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Dependence of Mesomorphism on Terminal End Group of a Molecule

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A novel azoester homologous series of liquid crystals consisting of 12 members is majorly nematogenic without the exhibition of smectic mesomorphism, except for the hexadecyloxy derivative. The methoxy and ethoxy members are monotropically nematic and the rest of the homologs are enantiotropically nematogenic. Transition temperatures and mesophase morphology were determined on an optical polarizing microscope equipped with a heating stage. The textures of the nematic mesophase are threaded or Schlieren in type. Infra red, ^{1}H NMR, mass spectral data, and elemental analysis data confirm the molecular structures of the novel homologs. The mesophase length varies from 00 to 72°C and the average thermal stability for the nematic phase is 133.5°C. Liquid crystal properties vary from homolog to homolog in present novel series. The liquid crystal behavior of the presently investigated novel series is compared with structurally similar known series. The transition curves (Cr-N/Cr-I and N-I/I-N) behave in a normal manner. The N-I/I-N transition curve exhibit an odd-even effect. The series is majorly nematogenic without exhibition of smectogenic character. Only the C_{16} homolog is nonmesogenic.

Keywords Azoester; liquid crystal; monotropy; mesogen; nematic

Introduction

Liquid crystal (LC) properties of substances have been exploited for the benefit of a mankind since its recognition [1] as a separate state between the crystalline solid and the isotropic liquid. Chloro substituted LC materials are useful as an optical imaging, LC displays, organic light-emitting diodes, semiconductor materials, anisotropic networks, hole transporting materials in organic light emitting devices, [2,3] etc. Azoester LC dyes and their benzoyloxy and cinnamoyloxy derivatives are also find equal importance as useful as other LC materials with reference to polarization of light and related study. Number of ester homologous series with –N = N- central groups have been reported [4–6]. The present investigation is planned with a view to understanding and establishing the effects of molecular structure on LC property [7,8] with the dichloro laterally substituted groups causing steric hindrance in space at the middle phenyl ring as well as $-OCH_3$ and –OR left and right terminal end groups on para positions of third and first phenyl rings. The study is

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Table 1. Elemental analysis for methoxy, butoxy, hexyloxy, and decyloxy derivatives

		Elements% found (calculated%)		
Sr. no.	Molecular formula	C	H	N
1	$C_{21}H_{16}N_2O_4Cl_2$	58.39(58.47)	3.78(3.71)	6.58(6.50)
2	$C_{24}H_{22}N_2O_4Cl_2$	60.80(60.89)	4.60(4.65)	5.90(5.92)
3	$C_{26}H_{26}N_2O_4Cl_2$	62.20(62.27)	5.11(5.19)	5.57(5.59)
4	$C_{30}H_{34}N_2O_4Cl_2$	64.60(64.63)	6.18(6.10)	5.12(5.03)

aimed to understand the effect of terminal end groups on mesomorphic behaviors keeping rest of the molecular part unchanged for the same homolog among the structurally similar series, in terms of molecular rigidity and flexibility, dipole moment, dispersion forces, etc. [9–12].

Experimental

Synthesis

4-*n*-Alkoxy benzoic acid was alkylated by suitable alkylating agents (*R-X*) by the modified method of Dave and Vora [13]. Azodye 4-Hydroxy 3,5-dichloro phenyl azo-4'-methoxy benzene was prepared by a usual established method (M.P is 102.0°C and Yield is 69.5%) [14]. 4-*n*-Alkoxy benzoic acids and azodye were individually condensed in ice-cooled pyridine to get a series of final azoester products [15]. Final products were individually decomposed, filtered, washed, dried, and purified till constant transition temperature, obtained.

