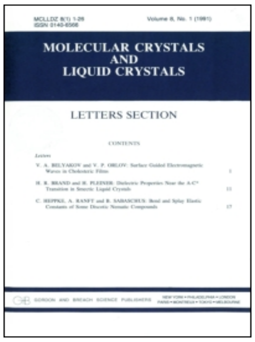

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The effect of geometrical shape and molecular rigidity on mesomorphism

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ABSTRACT
A novel nonlinear homologous series RO–C_6H_4–CH=CH–COO–C_6H_4 (meta) –CO–CH=CH–C_6H_4–$OC_{12}H_{25(n)}$ (para) consisting of three phenyl rings, two central bridges –CH=CH–COO– and –CO–CH=CH– as well as –OR and –$OC_{12}H_{25(n)}$ as flexible and constant terminal end groups respectively. The object in view is aimed to understand and establish the effect of molecular structure on LC properties of nonlinear inverted "V" shaped molecules. Novel homologous series consists of thirteen homologues. Transition temperatures and textures were determined by polarizing optical microscopy (POM) equipped with a heating stage. Textures of nematic phases are threaded or schlieren and that of a smectic phases are of the type-A or C. Transition curves of a phase diagram behaved in a normal manner. Sm-N and N-I transition curves exhibited odd-even effect. Analytical, Thermal and Spectral data confirms the molecular structure of homologues.

KEYWORDS
Chalconyl LC; liquid crystals; mesogens; nematic; smectic

Introduction

Mesomorphic behaviors of a liquid crystalline (LC) substance [1] of either thermotropic or lyotropic type are dependent on the number of variable factors like aromaticity through the number of phenyl rings involved, polarities of terminal and/or central bridge or bridges, shape and size, ratios of length to breadth and the molecular polarity and polarizability, magnitudes of dipole–dipole interactions and intermolecular dispersion forces, substitution of functional group or groups on same or different phenyl ring or rings of isomeric or nonisomeric molecules, etc., or in general molecular rigidity and/or flexibility [2,3,4,5] of the differing molecular structure [6,7,8,9,10,11,12]. Present investigation is planed with a view to understand the relation between molecular structure and mesomorphism with reference to the geometrical shape of a molecule and the functional groups involved at central bridge liking phenyl rings and terminally situated end groups. Proposed novel substances will contain three phenyl rings, two central bridges, and two terminal group with inverted "V" shape of molecules. Study will involve synthesis, characterization of novel substances through elemental analysis, spectral data, and thermometric data obtained through an optical polarizing microscopy (POM) equipped with a heating stage. Evaluated thermal data will be discussed and interpreted in terms of molecular rigidity and flexibility. Group efficiency order will be derived from

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comparative study of structurally similar analogous series. Numbers of homologous series with thermotropic LC ester linkages have been reported to date [13,14,15,16,17,18].

Experimental

Synthesis

4-Hydroxy benzaldehyde was alkylated by using suitable alkyl halides (R-X) to convert it into 4-n alkoxy benzaldehyde (A), which reacts with malonic acid, in presence of piperidine and pyridine to form 4-n alkoxy cinnamic acid (B) [19].

α-3-Hydroxyl benzoyl β-4′-dodecyloxy phenyl ethylene (C) was prepared by usual established method [20]. Chalconyl esters were synthesized by condensing (B) and (C) using literature method [21]. Thus, the Chalconyl–ester homolog derivatives were filtered, washed with sodium bicarbonate solution followed by distilled water, dried, and purified till constant transition temperatures obtained using an optical polarizing microscope equipped with a heating stage (POM). Alkyl halides, 4- hydroxy benzaldehyde, 4-hydroxy acetophenone, dicyclohexyl carbodimide, dimethyl amino pyridine, DCM, MeOH, acetone, malonic acid, pyridine, piperidine, etc., required for synthesis were used as received except solvents that were dried and distilled prior to use. The synthetic route to a series is shown in Scheme 1.

