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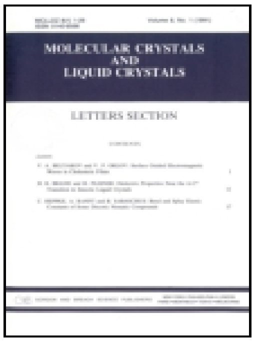

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Mesomorphism dependence on geometric shapes in isomeric molecules

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ABSTRACT

A novel homologous series of symmetrical dimers RO-C_6H_4-CH=CH-COO-C_6H_4-OOC-CH=CH-C_6H_4-OR of liquid crystalline (LC) characteristics have been synthesized and studied with a view to understand and establish the effects of the molecular structure on the LC property or properties with special reference to geometrical shape in case of isomeric series. Homologous series consisted of 13 dimers (C_1 to C_{18}). C_1 to C_8 are only enantiotropic nematic and the rest of the dimer homologues from C_{10} to C_{18} are enantiotropically smectogenic in addition to nematogenic. Textures of the nematic phase are threaded or Schlieren and that of the smectic phase are of the type smectic A or C. Transition temperatures and the textures were determined by an optical polarizing microscopy equipped with a heating stage. Thermal stability for smectic and nematic are 161.0 °C and 237.6 °C, respectively, whose total mesophase (Sm+N) length ranges from 71.0 °C to 126.0 °C. Cr–M, Sm–N, and N–I transition curves of a phase diagram behaved in normal manner except negligible abnormality at C_{14} dimer of N–I transition curve. N–I transition curve exhibited odd– even effect nearby up to C_7 dimer. Analytical and spectral data supported molecular structures of homologue dimers. Thus, present homologue dimer series is predominantly nematogenic and partly smectogenic and high-ordered melting type. LC properties of present novel series are compared with structurally similar series.

KEYWORDS
Enantiotropic; liquid crystals; nematic; smectic; symmetric dimer

Introduction

Liquid crystalline state (LC) [1] of a substance is well known for utility in the benefit of mankind [2–7]. Among them, the LC dimers have played an important role and contribution [8–10]. Present investigation was planned to synthesize a homologous series of symmetric dimers in which two mesogenic units are bonded to a phenyl ring to study the effect of the molecular structure on LC properties of the dimer with special reference to the geometrical shape of the isomeric dimers. Number of such dimers and monomer ester series with LC properties have been reported till date [11–22]. The present study will include synthesis, characterization, thermal properties, texture determination, and the comparison of some LC properties with structurally similar dimer isomeric series. The characteristics of present thermotropic dimer series will be explained and interpreted in terms of molecular rigidity and flexibility [23–30].

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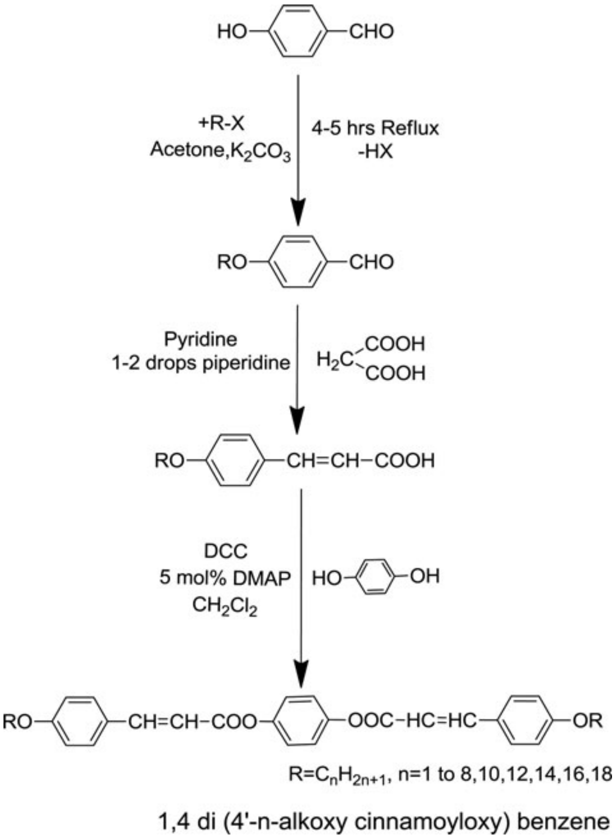

Scheme 1. Synthetic route to the series.