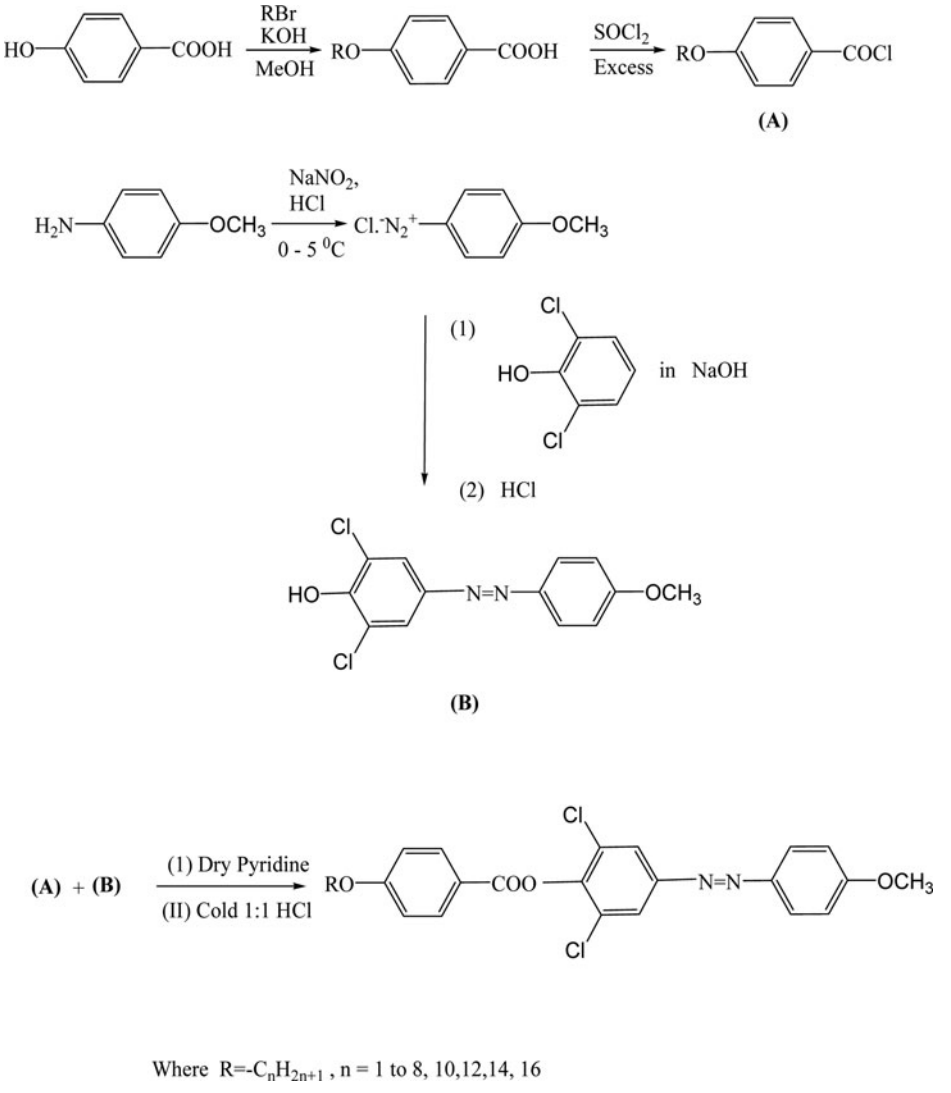
The chemicals, 4-hydroxy benzoic acid, alkyl halides [*R-X*], methanol, ethanol, KOH, thionyl chloride, pyridine, 2,6 dichloro phenol, 4-methoxyaniline, HCl, $NaNO_2$, etc. required for synthesis were used as received excepts solvents, which were dried and distilled prior to use. The synthetic route 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, infra red spectra, ^{1}H NMR spectra, texture determination by a 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 n-*heptyl derivative.* 2933.0, 2867.0, 1455.0, 1386.7 (alkyl group), 1733.9, 1241.1 (ester group), 1601.0 (−N=N−), 1582.5 (−C=C− aromatic stre.), 1142.7 and 1164.9 (ether group), 839.0 (p-sub. benzene ring), 724.2 (poly -CH_2- rocking bending), 1037.6 (C−Cl aromatic).



Scheme 1. Synthetic route to the series.