Characterization

Some selected representative homologs of the series were characterized by infrared [IR], ^{1}H NMR technique, and elemental analysis. IR spectra were recorded on a Perkin Elmer spectrum GX. ^{1}H NMR spectra were recorded on a Bruker using $CDCl_3$ as solvent. Elemental analysis was performed on Perkin Elmer PE 2400 CHN analyzer (Table 1). Liquid crystal properties, i.e., transition and melting temperatures of homologs were investigated by an optical polarizing microscopy with heating stage. Textures of the novel homologs were determined by miscibility method.

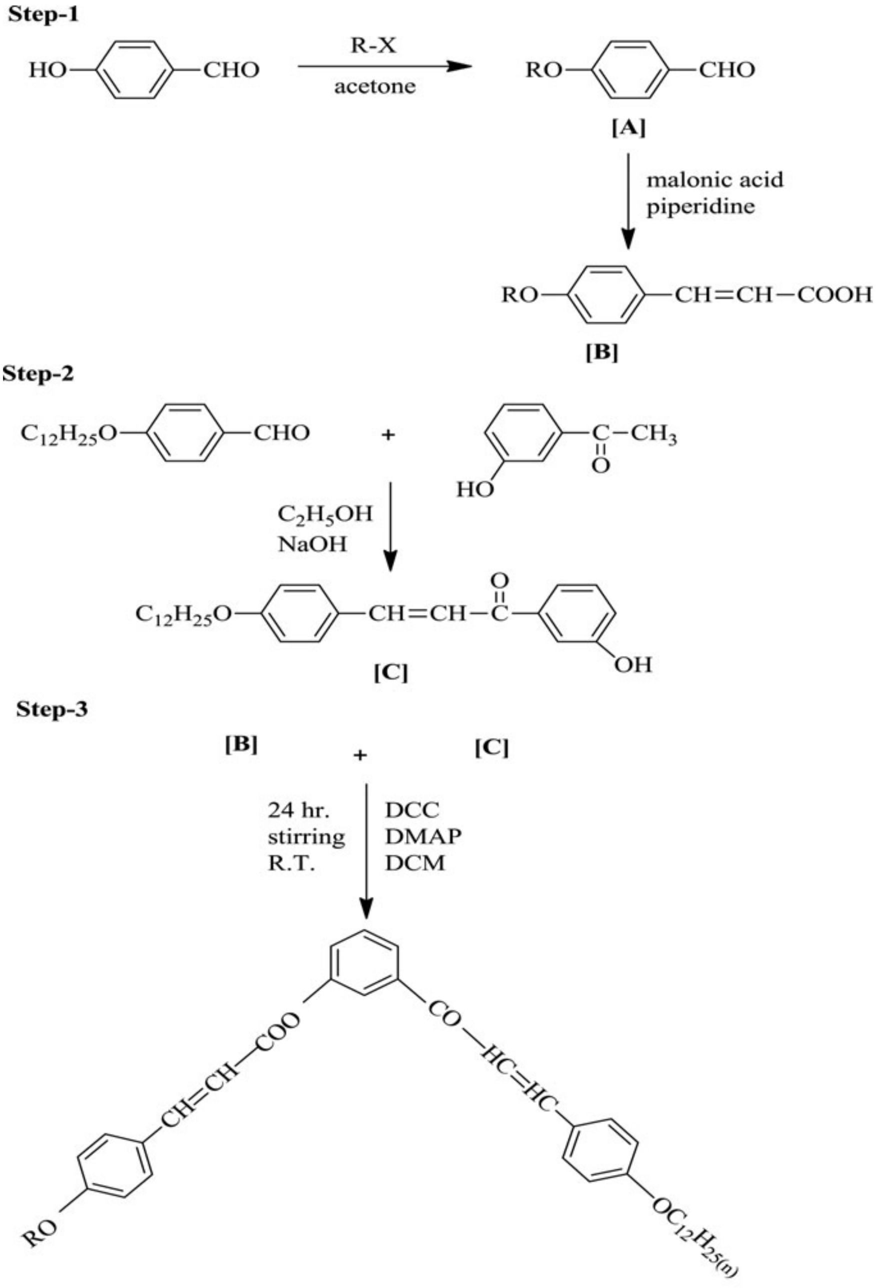
Analytical data

Table 1. Elemental analysis for butyloxy, hexyloxy, decyloxy, and dodecyloxy.

