-OC_2H_5$ and phenyl ring $-NO_2$ covalent bond (C—O and C—N bond) polarity. Therefore, total molecular rigidity and flexibility of the same homolog from series to series under comparative study and the homolog to homolog in the same series acquires difference of liquid crystal state inducing capacity or resistivity toward exposed thermal vibrations. Thus, mesomorphism and the degree of mesomorphism for the same homolog from series to series and from homolog to homolog in the same series depend upon changing suitable magnitudes of anisotropic forces of intermolecular end to end attractions as a consequence of resultant molecular rigidity and flexibility offered by individual molecular structure. Following Table 3 represents some liquid crystal properties of series 1 and X in a comparative manner.

Careful observation of Table 3 indicates that

- Azoester homologous series of liquid crystals of present investigation 1 and series X are only nematogenic.
- Smectogenic character is totally absent.
- Thermal stability for nematic of Series 1 and X are 158.0 and 113.25 as calculated on the basis of enantiotropic homologs, i.e., thermal stability of series 1 is higher than a series X.
- Nematogenic mesophase commences from very first member (C_1) of a series 1 to last C_{16} member and it commences from second member (C_2) of series X to dodecyloxy (C_{12}) member of a series.
- Mesophase length of series 1 is greater than a series X chosen for comparison.

Nematogenic mesophase formation and the degree of mesomorphism being attributed to the differing characteristics of right terminals $-OC_2H_5$ and $-NO_2$; the group efficiency order and mesophase stabilization are related to the group polarity of functional group $-OC_2H_5$ and $-NO_2$. A covalent bond between carbon of phenyl ring and oxygen atom of $-OC_2H_5$ is more polar than a covalent bond between a carbon of phenyl ring and Nitrogen atom of $-NO_2$ due to the difference between electron affinities of oxygen and Nitrogen

atom. Thus, on thinking the bond polarities concept between O and C, C and H of $-OC_2H_5$ as well as N and O of $-NO_2$, the $-OC_2H_5$ group releases electron clouds toward phenyl ring, whereas $-NO_2$ group instead of releasing toward phenyl ring it withdraws electron clouds from phenyl ring. Therefore, molecular rigidity and the end-to-end attractions among the molecules of series 1 for the same homolog are strengthened and therefore the relative thermal stability of series 1 is more than the thermal stability of series X. Thus, enthalpy (ΔH) value as related to thermal stability at a given temperature, i.e., energy stored in a homolog substance for the same homolog from series to series is relatively more for a series 1 than a series X, which facilitated the more resistivity against externally exposed thermal vibrations from thermodynamic surroundings for the molecules of series 1, than the corresponding molecules of series X. Therefore, comparatively mesophase length range and early commencement of nematic mesophase in case of series 1 are relatively superior to series X.

Conclusions

- Presently investigated novel series is entirely nematogenic without exhibition of smectic mesophase formation whose mesophase (nematic) commences from very first member of a series to the last member (C_1–C_{16}) of a series.
- Group efficiency order derived on the basis of (i) thermal stability, (ii) early commencement of mesophase, and (iii) the mesophase length range for nematic are as under.

(i) **Nematic** : $-OC_2H_5 > -NO_2$
(ii) **Nematic** : $-OC_2H_5 > -NO_2$
(iii) **Nematic** : $-OC_2H_5 > -NO_2$

- Suitable magnitudes of molecular rigidity and flexibility are important to induce LC state formation.
- Molecular rigidity and flexibility are very sensitive and susceptible to molecular structure.
- Novel azoester substances of present investigation may be useful for photoinduced study and optical imaging LC displays, etc.

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