Experimental

Synthesis

4-Hydroxy benzaldehyde was alkylated by suitable alkylating agent R-X by refluxing for 4–5 hr with acetone and K_2CO_3 by the established method [31]. 4-*n*-Alkoxy benzaldehydes were individually condensed with malonic acid in pyridine in the presence of few drops of piperidine to obtain trans 4-*n*-alkoxy cinnamic acids [32]. Transition temperatures of dimeric 4-*n*-alkoxy cinnamic acids matched with the reported values. Trans *n*-alkoxy cinnamic acids were individually treated with hydroquinone (1, 4 dihydroxy benzene) in the presence of DCC, 5 mol% DMAP and CH_2Cl_2 in a usual method [33]. Final products were washed with methanol in vacuum filter then recrystallized till constant transition temperatures obtained. The synthetic route to the series is mentioned in Scheme 1.

The chemicals 4-hydroxy benzaldehyde, R-X (alkyl halides), K_2CO_3, acetone, DCC, DMAP, CH_2Cl_2, hydroquinone etc., were used as received except solvents which were dried and distilled prior to use.

Characterization

Some selected members of a series were characterized by elemental analysis (Table 1), Infrared spectroscopy, ^{1}HNMR spectra and mass spectroscopy. Microanalysis was performed on

Table 1. Elemental analysis for (1) Butyloxy (2) Hexyloxy (3) Dodecyloxy derivatives.

		Elements % Found			Elements % Calculated		
S. No.	Molecular formula	C	H	O	C	H	O
1	$C_{32}H_{34}O_6$	74.75	6.62	18.63	74.69	6.66	18.65
2	$C_{36}H_{42}O_6$	75.69	7.38	16.79	75.76	7.42	16.82
3	$C_{48}H_{66}O_6$	77.93	8.96	12.95	78.01	9.00	12.99

EuroEA Elemental Analyzer. IR spectra were recorded on Shimadzu FTIR Model -IRAffinity-1S (MIRacle 10), ^{1}HNMR spectra were recorded on Bruker Avance-III (400 MHz) spectrometer using $CDCl_3$ as a solvent, Mass spectra were recorded on Shimadzu GC–MS Model No. QP-2010. The liquid crystal behavior and the type of textures were determined by the miscibility method on microscopic observations.

Analytical data

Spectral data

^{1}HNMR in ppm for propyloxy derivative

0.95–0.99 (t, 6H,-CH_3 of both -OC_3H_7 group), 3.85–3.91 (t, 4H,CH_3-CH_2-$\underline{CH_2}$-O- of both alkoxy chain), 1.72–1.78 (m, 4H, CH_3-$\underline{CH_2}$-CH_2-O- of both alkoxy chain), 6.39–6.43 (d, 2H, -OOC-C$\underline{H}$ =CH- of both cinnamate group), 7.47–7.45 (d,2H, -OOC-CH=C$\underline{H}$- of both cinnamate group), 7.12–7.34 (4H, middle phenyl ring), 6.87–7.73 (8H, both phenyl ring with alkoxy chain). The NMR data are reliable with the molecular structure.

^{1}HNMR in ppm for pentyloxy derivative

0.92–0.95 (t, 6H,-CH_3 of both -OC_5H_{11} group), 1.28–1.34 (m, 4H,CH_3-$\underline{CH_2}$-$(CH_2)_3$-O- of both alkoxy chain), 1.38–1.43 (m, 4H, CH_3-CH_2-$\underline{CH_2}$-$(CH_2)_2$-O- of both alkoxy chain), 1.74-1.78 (m, 4H, CH_3-$(CH_2)_2$-$\underline{CH_2}$-CH_2-O- of both alkoxy chain), 3.96–4.10 (t, 4H, CH_3-$(CH_2)_3$-$\underline{CH_2}$-O- of both alkoxy chain), 6.46–6.50 (d, 2H, -OOC-C$\underline{H}$ =CH- of both cinnamate group), 7.60–7.64 (d,2H, -OOC-CH=C$\underline{H}$- of both cinnamate group), 7.39–7.54 (4H, middle phenyl ring), 6.57–7.84 (8H, both phenyl ring with alkoxy chain). The NMR data are reliable with the molecular structure.