	Element % found		Element % calculated	
Molecular formula	C	H	C	H
$C_{40}H_{50}O_5$	78.18%	7.86%	78.68%	8.19%
$C_{42}H_{54}O_5$	77.03%	7.92%	78.99%	8.46%
$C_{46}H_{62}O_5$	78.10%	8.74%	79.71%	8.85%
$C_{48}H_{66}O_5$	78.52%	8.66%	79.77%	9.14%

IR Spectra in cm^{-1} for pentyloxy and tetradecyloxy derivatives:

Pentyloxy: 640.37, 734.88, 823.60 (polymethylene of $(-CH_2)_n$ of $-OC_5H_{11}$), 937.40, 974.05 (–CH=CH–), 1336.67, 1251.80, 1168.86 (–C–O stretching in $(-CH_2)$ chain), 1510.26 (C=C stretching), 1602.85 (–C=O group, –COO ester group), 2848.86 (–CH stretching in $-CH_3$), 3032.10 confirms the =C–H of aromatic. The IR data are consistent with the molecular structure.



where, R = CnH2n+1, n=1 to 8, 10, 12, 14, 16, 18

Scheme 1. Synthetic route to the series.

Tetradecyloxy: 638.44, 734.88, 831.32 (polymethylene $(-CH_2)_n$ of $-OC_{14}H_{29}$), 937.40 (−CH=CH−), 981.77 (−CH def. in hydrocarbon), 1099.43 (−C=O stretching), 1390.68, 1253.73, 1168.86 (−C−O stretching in (−CH2) chain), 1510.26(−C=C− stretching), 1600.92 (−C=O group, −COO ester group), 2850.79, 2920.23 (−CH stretching in $-CH_3$), 3502.73 confirms the =C−H of aromatic. The IR data are consistent with the molecular structure.

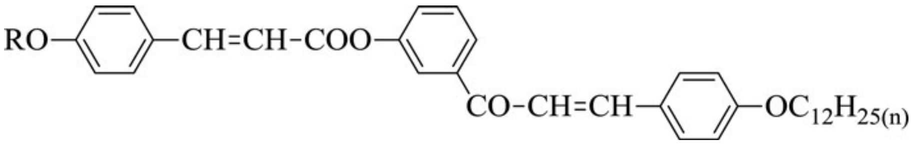
^{1}H NMR spectra in $CDCl_3$ in δ ppm for heptyloxy and octadecyloxy derivatives:

Heptyloxy: 0.72–0.53 (t, $-CH_3$ of $-OC_7H_{15}$), 1.8–1.1 (m, n-polymethylene group of $-OC_7H_{15}$), 2.7–2.0 (m, n-polymethylene group of $-OC_7H_{15}$), 3.4–3.0 (s, $-O-CH_2-CH_2$ of $-OC_7H_{15}$), 5.4–5.1 ($-O-CH_2-CH_2$ of $-OC_7H_{15}$), 6.9–6.02 (s, $-O-CH{=}CH$), 11.3 (s, p-disubstituted phenyl ring). The NMR data are consistent with the molecular structure.

Octadecyloxy: 0.42–0.99 (t, $-CH_3$ of $-OC_{18}H_{37}$), 1.40–1.00 (m, n-polymethylene group of $-OC_{18}H_{37}$), 2.48–1.59 (m, n-polymethylene group of $-OC_{18}H_{37}$), 3.13 (s, $-O-CH_2-CH_2$ of $-C_{18}H_{37}$), 7.76 (s, $-O-CH{=}CH-$). The NMR data are consistent with the molecular structure.

Table 2. Textures of nematic phase of C_4, C_8, C_{12}, C_{16} by miscibility method.

Sr. no.	Homolog	Texture
1	C_4	Threaded nematic
2	C_8	Threaded nematic
3	C_{12}	Smectic-A
4	C_{16}	Smectic-C



Homologous series: α-3 [4′-n-alkoxy cinnamoyloxy] benzoyl β-4″-dodecyloxy phenyl ethylenes.

Table 3. Transition temperature in °C.

