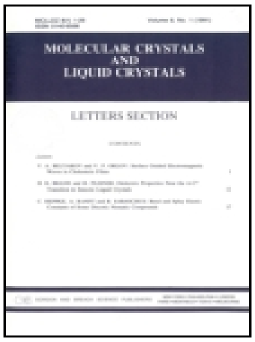

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Synthesis and Mesomorphic Phase Behavior of Laterally Substituted Novel Azoesters

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A novel homologous series of 4(4′-n-alkoxy benzoyloxy)phenylazo 2″-chloro-3″-methyl benzenes was synthesized and studied for mesophase behavior dependence on molecular structure. The nematogenic mesophase is exhibited from the first to the last member and the smectogenic mesophase from the hexyloxy to the tetradecyloxy member of the series. The nematic mesophase is of a threaded or Schlieren type, and the smectic mesophase is of a focal conic fan of the type A or C. Mesomorphic properties of the present novel homologous series are compared with other structurally similar homologous series.

Keywords Liquid crystal; mesomorphic; monotropic; nematic; smectic

Introduction

Looking to the utility of liquid crystalline (LC) materials of definite range of temperature or concentration in the manufacture of various articles such as pharmaceutical preparations, medical instruments, engineering, physical and chemical processes, display devices, biology, and biological systems requires the synthesis and evaluation of novel materials. The formulation of LC materials of definite temperature range or the concentration range needs the construction of a molecule with a novel geometrical shape, size, polarity of functional group or groups linked at the lateral and/or terminal positions of a phenyl ring to maintain suitable magnitudes of anisotropic forces of intermolecular attractions [1], as a consequence of favorable molecular rigidity and/or flexibility [2–4]. Thus, the present investigation is planned with a view to synthesize novel LC substances that can have three phenyl rings bonded through –COO– and –N=N– central bridges as a rigid core and -OR, -Cl, -CH_3 groups as terminal and lateral groups that act as a flexible part of a molecule. Thus, the role of molecular shape, size, polarity of functional groups, molecular polarizability, etc., can be correlated with mesophase formation and degree of mesomorphism. Hence, the present study can evolve an idea to understand and establish the relation between molecular structure and liquid crystal behavior of a newly constructed molecule.

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Table 1. Elemental analysis for (1) ethyloxy, (2) propyloxy, and (3) octyloxy derivatives

		Elements % found			Elements % calculated		
Sr. no.	Molecular formula	C	H	N	C	H	N
1	$C_{22}H_{19}ClN_2O_3$	66.95	4.80	7.27	66.92	4.85	7.09
2	$C_{23}H_{21}ClN_2O_3$	62.74	5.20	6.80	67.56	5.18	6.85
3	$C_{22}H_{19}ClN_2O_3$	69.58	6.79	6.73	70.21	6.52	5.85

Experimental

Synthesis

Alkylation of 4-hydroxy benzoic acid was carried out by appropriate alkylating agents (R-X) to form 4-*n*-alkoxy benzoic acids [5]. The *n*-alkoxy benzoic acids were converted to their corresponding acid chlorides using freshly distilled thionyl chloride [A] and used directly for further reaction without purification. Azo dye, 4-hydroxy phenyl azo-2′-chloro-3′-methyl benzene [B] of melting point 106°C was prepared by the usual established method of diazotization [6]. Component [A], i.e., 4-*n*-alkoxy benzoyl chloride and component [B], i.e., the azo dye were condensed in dry cold pyridine to prepare final azoester molecule by a usual etherification method [7,8]. Final products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained. Transition temperatures of the homologues were determined by optical polarizing microscopy. The chemicals, viz., 4-hydroxy benzoic acids, alkyl halides (R-X), methanol, ethanol, KOH, thionyl chloride, phenol, 2-chloro-3-methyl aniline, pyridine, and NaOH required for synthesis were used as received excepted solvents that were dried and purified prior to use.