^{I}R in cm^{-1} for methyloxy derivative

3062 (C-H str. of aromatic), 2924 & 2846 (C-H str. of (-CH_2-)$_n$ group of -OC_6H_{13}), 1705 (C=O str. of carbonyl carbon of ester group), 1643 (C=O str. of α,β unsaturated ketone), 1589 (C=C str. of alkene), 1543 &1512 (C=C str. of aromatic ring), 1450 (C-H bending of –CH_2 alkane group), 1381 & 1303 (C-H bending of alkene), 1249 (C-O str. of ester group), 1026, 987 & 702 (C-H bending of alkene disubstituted). The IR data are consistent with the molecular structure.

^{I}R in cm^{-1} for decyloxy derivative

3056 (C-H str. of aromatic), 2924 & 2846 (C-H str. of (-CH_2-)$_n$ group of -$OC_{10}H_{21}$), 1720 (C=O str. of carbonyl carbon of ester group), 1627 (C=O str. of α,β unsaturated ketone), 1597 (C=C str. of alkene), 1566 & 1504 (C=C str. of aromatic ring), 1465 (C-H bending of –CH_2 alkane group), 1427 (C-H bending of alkene), 1288, 1249 & 1180 (C-O str. of ester

Table 2. Transition temperatures in °C.

Compound No.	*n*-alkyl chain C_nH_{2n+1} (*n*)	Sm	N	Isotropic
1	1	–	208	293
2	2	–	201	284
3	3	–	179	277
4	4	–	161	266
5	5	–	141	261
6	6	–	132	249
7	7	–	122	248
8	8	–	137	236
9	10	123	144	215
10	12	107	149	205
11	14	100	185	202
12	16	98	179	186
13	18	96	148	167

Sm-Smectic; N-Nematic

group), 1010, 995 & 825 (C-H bending of alkene disubstituted). The IR data are consistent with the molecular structure.

Mass spectra of ethyloxy derivative

m/*z* (rel. int%): 458$(M)^+$, 398, 316, 273, 245, 175 (base peak), 147, 119, 91

Mass spectra of heptyloxy derivative

m/*z* (rel. int%): 598 $(M)^{+,}$ 343, 245 (base peak), 218, 187, 147, 119, 91, 57

Results and discussion

1, 4 Dihydroxy benzene unit is a nonmesogenic unit (M.P. 172°C) which on condensation with two symmetric mesogenic spacer units which yielded liquid crystalline symmetric dimers for entire series from C_1 to C_{18}. Trans 4-n-alkoxy cinnamic acid acted as mesogenic units linked to 1, 4 dihydroxy benzene unit. Mesomorphism commences from very first member of a series as nematogenic character and contained up to last (C_{18}) homologue dimer. However smectogenic property commenced from C_{10} homologue dimer to the last C_{18} dimer derivatives in addition to nematogenic character. Transition temperatures as determined from an optical polarizing microscopy (Table 2) were plotted for the number of carbon atoms present in *n*-alkyl chain of left and right *n*-alkoxy identical terminal end groups versus the transition temperatures of homologue dimers C_1 to C_{18}. Cr–M, Sm–N, and N–I transition curves are obtained on linking, like or related points as shown in a phase diagram of Figure 1. The Cr–M transition curve continuously falls up to C_7 dimer and rises in zigzag manner at the C_8 dimer and then continuously descended to C_{18} homologue. Thus, it shows falling tendency from C_1 to C_{18} and behaved in a normal manner. The Sm–N transition curve rises from C_{10} to C_{12} and then passes through maxima at the C_{14} homologue dimer and then descended to C_{18} homologue dimer through C_{16}. Thus, it behaved in a normal expected manner, without exhibition of the odd–even effect. The N–I transition curve continuously descended from C_1 to C_{18} except C_{14}, where negligible rise of one or two degree is observed. Thus, it behaved in a normal manner with the exhibition of the odd–even effect in very very narrow range of temperature. The odd–even effect diminished as series is ascended from and beyond a point between C_7 and C_8 for homologue dimers of longer *n*-alkyl chain. The odd members of the N–I transition curve occupy higher position than the even members of the transition curve. The changing trend in mesogenic properties from homologue to homologue for the same series