Compound no.	Homolog (*n*-alkyl chain)	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	C_1	—	—	186.0
2	C_2	—	—	180.0
3	C_3	—	—	172.0
4	C_4	—	158.0	164.0
5	C_5	128.0	137.0	160.0
6	C_6	120.0	130.0	156.0
7	C_7	118.0	124.0	144.0
8	C_8	92.0	120.0	138.0
9	C_{10}	88.0	121.0	132.0
10	C_{12}	72.0	112.0	126.0
11	C_{14}	66.0	90.0	118.0
12	C_{16}	71.0	83.0	114.0
13	C_{18}	62.0	81.0	110.0

Homologous series: α-3 [4′-n-alkoxy cinnamoyloxy] benzoyl β-4″-dodecyloxy phenyl ethylenes.

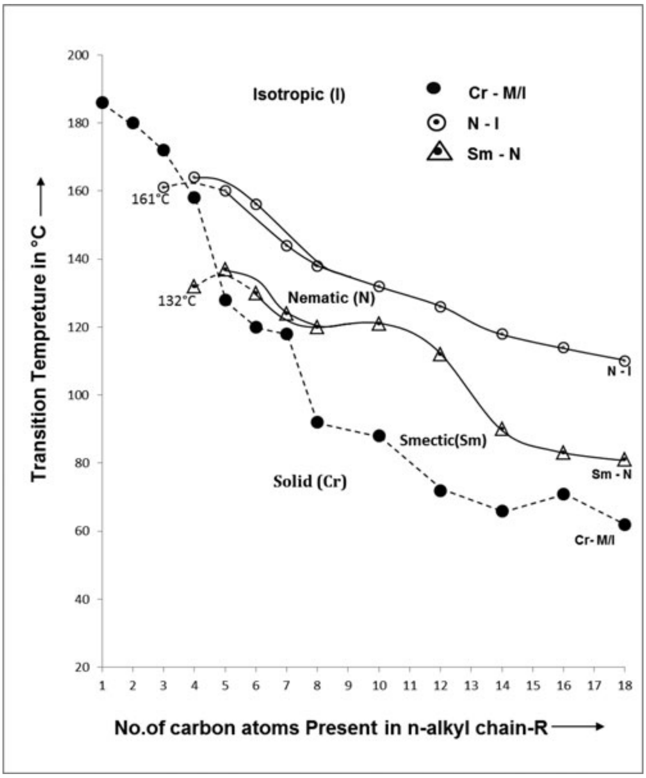


Figure 1. Phase behavior of series.

Results and discussion

Novel LC materials with 62.0°C to 164.0°C transition temperature range are synthesized by condensation of trans 4-n-alkoxy cinnamic acids and nonmesogenic meta substituted chalconyl derivative containing hydroxy group (m.p.: 96°C, yield: 68%), which yielded α-3-(4′-n-alkoxy cinnamoyloxy) benzoyl β-4″-dodecyloxy phenyl ethylenes. Dimerization of n-alkoxy cinnamic acids disappears on esterification and transition temperatures are lowered as compared to corresponding n-alkoxy cinnamic acids. Nematogenic mesomorphism commences from C_4 homolog and continued up to last C_{18} homolog. Smectogenic mesophase commences from C_5 homolog and maintained up to C_{18} homolog prior to nematogenic mesophase formation. Transition and melting temperatures (Table 3) as determined by POM equipped with a heating stage, were plotted against the number of carbon atoms present in n-alkyl chain R of −OR group. The transition curves, Cr-M/I, Sm-N, and N-I are obtained on linking like or related transition points as depicted in a phase diagram (Fig. 1) showing their phase behaviors of novel series. Cr-M/I transition curve follows zigzag path of rising and falling with overall descending tendency and behaved in normal manner. Sm-N transition curve descends and then passes through maxima at C_{10} homolog and descended up to C_{18} homolog with exhibition of very narrow and sharp odd-even effect. N-I transition curve continuously descended from C_4 to C_{18} homolog with exhibition of narrow and sharp odd-even effect. Thus, Sm-N and N-I transition curves behaved in usual established expected normal manner. Curves involved in odd-even effect for Sm-N and N-I are merging into each other at C_9 homolog. N-I transition curves for odd members are occupying lower position, whereas, in Sm-N transition curve it (odd) occupies higher position as compared to even members. The odd-even effect diminishes as series is ascended from and beyond C_9 homolog for longer n-alkyl chain “R” of higher homologs of −OR and tailed ended $-OC_{12}H_{25(n)}$ hydrocarbon chain bonded through oxygen atom with third phenyl ring. Mesomorphic properties from homolog to homolog in present novel series undergoes variations. Molecular structures of homologs are confirmed by analytical, thermal, and spectral methods. The smectic and nematic thermal stabilities of present novel series are 110.88 and 136.2, respectively. The total mesophase lengths are varied from maximum to minimum, which is 54.0°C to 6.0°C at the C_{12} and C_4 homolog, respectively. Thus, present novel inverted “V”-shaped chalconyl ester series is predominantly nematogenic and partly smectogenic. The extrapolation [22,23,24,25] of Sm-N and N-I transition curves predicts latent transition temperatures (LTT) for smectic and nematic, as monotropic 132°C and 161°C, respectively, of C_4 and C_3 homologs.