IR in cm^{-1} for n-*octyloxy derivative.* 2922.0, 2852.5, 1473.0, 1386.7 (alkyl group), 1733.9, 1242.1 (ester group), 1599.0 (−N=N−), 1581.5 (−C=C− aromatic stre.), 1142.7 and 1164.0 (ether group), 839.9 (p-sub. benzene ring), 723.3 (poly-CH_2- rocking bending), 1033.8 (C−Cl aromatic).

^{1}H-NMR in $CDCl_3$, δ ppm for n-*propyloxy derivative.* 1.07 (t, 3H, $-CH_3$), 1.88 (m, 2H, $-OCH_2-\underline{CH_2}-$), 3.9 (s, 3H, $-OCH_3$), 4.02 (t, 2H, $-OCH_2-$), 6.98–7.04 (d, 4H, Ar-H), 7.9 (s, 2H, Ar-H), 8.19 and 8.23 (d, 4H, Ar-H).

^{1}H-NMR in $CDCl_3$, δ ppm for n-*hexyloxy derivative.* 0.92 (t, 3H, $-CH_3$), 1.35–1.47 (m, 6H, 3x $-CH_2-$), 1.83 (m, 2H, $-OCH_2-\underline{CH_2}-$), 3.9 (s, 3H, $-OCH_3$), 4.06 (t, 2H, $-OCH_2-$), 6.90–7.04 (d, 4H, Ar-H), 7.94 (s, 2H, Ar-H), 8.18 and 8.23 (d, 4H, Ar-H).

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

Compound no.	*n*-Alkyl group C_nH_{2n+1} (*n*)	Transition temperatures in °C		
		Sm	*N*	Isotropic
1	C_1	—	(208.0)	210.0
2	C_2	—	(205.0)	207.0
3	C_3	—	142.0	172.0
4	C_4	—	147.0	171.0
5	C_5	—	100.0	146.0
6	C_6	—	97.0	147.0
7	C_7	—	86.0	131.0
8	C_8	—	75.0	126.0
9	C_{10}	—	80.0	117.0
10	C_{12}	—	40.0	112.0
11	C_{14}	—	71.0	80.0
12	C_{16}	—	—	60.0

Mass Spectra (Molecular Weight) Pentyloxy Homolog

Theoritical – 487.
Experimental – 487.

Textures by Miscibility Method

Pentyloxy homolog – Threaded texture
Heptyloxy homolog – Threaded texture
Tetradecyloxy homolog – Schlieren texture

Results and Discussion

Azodye 4-hydroxy 3,5-dichlorophenyl azo-4′-methoxy benzene is nonmesomorphic (M.P. is 102.0°C). However on condensing it with dimerized 4-*n*-alkoxy benzoic acids through their corresponding acid chlorides yielded azoester molecules with nematic type liquid crystalline behaviors throughout the series. Transition temperatures (Table 2) as determined by an optical polarizing microscopy equipped with a heating stage were plotted against the number of carbon atoms present in n-alkyl chain of the left *n*-alkoxy terminal end group to construct a phase diagram showing mesophase behaviors of a novel series. Transition curves were drawn by linking like or related points of a phase diagram (Fig. 1). Solid-isotropic (Cr–I) or Solid-Nematic (Cr–N) transition curve follows a zigzag path of rising and falling in usual established manner and behaved with normal behavior. Nematic-Isotropic (N-I) or Isotropic-Nematic (I-N) transition curve continuously descended as series is ascended up to tetradecyloxy(C_{14}) derivative. Hexadecyloxy (C_{16}) homolog derivative being nonliquid crystal, the N-I/I-N transition curve is extended [16] upto C_{16} homolog and it merges into Cr-I point of it, indicating that Cr-I and N-I point of C_{16} is the same and its mesophase length is zero, i.e., nonmorphicity of C_{16} is supported by the trend of N-I/I-N transition curve. And I-N/N-I transition curve exhibited odd-even effect with odd member's curve