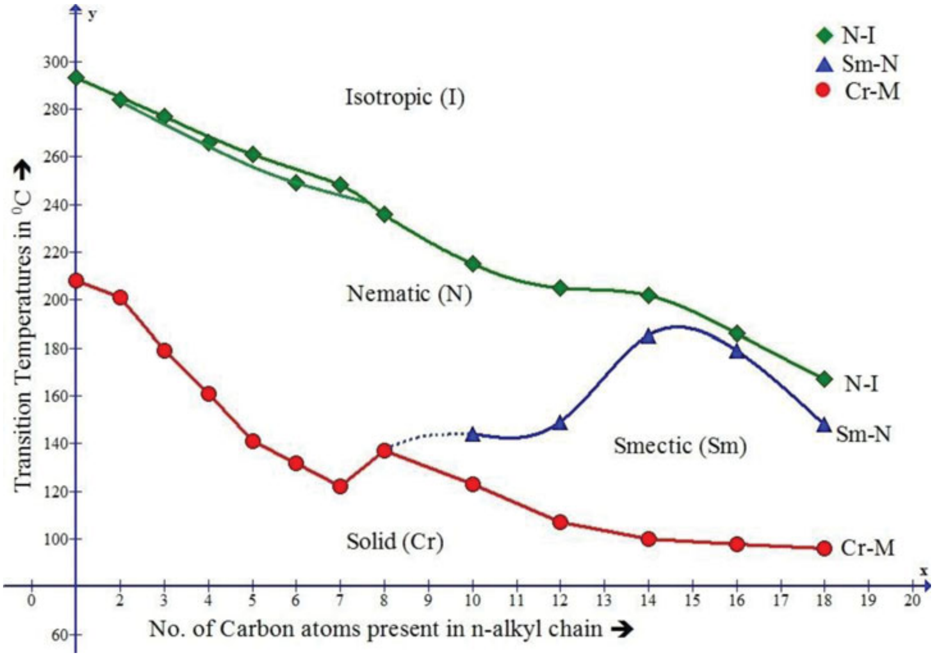

Figure 1. Phase Behavior of Series.

occurs because of changing the molecular length and the permanent dipole moment across the long molecular axis, length to breadth ratio, ratio of the polarity to polarizability, suitable magnitude of anisotropic forces of intermolecular end to end or/and lateral attractions as well as cohesive forces etc. also changes from homologue to homologue as a consequence of molecular rigidity and flexibility of individual homologue, which varies accordingly and hence the mesogenic tendency are differ from homologue to homologue in the same series. The Sm–N transition curve is extrapolated to C_8 nonsmectogenic [34–37] dimer homologue to understand its nonsmectogenic behaviors. Thus, present homologous dimer series is predominantly nematogenic and partly smectogenic of high-ordered melting type.

High-ordered transition temperatures of homologue dimers are attributed to the molecular rigidity possessed by three phenyl rings, two conjugated double bonds. Linearity of molecule and high magnitude of length to breadth ratio, including the effect due to molecular flexibility induced by left and right identical *n*-alkoxy terminal end groups, which causes suitable magnitudes of anisotropic dispersion forces of intermolecular end to end and lateral attractions and favorable intermolecular closeness. The highly polar *n*-alkoxy terminals on both sides of a molecule maintains end-to-end attractions and molecular polarizibility throughout the dimer homologous series which permits the all homologue molecules to float on the surface with statistically parallel orientational order within definite range of temperature to exhibit nematogenic character. However, on sequential addition of methylene unit or units from and beyond C_{10} homologue, the intermolecular cohesion and closeness encourages lamellar packing of molecules in the preoccupied crystal lattices in rigid crystals, which allows sliding layered molecular arrangement under floating condition within definite range of temperature to exhibit smectogenic character and then residual end-to-end dispersion forces and C-OR dipolarities causes to induce nematogenic character from and beyond C_{10} to C_{18} homologue dimers. The all molecules of all the homologues of a present dimer series are randomly oriented in all possible directions from and beyond their isotropic temperatures. But on cooling