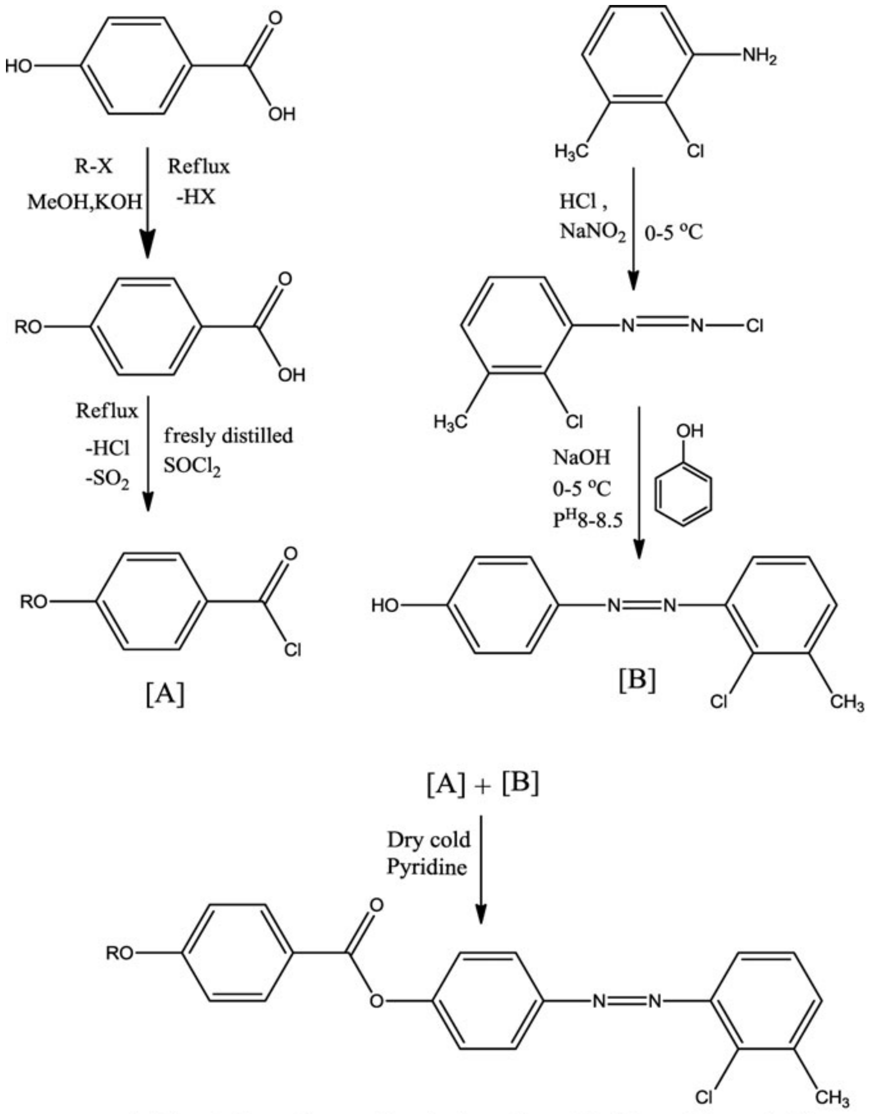
The synthetic route to the series is shown in Scheme 1.

Characterization

Some of members of a novel series as the representative member of a series were characterized by elemental analysis (Table 1), infrared spectroscopy, ^{1}H NMR spectra, mass spectrometry, and textural identification. Microanalysis was performed on a EuroEA Elemental Analyzer (Waltham, Massachusetts, U.S.A.). IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer (Nishinokyou Kuwabara-cho, Nakagyo-Ku Kyoto, Japan), ^{1}H NMR spectra were recorded on Bruker spectrometer (Billerica, Massachusetts, U.S.A.) using DMSO-d_6 as a solvent, and mass spectra were recorded on a Shimatzu GC-MS Model No. QP-2010 (Nishinokyou Kuwabara-cho, Nakagyo-Ku Kyoto, Japan). The liquid crystal behavior and the type of textures were determined by a miscibility method through microscopic observations. Thermodynamic properties enthalpy (ΔH) and entropy ($\Delta S = \Delta H/T$) are discussed qualitatively.