The lowering of transition temperatures of present novel homologs as compared to the corresponding trans n-alkoxy cinnamic acids is attributed to the breaking of hydrogen bonding between two molecules of aromatic acid through esterification process. The absence of mesogenic tendency of C_1 and C_2 homologs is attributed to low magnitudes of dispersion forces and low magnitudes of dipole–dipole interactions, which, induces unsuitable magnitudes of intermolecular anisotropic forces of attractions and closeness as well as high crystallizing tendency and inability to resist exposed thermal vibrations, which transforms the homologs C_1, C_2, and C_3 from crystalline solid state to direct isotropic state without passing through LC state and vice versa on cooling the isotropic mass of the same, none of the mesomorphic homolog for monotropic mesophase in irreversible manner due to their high crystallizing tendency. The exhibition of nematic or/and smectogenic character is attributed to the suitable magnitudes of anisotropic forces of intermolecular attractions and closeness as a consequence of favorable molecular rigidity and/or flexibility, which disalign the molecules of C_4 to C_{18} homologs at an angle less than 90 or/and at 90° with the plane of a floating surface. The molecules that disaligned at an angle 90° (perpendicular to floating surface) possess lamellar packing of molecules in their preoccupied crystal lattices, which forms layered structured molecular arrangement in solid crystals and high order of regularity and low entropy (ΔS) toward exposed thermal vibrations. Thus, on exposure of heat energy from exterior source, the intermolecular forces are loosened, but sliding layered molecular arrangement is maintained on floating surface for a range or ranges of temperatures depending upon thermal resistivity of sample homolog facilitating smectic mesophase formation (C_5 to C_{18}) but, the molecules that disaligned at an angle less than 90° (C_4) or facilitated smectic mesophase and possessed residual suitable magnitudes of anisotropic forces of intermolecular cohesion (C_5 to C_{18}), which maintained the statistically parallel orientational order of molecules facilitated nematogenic (C_4 to C_{18}) mesophase formation for a range of temperature (only C_4) and for another higher range of temperature including smectic mesophase (C_5 to C_{18}). However, all the mesogenic homologs (C_4 to C_{18}) on further heating exhibit isotropic state from and beyond isotropic temperature at which molecules are randomly oriented in all possible directions with high order of disorder or randomness or high entropy ($\Delta S = \Delta H/T$) in uncontrolled manner. However, on cooling the same from and below isotropic temperature, the mesogenic molecules exhibited only nematic (C_4) or nematic plus smectic mesophases reappearance (C_5 to C_{18}) exactly at a temperature and for temperature range at or during which it appeared on heating in reversible manner. Such phase transitions are called enantiotropic transitions and temperatures are known as enantiotropic transition temperatures. The odd-even effect observed for N-I and Sm-N transition curves is attributed to the odd and even numbered carbon atoms present in n-alkyl chain “R” of −OR. The normal behaviors of transition curves of a phase diagram indicates expected status of n-alkyl chain "R" of –OR and $-OC_{12}H_{25(n)}$ terminal groups without any unexpected deviation. Occupation of higher or lower positions of odd and even N-I or Sm-N transition curves depend upon molecular resistivity (ΔH), as a result of effective molecular rigidity and flexibility of odd or even homologs concerned. The variations in mesomorphic properties of thermotropic LC substances from homolog to homolog in the same series is attributed to the changing number of methylene ($-CH_2$-) unit or units whose progressive and sequential addition increases molecular length, permanent dipole moment across the long molecular axes, length to breadth ratio, intermolecular cohesions, molecular polarity and polarizability, or the ratio of the polarity to polarizability, ratio of the molecular rigidity to flexibility, etc. The extrapolation of N-I and Sm-N transition curves, keeping in view of the trend of respective curve to determine and predict LTT are 132°C (Smectic) and 161°C (Nematic), which shows the latent ability of C_3 and C_4 homolog, and predicted LTTs are hypothetical and not real or not realizable because, they are far below the isotropic temperature and no sooner they exhibit predicted mesophase, they undergo crystallization due to their high crystallizing tendency. Some thermometric properties of present inverted "V"-shaped novel chalconyl ester series-1 are compared with structurally similar analogous nonisomeric series-X [26] and Y [27] as shown below in Fig. 2.