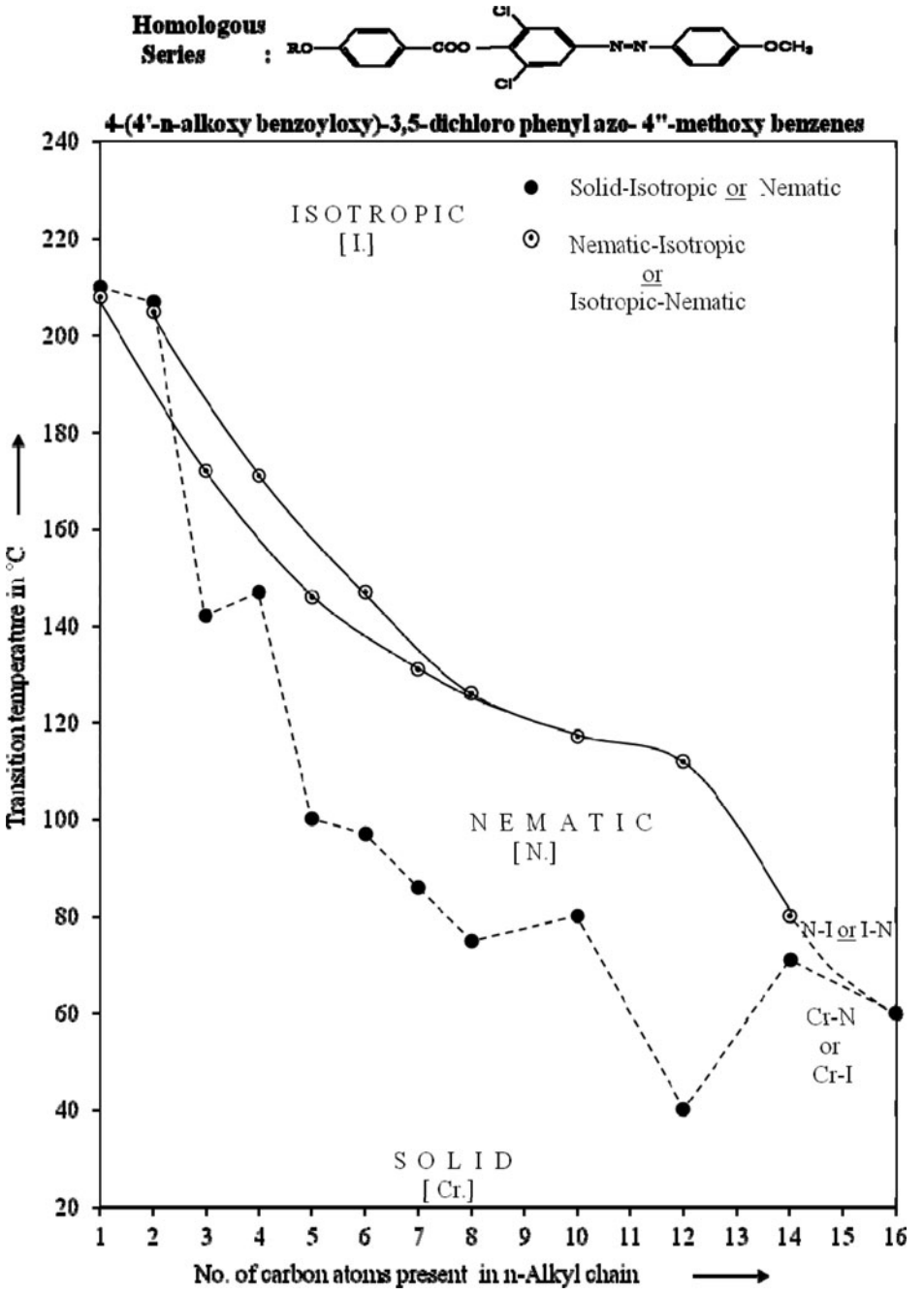


Figure 1. Phase behaviors of series.

lower than even member's curve. Curves for odd and even members merge into each other nearby nonyloxy (C_9) homologue and then from and beyond merging of each other, it follows into single N-I transition curve for higher homologs (C_{10}–C_{16}). Thus, odd-even effect diminishes for higher homologues from and beyond merging (C_9) of N-I curves for

odd and even homologues. Average Thermal Stability for nematic mesophase formation (C_3–C_{14}) is 133.5 ^{0}C and mesomorphic phase length ranges from 0 to 72°C. Mesomorphism commences from very first member of a novel series. Mesomorphic properties of a novel azoester series undergo variations from homologue to homologue with varying *n*-alkyl chain length keeping right terminal and other molecular part unchanged. Thus, presently investigated novel series is predominantly nematogenic (C_1–C_{14}), with partly high melting and partly middle ordered melting type, without exhibition of any smectic property.