Analytical Data

Elemental Analysis (Table 1).



4-(4'-n-Alkoxy benzoyloxy) phenylazo-2"-chloro-3"-methyl benzenes

Where, R= C_nH_{2n+1} and n= 1to8,10,12,14and 16.

Scheme 1. Synthetic route to the series

Spectral Data

NMR in ppm for the Butoxy Derivative. 0.93–0.97 (t, 3H, -CH_3 of –OC_4H_9 group), 1.26–1.77 (q, 2H, CH_3-CH_2-), 1.73–1.77 (t, 2H, -CH_2-CH_2-O-), 4.06–4.13 (t, 2H, -CH_2-O-), 2.72–2.76 (s, 3H, CH_3-Ph), 7.13–7.15 (d, 2H, *ortho* to –OC_4H_9 group in phenyl ring), 7.38–7.41 (t, 1H, *para* to –Cl group in phenyl ring), 7.52–7.58 (m, 3H, phenyl ring), 7.66–7.67 (d, 1H, in phenyl ring *ortho* to –N=N– group), 8.02–8.12 (m, 4H, *ortho* to

–COO– and –N=N– group in phenyl ring). The NMR data are consistent with the molecular structure.

NMR in ppm for the Decyloxy Derivative. 0.82–0.85 (t, 3H, -CH_3 of –$OC_{10}H_{21}$ group), 1.24 (m, 12H, CH_3-CH_2-(-CH_2-)$_6$-CH_2-CH_2-O-), 1.39–1.40 (q, 2H, CH_3-CH_2-), 1.73–1.77 (t, 2H, -CH_2-CH_2-O-), 2.71 (s, 3H, CH_3-Ph), 4.06–4.13 (t, 2H, -CH_2-O-), 7.10–7.12 (d, 2H, *ortho* to –$OC_{10}H_{21}$ group in phenyl ring), 7.36–7.40 (t, 1H, *para* to –Cl group in phenyl ring), 7.50–7.56 (m, 3H, phenyl ring), 7.64–7.65 (d, 1H, in phenyl ring *ortho* to –N=N– group), 8.00–8.10 (m, 4H, *ortho* to –COO– and –N=N– group in phenyl ring). The NMR data are consistent with the molecular structure.

IR in cm^{-1} for the Heptyloxy Derivative. 2852, 2920 (C-H Str. of (-CH_2-)$_n$ group of –OC_7H_{15}), 1440, 1604 (aromatic C=C Str.), 3068 (C-H Str. of aromatic ring), 1010, 1068, 1168, 1267 (C-O Str. of –COO– group), 1728 (C=O, Str. of –COO– group), 1139 (C-O-C-), 648 (C-Cl Str.), 750, 848, 698 (phenyl ring), 1604 (–N=N– Str.). The IR data are consistent with the molecular structure.

IR in cm^{-1} for the Dodecyloxy Derivative. 2852, 2933 (C-H Str. of (-CH_2-)$_n$ group of –$OC_{12}H_{25}$), 1465, 1506, 1579 (aromatic C=C Str.), 3070 (C-H Str. of aromatic ring), 1066, 1170 (C-O Str. of –COO– group), 1732 (C=O, Str. of –COO– group), 1143 (C-O-C-), 626 (C-Cl Str.), 750, 842, 692 (phenyl ring), 1604 (–N=N– Str.). The IR data are consistent with the molecular structure.

Mass Spectra of the Hexyloxy Derivative. *m/z* (rel. int.%): 450 $(M)^+$, 245, 205, 121, 93.