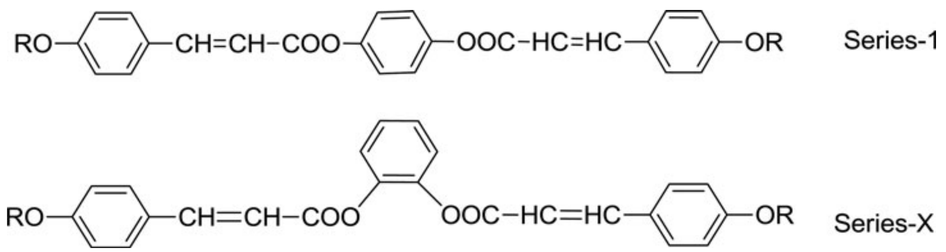

Figure 2. Structurally similar series.

the same, they show corresponding mesophase or mesophases in a reversible manner. The appearance of mesophase or mesophases (smectic or/and nematic) is attributes to the favorable molecular rigidity and flexibility caused by the individual molecular structure of each dimer of a novel series. The disappearance of the odd–even effect from and beyond the point of merging the odd and even members N–I transition curves for longer *n*-alkyl chain of higher homologues, is due to the coiling or bonding or flexing or coupling of *n*-alkyl chain with the major axis of a core structure of a molecule. The unexpected positional status of the N–I curves for odd and even members may be due to the presence of the exactly same -OR group, but the difference of N–I transition points being very very small and the difference of their positional status is less effective and negligible. Sm–N transition curve on extrapolation to nonsmectogenic C_8 homologue merges into Cr–N transition point, which indicates that, smectogenic mesophase length $137 - 137 =$ zero. Means there is no possibility of occurring the smectic phase or lamellar packing of molecules in the crystal lattices of C_8 homologue dimer. The observed change in mesomorphic behaviors from homologue to homologue in the present series is attributed to the sequential addition of methylene unit or units at the *n*-alkyl chain of both terminal end groups in equal manner. However, the magnitudes of flexible *n*-alkyl chain behavior and flexibility may differ and can cause variations in mesogenic behaviors and the degree of mesomorphism. Thermal stability for smectic and nematic are 161.0°C and 237.6°C attributed to their high magnitudes of molecular rigidity and intermolecular closeness. High thermal resistivity yielded longer smectogenic and nematogenic mesophase lengths of the order 21–85 °C and 08 ‾126 °C, respectively, and the total mesophase length ranges from 71 °C to 126 °C at the C_{18} and C_7 homologue dimer, respectively. Some mesogenic properties of present novel series of dimers are compared with the structurally similar other series-X [38] as shown in Figure 2.

Homologous series-1 of dimers of present investigation and a homologous series-X of dimers chosen for comparison are isomeric to each other with identical dihydroxy benzene as linking unit but series-1 is constructed with 1,4 dihydroxy benzene and series-X is constructed with 1, 2 dihydroxy benzene with common two mesogenic units in both the isomeric dimer series under comparison. Therefore, series-1 under discussion is linear lath like stratified molecular structural shape, whereas dimer series-X has nonlinear 'V' shaped unstraitified molecular structural shape. Thus, mesomorphic properties and the degree of mesomorphism depend upon the differing features like molecular shapes. Consequently, it results into changing molecular rigidity and flexibility, dispersion forces, permanent dipole moment across the long molecular axis, dipole–dipole interactions, C–OR bond dipolarity, molecular polarity and polarizibility, intermolecular cohesion and closeness, etc., for the same homologue dimer from series-1 to series-X.

Table 3. Average thermal stabilities in °C.

Dimer series →	1	X
Smectic–Isotropic or Smectic–Nematic Commencement of Smectic phase	161.0 °C (C_{10}–C_{18}) C_{10}	95.95 °C (C_8–C_{18}) C_7
Nematic–Isotropic Commencement of Smectic phase	237.6 °C (C_1–C_{18}) C_1	—
Total mesophase length range (Sm+N) in °C	71.0 °C (C_{18}) to 126.0 °C (C_7)	8.9 °C (C_{14}) to 32.9 °C (C_{10})

Isomeric homologous series-1 and X under comparative study differs with respect to geometrical shape and size which causes difference in the mesogenic behaviors as mentioned in Table 3.