4″-Methoxy Benzenes

Sm, Smectic; N, Nematic. Value in parenthesis indicate monotropy.

The molecular length increases on linking dimerized 4-*n*-alkoxy benzoic acids with azodye. Hence, the molecular length, length to breadth ratio, molecular polarity and polarizability, dipole–dipole interactions, dispersion forces, etc. are enhanced and attains to the suitable magnitudes of anisotropic forces of intermolecular end to end attractions as a consequence of favorable molecular rigidity and flexibility to induce nematogenic character in the members of a novel series from C_1 to C_{14} homolog derivatives. The dimerization of 4-*n*-alkoxy disappears on esterification through corresponding acid chlorides, due to breaking of hydrogen bonding between two acid molecules. Azoester molecules from C_3 to C_{14} homologs resist exposed thermal vibrations and disalign at an angle less than ninety degree for some temperature range on floating surface with statistically parallel orientational order. However, on continued further heating beyond certain temperature limit intermolecular anisotropic forces are loosened and a sample substance exhibit isotropic state of existence from and beyond isotropic temperature at which molecules are randomly oriented in all possible directions with high order of disorder or high entropy($\Delta S = \Delta H/T$). However, on cooling the isotropic melt, the C_1–C_2 homologs undergo exhibition of statistically parallel orientational molecular order and showed monotropic nematic mesophase formation below isotropic temperature in irreversible manner. Rest of the enantiotropic nematogenic azoester molecules from C_3 to C_{14}, on cooling the isotropic melt, showed nematic mesophase formation from and below isotropic temperature in reversible manner till solidification. Hexadecyloxy (C_{16}) derivative of a series is unable to resist exposed thermal vibrations and abruptly breaking its crystal lattices. Thus, C_{16} homolog sharply and smoothly transform into isotropic liquid from solid state without passing through an intermediate state of existence between crystalline solid and isotropic liquid, i.e., liquid crystalline state of a substance is missing. The inadequate magnitudes of end-to-end intermolecular adhesion and closeness hinder the exhibition of mesophase by C_{16} homolog. The absence of smectogenic character is attributed to the absence of lamellar packing of molecules in the crystal lattices of the homologs C_1–C_{16} and the unsuitable extent of molecular noncoplanarity and steric hindrance caused by laterally substituted two chloro groups bonded to middle phenyl ring towards smectogenic –COO- central group. The exhibition of odd-even effect by N-I/I-N transition curve is attributed to the sequentially added methylene unit to *n*-alkoxy terminal end group making *n*-alkyl chain with odd and even numbered carbon atoms. The disappearance of odd-even effect from and beyond C_9 homolog for higher homolog is attributed to the coiling or bending or flexing or coupling of longer *n*-alkyl chain with principal axis of a core structure of molecules (C_{10}–C_{14}). The variations of liquid crystalline properties from homologue to homologue in the present series is attributed to the changing number of $-CH_2-$ unit or units in *n*-alkyl chain which alters the degree of intermolecular cohesive forces from homolog to homolog in the same series. Thus, transition and melting temperatures undergo depression as series is ascended