Mass Spectra of the Tetradecyloxy Derivative. *m/z* (rel. int.%): 562 $(M)^+$, 345, 425, 317, 121.

Texture Determination by Miscibility Method.

- Propoxy homologue: threaded nematic
- pentyloxy homologue: Schlieren nematic
- octyloxy homologue: smectic-A
- tetradecyloxy homologue: smectic-C

Result and Discussion

4-Hydroxy benzoic acid is dimeric, which on linking through the acid chloride with the non-mesomorphic azo dye component resulted in the formation of mesomorphic products. The methoxy and ethoxy homologues are monotropic nematic, the propoxy, butoxy, pentyloxy, and hexadecyloxy homologues are enantiotropic nematic only, and the rest of the homologues also exhibit smectogenic mesomorphism in addition to nematogenic mesophase in an enantiotropic manner.

Thus, all the members of the novel series show LC behavior. A phase diagram (Fig. 1) shows the number of carbon atoms present in *n*-alkyl chain of the left *n*-alkoxy terminal end group versus the transition temperatures (Table 2) of the homologues showing mesophase behavior of the novel series. A solid-mesomorphic transition curve follows a zigzag path of rising and falling values with alternation of transition temperatures and behaves in

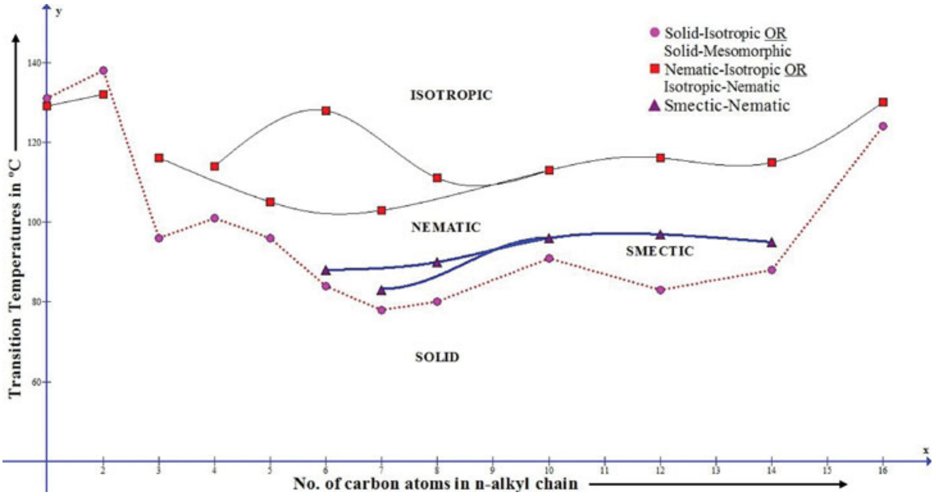


Figure 1. Phase behavior of series.

normal manner. The smectic-nematic transition curve initially rises and then descends after passing through a maxima, as series is ascended with exhibition of an odd–even effect. Hence, the smectic-nematic transition curve behaves in a usual manner. The nematic-isotropic transition curve descends as the series is ascended with a sudden steep rise at the hexadecyloxy homologue and exhibits an odd–even effect. The curve for odd and even members of the novel series merges into each other between the nonyloxy and decyloxy homologues and then a single curve propagated until the last hexadecyloxy homologue of the series and generally behaves in a normal manner except for the hexadecyloxy

Table 2. Transition temperatures in °C of series-1

		Transition temperature in °C		
Compound no.	R = *n*-alkyl group	Sm	Nm	Isotropic
1	Methyl	—	(129.0)	131.0
2	Ethyl	—	(132.0)	138.0
3	Propyl	—	96.0	116.0
4	Butyl	—	101.0	114.0
5	Pentyl	—	96.0	105.0
6	Hexyl	84.0	88.0	128.0
7	Heptyl	78.0	83.0	103.0
8	Octyl	80.0	90.0	111.0
9	Decyl	91.0	96.0	113.0
10	Dodecyl	83.0	97.0	116.0
11	Tetradecyl	88.0	95.0	115.0
12	Hexadecyloxy	—	124.0	130.0

