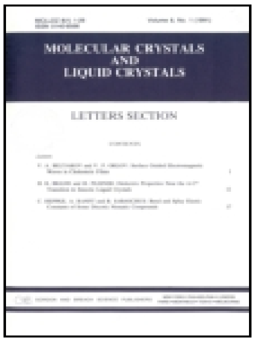


Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Mesomorphism dependence on molecular rigidity with reference to –CH=CH– unit of central bridge

R. B. Marathe & A. V. Doshi

To cite this article: R. B. Marathe & A. V. Doshi (2016) Mesomorphism dependence on molecular rigidity with reference to #CH#CH# unit of central bridge, Molecular Crystals and Liquid Crystals, 625:1, 81-92, DOI: 10.1080/15421406.2015.1069004

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1069004

MOL. CRYST. LIQ. CRYST.
2016, VOL. 625, 81–92
http://dx.doi.org/10.1080/15421406.2015.1069004

Taylor & Francis
Taylor & Francis Group

Mesomorphism dependence on molecular rigidity with reference to −CH=CH− unit of central bridge

R. B. Marathe[a] and A. V. Doshi[b]

[a]Huntsman International India Pvt. Ltd, Umraya village, Taluka: Padra, Vadodara, Gujarat, India; [b]Dr K. N. Modi University, Plot No.INS-1, RIICo Industrial Area Ph-II, Newai, Dist. Tonk, Rajasthan, India

ABSTRACT

A novel ester homologous series of rich mesomorphism and low temperatures with unexpected phase behaviors of eleven homologues was synthesized and studied with a view to understanding and establishing the relation between mesomorphic behaviour and the molecular structure of a series 4-(4′-*n*-alkoxybenzoyloxy)-4″-chlorobenzyl cinnamates. All the members of the novel series are enantiotropically smectogenic and the octyloxy (C_8) to hexadecyloxy (C_{16}) homologues are enantiotropically nematogenic, in addition to smectogenic. Odd–even effect is observed for Sm–I/Sm–N transition curve but it is absent for N–I transition curve. Textures of nematic phase are threaded or Schlieren and that of the smectic phase are fan shaped or batonates of smectic-A type phase or Smectic-C type for C_{16} homologues as judged directly from a heating stage of an optical polarizing microscopy. Analytical and spectral data confirmed the molecular structures of novel homologues. Mesomorphic properties of present series are compared with the structurally similar other known series. The average smectic and nematic thermal stabilities are 92.78°C and 100.8°C, respectively. Mesophase length minimum to maximum for smectic and nematic are 21.0°C to 31.1°C and 8.4°C to 42.6°C respectively. Thus, the present novel series is partly nematogenic and fully smectogenic with considerable degree of mesomorphism and low melting type.

KEYWORDS
Liquid crystals; mesogen; mesomorphism; nematic; smectic

Introduction

The mesogenic tendency of liquid crystalline (LC) substances [1] has been proven its ability to benefit mankind since 1888 [2–10]. The present investigation is planned with a view to understanding and establishing the effects of molecular structure on LC properties and the degree of mesomorphism through synthesis of novel LC substances by homologous series. The present investigation is aimed (i) to synthesize novel homologous series including their characterization, (ii) to evaluate thermal data in terms of thermal stability, commencement of mesophase, and mesophase length range, (iii) to compare the LC behaviors of present series with structurally similar other series, (iv) to interpret and discuss normal or abnormal behaviours in terms of molecular rigidity and flexibility [11–16] with reference to presence and absence of −CH=CH− unit in central bridge, and (v) conclude the effects of molecular structure on LC

CONTACT R. B. Marathe maratha79raj@gmail.com Huntsman International India Pvt. Ltd., Umraya village, Taluka, Padra, Vadodara, Gujarat, India.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

properties [17–20] including suggested possibility of application of novel substances to LC researchers working with aims, object and views other than present investigation. Number of homologous series of LC have been reported to date [21–25] but present novel series consists of three phenyl rings, two central bridges –COO– and –CH=CH–COO–CH_2- with two terminal end groups –OR and –Cl.