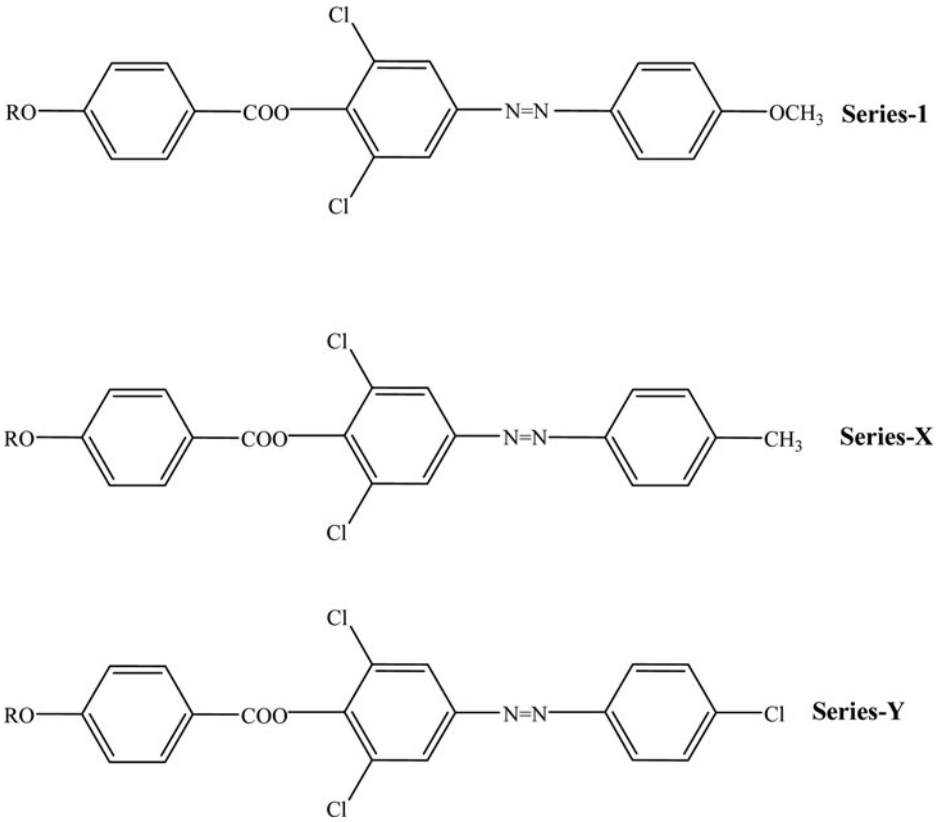


Figure 2. . Structurally Similar series.

from C_1 to C_{14} and only nematogenic mesophase acquires stabilization. The mesomorphic properties of presently investigated novel azoester homologous series 1 are compared with other structurally similar known homologous series X [17] and Y [18] as under in Fig. 2.

Homologous series of present investigation series 1 and the homologous series X and Y chosen for comparative study are identical and structurally similar with respect to three phenyl rings, two central bridges −COO− and −N=N− as well as laterally substituted two flexible 3,5-dichloro groups. Moreover flexible *n*-alkoxy (-OR-) terminal end groups are also identical for the same homologue from series to series. However series 1, X, and Y differ with respect to right handed terminal end groups $-OCH_3$, $-CH_3$, and −Cl, whose individual group polarity and hence the molecular polarity as well as related degree of cohesive intermolecular suitable magnitudes of anisotropic forces as a consequence of combine effect of molecular rigidity and flexibility undergo variations. Thus, changing molecular flexibility and rigidity for the same homolog from series to series vary accordingly. Thus, changing trend of mesomorphic properties from series to series or homolog to homolog in the same series depends upon the differing or changing part of structurally similar homologous series selected for comparative study. Thus, mesomorphic behaviors and the degree of mesomorphism of any individual or structurally similar homologous series depends upon the suitable or favorable magnitudes of molecular rigidity and flexibility as emerged from its molecular structure. Following Table 3 represents some mesomorphic properties like

Table 3. Average thermal stabilizes in °C

Series →	1	X	Y
Smectic-Isotropic or Smectic-Nematic Commencement of Smectic phase	—	—	—
Nematic-Isotropic or Isotropic-Nematic Commencement of Nematic phase	133.5 (C_3-C_{14}) C_1	111.2 (C_5-C_{10}) C_4	96.3 (C_4-C_{10}) C_4
Mesophase length range in °c	00 to 72——Nm	00 to 31	00 to 21

thermal stabilities, commencement of mesophase, mesophase length range, etc. in comparative manner for presently investigated novel series 1 and the structurally similar series X and Y as chosen for comparison.