Note: () indicate monotropy.
Sm – Smectic: Nm – Nematic.

derivative. Thus, the phase diagram as a whole behaves in the usual established manner, for the novel homologous series under discussion. The nematogenic phase length ranges from 6°C to 40°C and smectogenic phase length varies between 4°C and 14°C. The smectic and nematic average thermal stabilities are 91.5°C and 113.4°C, respectively. All the members of the novel series exhibit nematogenic character and the homologues from and beyond hexyloxy homologue additionally exhibit smectogenic character except for the hexadecyloxy homologue. Thus, the novel series under present investigation is predominantly nematogenic and partly smectogenic and is of a low melting type.

The esterification process breaks hydrogen bonding of dimerized 4-*n*-alkoxy benzoic acids through their acid chlorides. The methoxy and ethoxy homologues sharply transform into isotropic state on heating but on cooling they show a nematic mesophase below their isotropic temperature in an irreversible manner at the respective monotropic temperature. The molecules arrange themselves in a statistically parallel orientational order under a floating condition with favorable molecular rigidity and flexibility, which causes the molecular disalignment on the plane of a surface at an angle less than 90° under the influence of suitable magnitudes of anisotropic forces of intermolecular adhesion resisting thermal environment. The remaining homologues, i.e., propoxy to hexadecyloxy of the novel homologous series resist externally exposed thermal vibrations for a definite range of temperature causing nematic and/or smectic mesophase formation by arranging the molecules as statistically parallel orientational order of molecular and/or in a sliding layered molecular arrangement in a floating condition. The butoxy, pentyloxy, and hexadecyloxy homologues do adopt only parallel orientational order of molecules within definite temperature range giving rise to only nematic mesophase formation, while the hexyloxy to tetradecyloxy homologues show a sliding layered arrangement of molecules due to the lamellar packing of molecules in their crystal lattices at first, for definite temperature range showing smectic mesophase formation and then they arrange themselves in a statically parallel orientational order in floating condition for another higher temperature range showing nematogenic mesophase formation [9,10]. Every substance does have the capacity to resist thermal vibrations exposed upon it up to a definite temperature, limit depending upon energy stored (ΔH) due to its mass and characteristics. However, since its heat resisting capacity crosses the limit, the molecules of a substance under thermal energy exposure loses intermolecular attractions and molecules are randomly oriented in all possible directions without any ordered manner. Thus, high order of molecular disorder or molecular randomness or entropy ($\Delta S = \Delta H/T$) occurs from and beyond isotropic temperature, i.e., mesophase formation destabilizes and ceases to appear. Thus, the thermal behavior of a thermotropic liquid crystal substance varies with temperature giving rise to various stabilized physical states of a substance. An odd–even effect is observed for the smectic-nematic and the nematic-isotropic transition curves that are attributed to the sequentially added methylene units at the left *n*-alkoxy terminal end group. The odd–even effect for both the transition curves of the phase diagram diminishes as series is ascended from and beyond a point between the nonyloxy and the decyloxy homologues because the longer *n*-alkyl chain may coil, bend, flex, or couple to lie with major axis of the core [1]. Thus, molecular rigidity and flexibility [2–4] are reduced or ineffective. The variations in mesomorphic properties from homologue to homologue in the novel homologous series are attributed to the gradual addition of -CH_2- unit at the left *n*-alkoxy terminal end group keeping the right side laterally substituted almost equipolar and flexible groups -Cl and -CH_3 that contribute to increased molecular polarizability and flexibility. Thus, the intermolecular adhering anisotropic forces of attractions are favorably enhanced to induce mesophase formation right from the first member of the series to the last member of the series. The mesomorphic behavior of the presently investigated novel