Experimental

Synthesis

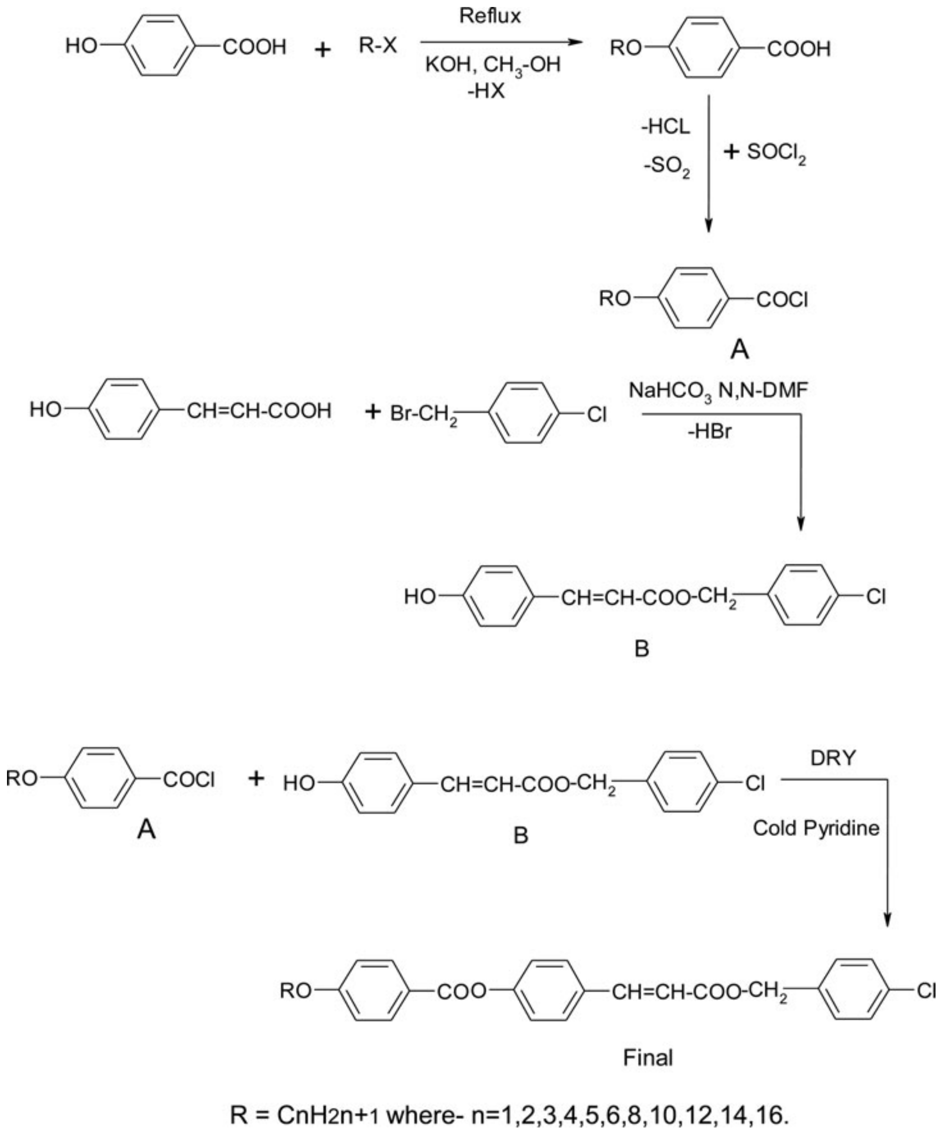
4-Hydroxy benzoic acid was alkylated by suitable alkylating agents R-X to form *n*-alkoxy benzoic acid by a modified method of Dave and Vora [26] as main component of a series. 4-Hydroxy-4′-chlorobenzyl cinnamate (m.p.: 98°C, Yield: 80%) was prepared from 4-chlorobenzyl bromide and 4-hydroxycinnamic acid by applying the method of a US patent No. 0053964, European patent and the modified method of Doshi, Patel and Marathe [27]. The detailed process includes preparation of sodium salts of 4-hydroxy cinnamic acid by dissolving in the solvent *N*,*N*-dimethyl formamide and $NaHCO_3$ at room temperature and sodium salt of 4-hydroxycinnamic acid is condensed with 4-chlorobenzyl bromide by dissolving in *N*,*N*-dimethyl formamide at room temperature. The solution was added to the solution of 4-hydroxycinnamic acid slowly at room temperature. The reaction mass was stirred for 24 hr at room temperature after addition of 4-chlorobenzyl bromide. After heating to 70–80°C for 2–3 hr the mass was allowed to cool at room temperature. The inorganic salt (NaBr) isolated by filtration. The filtrate containing the product decomposed in cold water under vigorous stirring. The off-white precipitate formed and the *N*,*N*-dimethyl formamide dissolved in excess water. The precipitated product was separated by a simple filtration method. The product was washed with excess of water to remove the salts and solvents. The product was dried and purified in toluene until constant melting point was obtained.