Characteristics of phase behaviors are as under

- Homologous series-1 is linear in which two arms of same mesogenic units are bonded to 1,4 position (180°) of nonpolar phenyl ring; whereas homologous series-X is nonlinear 'V' shaped in which exactly same as above two mesogenic arms are bonded to 1,2 position of a phenyl ring at 60° angle.
- Homologous series-1 is smectogenic in addition to nematogenic, whereas series-X is only smectogenic without exhibition of nematogenic property.
- Smectogenic mesophase commences from C10 homologue of a series-1, whereas it commences early from C7 member of a series-X.
- Nematic mesophase commences from very first member of a series-1, but it does not commence till the last (C18) homologue member of a series-X.
- Thermal stability for smectic for series-1 and X are 161°C and 95.95°C, respectively.
- Thermal stability for nematic of series-1 is 237.6 oC, whereas nematic mesophase did not facilitate at all for series-X.
- Odd–even effect is exhibited by M–I (N–I or Sm–I) transition curve in both the series under comparison.
- Total mesophase length (Sm+N) range of novel dimer series-1 is much greater than a series-X under comparison.

The polarity of chemical bond between two atoms depends upon the distribution of electron clouds concentrations on each end of a chemical bond, as a result of the difference of electronegativities of two atoms constituting a chemical bond. Therefore, greater the difference of electronegativities, the greater will be the bond polarity. Thus, a chemical bond between unlike atoms (e.g., H–Cl) will be more polar than a chemical bond between like atoms. Thus, a chemical bond between unlike atoms will be polar, whose magnitudes of polarity will depend upon the difference of electronegativity of individual atoms forming a chemical bond. Now, the polarity of a molecule is a vector sum (not algebraic sum) of the polarities of all bonds in a molecule, depending upon the angle between the bonds or a geometrical shape. The molecules of series-1 in which two mesogenic units of ester derived from trans cinnamic acid, bonded to nonpolar phenyl unit linearly at angle 180°, exactly in opposite directions. Therefore, all bonds of a mesogenic unit whose vector sum of polarities of all bonds will be equal in magnitudes and opposite in direction, for exactly same second mesogenic unit. Thus, the vector sum of polarities due to two mesogenic units will cancel to each other. Moreover, nonpolar phenyl ring will not contribute to total molecular polarity due to para substitution of mesogenic units. Hence, total polarity of the molecules of series-1 are almost near to zero, whereas the total polarity of the molecules of 'V' shaped series-X has the resultant value of molecular polarity due to 1, 2 substitution of the same two mesogenic units bonded to ortho substituted dihydroxy phenyl ring at 60° angle, i.e., series-X is more polar, polarizable and noncoplaner than an isomeric series-1 of present investigation. Moreover, the intermolecular distance as related to intermolecular closeness and suitable magnitudes of anisotropic dispersive forces of end to end as well as lateral attractions, causing occurrence of smectic and/or nematic phase, differs to a considerable extent due to the difference of the geometrical shapes for the same homologue from series-1 to series-X. Thus, molecular rigidity and/or flexibility including the positional status of the *n*-alkyl chains of *n*-alkoxy terminal end groups of series-1 and X differs. Consequently, the mesophase behaviors like commencement of smectic and/or nematic phase, facilitating of only smectic or smectic plus nematic phase, thermal stabilities for smectic and nematic, degree of mesomorphism or thermal resistivity against externally exposed thermal vibrations, facilitation of lamellar packing of molecules in their rigid crystal lattices, thermodynamically enthalpy (ΔH) values, the extent of noncoplanarity of the molecules etc. for the same homologue from series to series and from homologue to homologue in the same series undergo variations as observed in Table 3. Hence, the mesogenic behaviors of isomeric homologue dimer series vary with the geometrical shapes of the molecular structure.

Conclusions

- Presently investigated novel dimer series is predominantly and entirely nematogenic and partly smectogenic whose mesophase length is relatively higher and of high melting type.
- The group efficiency order derived on the basis of (a) thermal stability (b) commencement of mesophase and (c) mesophase length range for smectic and nematic are as under.

(a) Smectic: Linear series-1> 'V' shaped series-X
Nematic: Linear series-1> 'V' shaped series-X
(b) Smectic: 'V' shaped series-X > Linear series-1
Nematic: Linear series-1 > 'V' shaped series-X
(c) Sm+N: Linear series-1 > 'V' shaped series-X

- Mesomorphism in isomeric series is very sensitive and susceptible to molecular shapes of molecular structure.
- Present novel investigation may be useful to the scientists and technologist working in LC applications.
- Thus, present investigation supports and raised credibility to the conclusions drawn earlier.

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