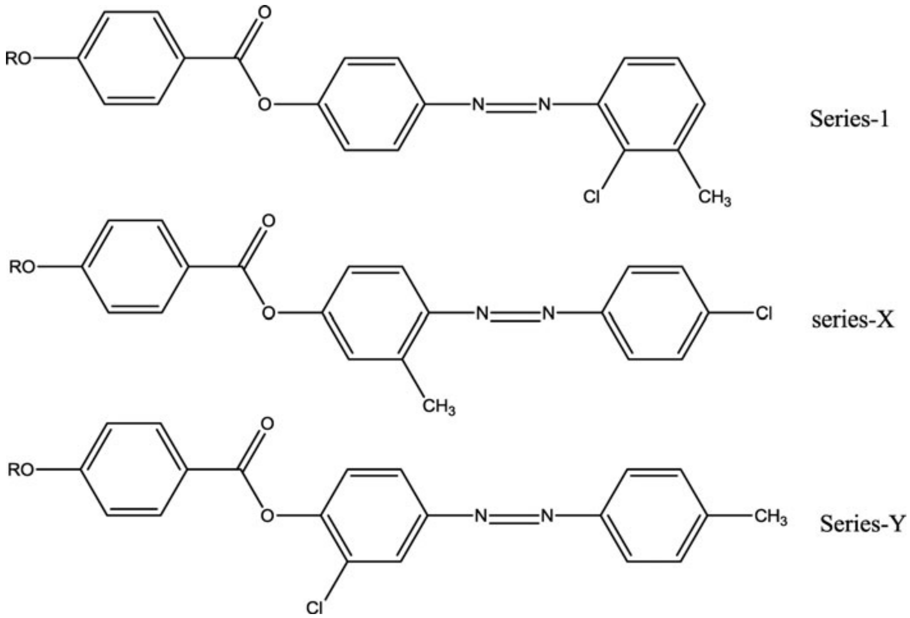


Figure 2. Structurally similar homologous series.

series-1 is compared with structurally similar other known homologous series X [11] and Y [12] as shown in Fig. 2.

All the homologous series 1, X, and Y are structurally similar with respect to three phenyl rings bonded through –COO– and –N=N– central bridges that contribute to the molecular rigidity as well as the left *n*-alkoxy terminal end group that contributes to the molecular flexibility [2–4]. However, they differ in their position of substituted functional groups -Cl and -CH_3 that are contributing to the total molecular flexibility, keeping rest of the molecular part unchanged. Thus, variations in mesomorphic properties can be linked with changing molecular structure, i.e., changing molecular flexibility with unchanged molecular rigidity. Homologous series 1, X, and Y are isomeric with respect to their molecular formula and changing and/or unchanging molecular part, but their positional difference of substitution on the middle and/or third phenyl ring or rings differs and causes a difference in their mesomorphic behavior. Homologous series 1 and Y are also isomeric, but differ in the position of substitution in which -Cl is bonded at the *ortho* position to the –COO– and the *meta* position to the –N=N– at the middle phenyl ring as well as the -CH_3 at the *para* position to the –N=N– at the third phenyl ring. Thus, the observed variations in mesomorphic behavior and the degree of mesomorphism are considered due to varied molecular flexibility, while keeping molecular rigidity intact for series 1, X, and Y.

Table 3 shows the average thermal stabilities for the smectic and the nematic phases, the commencement of mesophase, and series to series for the present series-1 and X or Y chosen for comparison.

Table 3 indicates the following.

(i) The smectic thermal stability of the novel series-1 is lower than that of series X, but higher than that of series Y because the smectic mesophase does not stabilize in the case of series Y.