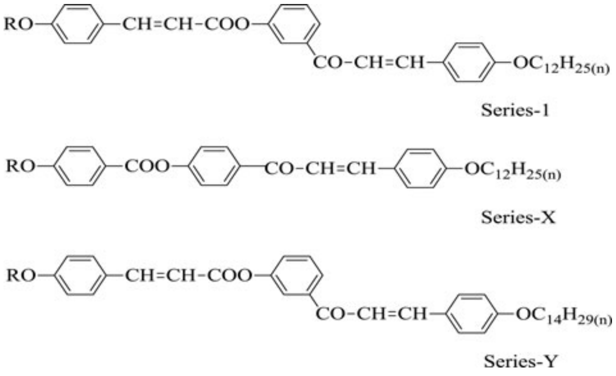


Figure 2. Structurally similar analogous series.

A novel homologous series-1 and X are nonisomeric to each other and identical with respect to three phenyl rings, one (–CO–CH=CH) central bridge linking middle and third phenyl rings, and left –OR end group as well as right $-OC_{12}H_{25(n)}$ tailed end group for the same homolog from series to series. But they differ with respect to their geometrical shapes, viz., nonlinear and linear, respectively, and central bridges –CH=CH–COO– and –COO- linking first and middle phenyl rings, which causes variations in the magnitudes of molecular rigidity and flexibility reflecting into variations in mesogenic behaviors and the degree of mesomorphism between series-1 and X. A homologous series-1 of present investigation and a nonisomeric homologous series-Y selected for comparative study are identical with respect to the geometrical shape, three phenyl rings, two same central bridges, and left n-alkoxy (–OR) end group for the same homolog from series to series; but, they differ with respect to tailed end groups $-OC_{12}H_{25(n)}$ and $-OC_{14}H_{29(n)}$, which causes difference in the magnitudes of molecular flexibility, which reflects in the mesogenic behaviors and the degree of mesomorphism. Thus, the changing behaviors in mesomorphic properties and the degree of mesomorphism depend upon varying features for the same homolog from series to series. Following Table 4 represents some thermometric data for the series-1, X, and Y in comparative manner.

Table 4. Thermal stabilities in °C.

Series→	Series-1 (Nonlinear)	Series-X (Linear)	Series-Y (Nonlinear)
Sm-N or Sm-I	110.88 (C_5–C_{18})	—	—
Commencement of smectic phase	C_5		
N-I	136.2 (C_4–C_{18})	110.25 (C_6–C_{18})	92.5 (C_6–C_{18})
Commencement of nematic phase	C_4	C_6	C_6
Total mesophase length in °C	6.0 to 54.0 C_4 C_{12}	10.0 to 39.0 C_{18} C_{10}	19.0 to 32.0 C_{10} / C_{18} C_6

Above Table 4 indicates that,

- Homologous series-1 of present investigation is smectogenic plus nematogenic whereas series-X and Y chosen for comparison are only nematogenic without exhibition of smectogenic character.
- Smectic thermal stability of present series is 110.88 and it does not stabilize even in the monotropic condition for series-X and Y.
- Nematic thermal stability is in decreasing order from series-1 to X to Y.
- Smectic phase commences from C_5 homolog for present series-1 but it does not commence till the last homolog of series-X and Y.
- Nematic mesophase commences earlier from C_4 homolog of series-1 and it commences from C_6 homolog for the series X and Y in equal manner.
- Lower total mesophase lengths adopted increasing order, whereas, upper total mesophase lengths adopted decreasing order from series-1 to X and Y.