And *n*-Alkoxy benzoic acids were condensed through their corresponding acid chlorides with 4-hydroxy-4′-chlorobenzyl cinnamate in dry pyridine to form final products by a usual established method [28]. Final esterified products were individually decomposed, filtered, washed dried, and purified until constant transition temperatures were obtained.

The required chemicals for synthesis 4-hydroxycinnamic acid, 4-hydroxy benzoic acid, alkyl halides, methanol, KOH, 4-chlorobenzyl bromide in alcohol or *N*,*N*-dimethyl formamide, $NaHCO_3$, HCl, Dry Pyridine, Thionyl chloride, Fresh Toluene, EtOH, etc. All these were used as received, except solvents which were dried and purified prior to synthesis. Synthetic route to the series is mentioned below (on page 17) as Scheme 1.

Characterization

The selected members of a novel homologues series were characterized and analyzed by elemental analysis and the structure elucidation by Infra-red spectra, ^{1}HNMR spectra and mass spectra. Textures and transition temperatures of homologues as well as of related materials were determined by an optical polarizing microscope, equipped with a heating stage. Elemental analysis was performed on Perkin-Elmer PE 2400 C,H,N analyzer (Table 1). The percentage halide content is determined by usual analytical method. IR spectra were recorded on Shimadzu Spectrum analyzer. ^{1}HNMR spectra were determined on Bruker spectrometer using $CDCl_3$ solvent. Textures of smectic mesophase of some homologues were recognized either directly from the microscopic observations or by miscibility method. Table 1



Scheme 1. Synthetic route to the series-1.

Table 1. Elemental analysis for ethoxy, propyloxy and hexyloxy derivatives.

Sr. No.	Molecular formula	% Elements calculated (Experimental%)		
		C	H	Cl
1	$C_{25}H_{21}ClO_5$	68.72 (67.20)	4.81 (4.56)	8.13 (8.09)
2	$C_{26}H_{23}ClO_5$	69.25 (70.20)	5.10 (5.30)	7.88 (7.60)
3	$C_{29}H_{29}ClO_5$	70.65 (69.80)	5.88 (6.00)	7.20 (7.50)

Analytical data

Spectral data

^{1}HNMR in ppm for the dodecyloxy derivative

0.86–1.83 (–CH_3 of $C_{12}H_{25}$), 3.99–4.05 (–CH_2– of –$C_{12}H_{25}$), 5.19–5.22 (–CH=CH–), 6.29–6.99 (p-substituted phenyl ring), 7.33–7.40 (p-substituted benzene).

^{1}HNMR in ppm for the tetradecyloxy derivative

0.85–0.89 (–CH_3 of $C_{14}H_{29}$), 1.15–1.50 (–CH_2– of –$C_{14}H_{29}$), 3.97–4.05 (–O–CH_2–), 5.04–5.21 (–CH=CH–), 6.20–6.24 (p-substituted phenyl ring), 6.26–6.97 (p-substituted benzene).

NMR data confirm the structure.

IR in cm^{-1} for butyloxy derivative

690–771 polymethylene of C_4H_9, 840 para-substituted phenyl ring, 1083, 1253, 1508 ester linkage of (–COO–C_4H_9), 921–943 Trans of (–CH=CH–) 1161 ether linkage of (C_4H_9–O– of phenyl), 1014 Aromatic –Cl linkage, 758–775 (C–Cl stretch).

IR in cm^{-1} for pentyloxy derivative

725 poly methylene of C_5H_{11}, 802–833 para substituted benzene, 981 Trans (–CH=CH–), 1012 Aromatic –Cl linkage, 1220, 1315, 11676, 1728 (–COO– ester), 1074, 1157 ether linkage of (C_5H_{11}–O–C_6H_4), 758 (para substituted– Cl), 3437 (H– bonding of OH), 2872, –COOH.