Table 3. Average thermal stability in °C

Series	[1]	[X]	[Y]
Smectic-nematic	91.5 [C_6–C_{14}]	108.0 [C_{10}–C_{16}]	—
commencement of smectic phase	C_6	C_{10}	
Nematic–isotropic	113.4 [C_3–C_{14}]	148.8 [C_1–C_{16}]	175.75 [C_1–C_{16}]
commencement of nematic phase	C_1	C_1	C_1

(ii) The smectic mesophase commences earlier from hexyloxy homologue in case of the novel series-1, but it commences late from the decyloxy homologue in case of series X and is not exhibited by series Y.
(iii) The nematic thermal stability increases from series-1 to series X to series Y.
(iv) The nematic mesophase appears from very first member of all the series 1, X, and Y.
(v) Series-1 and X are predominantly nematogenic and partly smectogenic, while series Y is entirely nematogenic without the exhibition of any smectogenic character, even in the monotropic condition.

Homologous series 1, X, and Y all possess laterally or terminally substituted chloro and/or methyl groups, at the third phenyl ring in case of series-1 and at the middle phenyl ring in case of series X and Y. The terminally substituted end group increases the molecular length and end-to-end intermolecular attractions, while the lateral group increases molecular width and reduces intermolecular attractions; the same situation increases molecular polarizability and consequently increases intermolecular attraction. Thus, the length to breadth ratio varies from series to series. Moreover, an increase in the intermolecular forces of attraction is caused due to polarizability due to the increased molecular breadth at the laterally substituted positions. Thus, two opposing forces of intermolecular adhesion operate in all series 1, X, and Y. The net effect of intermolecular anisotropic forces of attractions depends upon the predominance of any one force out of the two opposing forces. However, the magnitudes of net effect of intermolecular attractions differ from series to series due to the type of functional group attached to middle or/and third phenyl ring or rings, their position of substitution, and their individual polarity. Thus, the observed variations in the mesomorphic behavior can be attributed to the varying magnitudes of anisotropic forces of intermolecular attractions for series-1 to series X to series Y, in spite of their same molecular formula but different structural formula. Series-1 and X exhibit smectic character but series Y does not. Smectic mesophase formation commences early from hexyloxy homologue in case of series-1 but the smectic mesophase commences from decyloxy homologue in series X, due to their difference in their extent of noncoplanarity [7], because of laterally substituted -CH_3 and -Cl group on same third phenyl ring which differs from series X and Y. The commencement of the nematic mesophase occurs from very first member of all the series 1, X, and Y under comparison, which indicates that end-to-end attractions operate equally irrespective of the position of substitution of the -CH_3 and -Cl groups. Therefore, magnitudes of anisotropic forces of attractions as a consequence of molecular rigidity and/or flexibility determine the mesomorphic behavior of a molecule [1–4]. Hence, the mesomorphic behavior from series to series not only depends upon the varied lateral and/or terminal end groups, but also depends upon their varied substitution on different positions of same or different phenyl rings, irrespective of the same polarity of the same functional groups.

Conclusions

- The group efficiency order derived on the basis of thermal stabilities is as follows.
  Smectic: series X > series-1 > series Y
  Nematic: series Y > series X > series-1
- The group efficiency order is derived on the basis of early commencement of the smectic and the nematic mesophase.
  Smectic: series-1 > series X > series Y
  Nematic: series-1 = series X = series Y
- The presently investigated novel series is predominantly nematogenic and partly smectogenic.
- The thermal stabilities for the smectic and the nematic mesophase formation are lowered by substituting same functional group if positioned on the same phenyl ring instead of on different phenyl rings of a molecule, keeping the rest of the molecular part unchanged.
- Molecular rigidity and flexibility play an important role in liquid crystal formation and LC behavior of a molecule.
- Variations in mesomorphic (LC) behavior of a molecule also depend upon the positional difference of the substitution of same functional group or groups in isomeric homologous series.
- Commencement of the smectic mesophase depends upon the position of substitution either middle or third phenyl ring as lateral and/or terminal end group.
- The commencement of the nematic phase does not depend upon the place of substitution either on middle or third phenyl ring as lateral or terminal end group.

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