A nonlinear homologous series-1 of present investigation does have longer central bridge –CH=CH–COO– containing conjugated double bond as compared to linear-shaped series-X containing shorter carboxylate –COO- central bridge. Therefore, the molecular rigidity and molecular polarizability of series-1 are comparatively enhanced and more than a series-X. Thus, enhanced molecular rigidity due to added –CH=CH– unit and molecular polarizability due to nonlinear inverted "V" shaped molecules facilitated the layered structure in preoccupied crystal lattices, through lamellar packing of molecules in rigid crystal, which under the influence of exposed thermal vibrations maintain sliding layered molecular arrangement on the floating surface for definite range of temperature and then residual intermolecular attractions after smectogenic character exhibition, the same homologs manages to float the molecules with statistically parallel orientational order to promote and facilitate nematic mesophase formation. The intermolecular attractions and closeness though favorable, but insufficient to maintain lamellar packing and subsequent formation and maintenance of sliding layered molecular arrangement under identical floating condition of molecules of series-X, due to comparatively low rigidity and low polarizability through –COO- in place of –CH=CH–COO– and linear geometrical shape. The geometrical shape and induced polarizability of series-1 and Y appears identical except tailed end groups, but the intermolecular suitable magnitudes of anisotropic forces due to wider intermolecular distance in series-Y undergo reduction and predominated to the effect due to intermolecular polarizability factor of molecules of series-Y as compared to series-1, which may be affected by unexpected and modified status of n-alkyl chain "R" of –OR and $-C_{14}H_{29(n)}$ of $-OC_{14}H_{29(n)}$ end groups together with modified lower molecular rigidity than series-1 giving rise to only nematic phase with absence of smectic phase. The molecules of series-1 and Y are relatively less noncoplanar as compared to series-X. Therefore, the smectic and nematic mesophases comparatively commence earlier for a series-1 and the late for the series-X and Y in equal manner. The longer length of –CH=CH–COO– is greater by –CH=CH– unit as compared to identically positioned –COO- central bridge, which causes more noncoplanarity due to a twist obtained as the oxygen atoms of the vinyl carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic rings. On account of these differences, the smectic-nematic or smectic-isotropic thermal stability of series-X and Y is lower or lowest than the corresponding smectic thermal stability of series-1. Thermal resistivity and thermal stabilities varies with energy stored by an individual molecule as heat of formation (ΔH). The transition temperatures for the same homolog from series to series vary with changing magnitudes of polarity, polarizability, effective rigidity and flexibility, dispersion forces, dipole–dipole interaction, etc. Therefore, thermal resistivity and phase stabilization vary accordingly. Thus, upper mesophase length and nematic thermal stabilities adopt decreasing order and lower mesophase lengths adopt increasing order from series-1 to X to Y.

Conclusions

- Homologous series of present investigation is predominantly nematogenic and partly smectogenic of moderate mesophase length and thermal stabilities with thermometric and biological importance in the benefit of mankind and middle ordered melting type.
- The group efficiency order derived on the basis of (i) thermal stabilities, (ii) early commencement of mesophases, and (iii) total mesophase lengths for smectic and nematic are as under.
  - (i) Smectic
    Series-1 > series-X = series-Y
    Nematic
    Series-1 > series-X > series-Y
  - (ii) Smectic
    Series-1 > series-X = series-Y
    Nematic
    Series-1 > series-X = series-Y
  - (iii) Total mesophase lengths
    Upper: series-1 > series-X > series-Y
    Lower: series-Y > series-X > series-1
- Mesomorphism is very sensitive and susceptible to molecular structure as a consequence of resulting molecular rigidity and flexibility.
- Thermometric mesophase lengths and biological activity of present novel series can be exploited in the benefit of mankind.
- Present investigation supports and raises the credibility to the conclusions drawn earlier.

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