Table 3 indicates that

- Azoester series 1, X, and Y are only nematogenic without exhibition of any smectogenic character.
- Nematogenic mesophase formation commences from very first member of a series 1, while it commences late from Butyloxy (C_4) homolog for series X and Y chosen for comparison.
- Thermal stability gradually undergo depressed from series 1 to X to Y.
- Mesogenic phase length is the highest for a series 1 of present investigation and it gradually reduced for series X and Y, respectively.

The nematogenic mesophase formation tendency of a substance depended upon the extent of suitable magnitudes of anisotropic forces of intermolecular end to end attractions as a consequence of favorable molecular rigidity and flexibility conducive to cohesive forces emerged, which maintain the statistically parallel orientational order of molecules, while floating on the surface.

Homologous series 1, X, and Y contain three phenyl rings, two central bridges viz., −COO− and −N=N− as well as two (3,5 – dichloro) chloro groups on middle phenyl ring perfectly equal, similar or identical. Moreover, *n*-alkoxy terminal (left) end group is also identical for the same homolog from series to series. Therefore, intermolecular cohesive forces playing their role due to identical molecular part which contribute almost in equal manner. However the right-handed terminally situated $-OCH_3$, $-CH_3$, and −Cl intermolecular cohesion end group differ for series 1, X, and Y, respectively. Therefore, molecular dipole moment across the long molecular axis, dipole–dipole interactions, and the magnitudes of dispersion forces differ from series to series depending upon group polarities, of $-OCH_3$, $-CH_3$, and −Cl. All the three terminal end groups viz., $-OCH_3$, $-CH_3$, and −Cl bonded to third phenyl ring occupying identical para position. But a bond

between carbon of phenyl ring and functional end groups, i.e.,  ,  , and  bear different values of bond polarity. Therefore, vector sum of polarities of all bonds of same homolog of different series under comparison causes difference in dipole moment across the long molecular axis, dipole–dipole interactions and magnitudes of dispersion forces or end to end attractions. Thus, intermolecular closeness and suitable magnitudes of anisotropic forces of end to end cohesion energy against the steric hindrance facilitates and stabilizes only nematic mesophase formation in all the series 1, X, and Y, Thus, the magnitudes of end to end attractions vary for the same homolog from series to series. Hence, the average thermal stabilities, commencement of nematic mesophase and mesophase length and missing of smectic phase for the same homologue vary from series to series $-OCH_3$ terminal end group is highly polar and bearing higher group efficiency order for nematic than $-CH_3$ and $-Cl$, which shows highest thermal stability, early commencement (from C_1) of nematic phase and the highest mesophase length $-CH_3$ and $-Cl$ groups are weakly polar than $-OCH_3$ and mutually almost equally polar [19] ($-CH_3 \approx -Cl$) have nearer values of group efficiency order for nematic, thermal stability as well as equal commencement (from C_4) of nematic mesophase formation with nearer values towards mesophase lengths. Thus, a phenomenon of mesomorphism and the degree of mesomorphism are very sensitive to molecular structure and its molecular rigidity and flexibility as related to molecular polarity, polarizability, intermolecular cohesive forces emerging from dipole–dipole interactions, dipole moment across the long molecular axis and the magnitudes of dispersion forces.

Conclusions

- Presently investigated novel azoester series is majorly nematogenic with middle ordered melting type whose mesogenic phase length is relatively high.
- The group efficiency order for nematic derived on the basis of (i) thermal stability (ii) early commencement of nematic mesophase and (iii) mesophase length is as under.

(i) **Nematic**: $-OCH_3 > -CH_3 > -Cl$
(ii) **Nematic**: $-OCH_3 > -CH_3 = -Cl$
(iii) **Nematic:** $-OCH_3 > -CH_3 > -Cl$

- The mesomorphic properties vary from homolog to homolog in the same series due to the sequentially added methylene unit or units.
- The mesomorphic properties for the same homolog of different series vary with the changing polarity of right-handed terminal end group which remains unchanged for same series.
- Mesomorphic properties of a substance are sensitive and susceptible to its molecular structure.

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