IR data confirm the structure.

Mass spectra

Mass Spectra for Hexyloxy Derivative:

Molecular weight: Calculated: 422. Molecular formula: $C_{24}H_{19}ClO_5$
Experimental: 422.

Texture of phase by miscibility method

Octyloxy (C_8) derivative ——————————→ Threaded nematic
Tetradecyloxy (C_{14}) derivative ——————————→ Schlieren nematic
Ethoxy (C_2) derivative——————————→ Battonate Smectic-A
Hexyloxy (C_6) derivative——————————→ Fan shaped Smectic–A
Tetradecyloxy (C_{14}) derivative——————————→ Smectic-C

Results and discussion

The non-mesomorphic component 4-Hydroy-4′-chlorobenzylcinnamate (m.p.-98°C, Yield: 80%) is linked to the dimeric 4-*n*-alkoxy benzoic acid, whose dimerization disappears with lowering and alternation of transition temperatures of resulted novel homologues. Mesomorphic behaviours are promoted by increasing molecular length through –CH_2–C_6H_4–Cl unit. The unusual pattern of order of the mesophase occurrence observed for a present series, because most of the ester or other homologous series follows usual pattern of mesophase sequence. But in present series C_1–C_6 are with smectic–isotropic transition temperatures,

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

Compound no.	R=C_nH_{2n+1} (n)	Transition temperature in °C Sm	N	Isotropic
1	C_1	89.3	–	111.4
2	C_2	82.0	–	145.9
3	C_3	83.7	–	120.9
4	C_4	69.2	–	99.1
5	C_5	67.8	–	96.3
6	C_6	51.3	–	73.0
7	C_8	42.8	72.4	115.0
8	C_{10}	51.5	82.6	91.0
9	C_{12}	59.1	87.8	109.9
10	C_{14}	55.5	76.5	90.3
11	C_{16}	49.9	74.7	97.8
Sm: Smectic	*N* :Nematic			

without nematic mesophase formation, whereas C_8–C_{16} homologues give rise to form smectic to isotropic phase change via nematic mesophase formation with alternation of isotropic transition temperatures of C_8, C_{10}, C_{12}, C_{14}, C_{16} homologues. Thus, the sequential order of mesophase occurrence in any series normally should be first nematic then smectic and nematic and finally smectic-isotropic in the most of the homologous series. Generally, the initial members may either nematic or isotropic or smectic. The odd–even effect may be observed for N–I or / and Sm–N / Sm–I transition curve, but in case of presently investigated novel series, the smectic-isotropic transition appears first and then smectic–nematic–isotropic transition temperatures practically observed. Hence, the sequence of mesophase pattern in present series is not maintained or followed in unexpected sequential ordered pattern or it followed in unusual or unexpected ordered of mesophase pattern for nematic–isotropic transition of higher homologues (C_8 to C_{16}); with longer *n*-alkyl chain bonded to first phenyl ring through oxygen atom. Transition temperatures (Table 2) are plotted versus the number of carbon atoms present in *n*-alkyl chain of left *n*-alkoxy terminal end group. Smooth curves are drawn through like or related points to draw phase transition curves as depicted in a phase diagram (Fig. 1) showing the phase behavior of present series. Smectic-isotropic or smectic–nematic transition curve initially descended and then rises from C_8 homologue, then passes through maxima at C_{12} homologue and finally descends till C_{16} through C_{14} homologue. Thus, Sm–I or Sm–N transition curve behaves in normal manner. Cr–Sm transition curve follows zigzag path of rising and falling with overall descending tendency and behaved in expected normal manner. N–I transition curve adopts wave like path as shown by dotted wave, in which dotted curve alternate its path C_8 to C_{10} to C_{12} to C_{14} to C_{16}, i.e. N–I points of C_8, C_{12}, C_{16} on linking show a N–I transition curve which descends as series is ascended. Similarly on linking N–I points of C_{10} and C_{14} homologue constitute N–I transition curve with descending tendency as series is ascended. These two hypothetical N–I curves mentioned above are just like odd–even effect curves. But here they are curves related to even–even members which may be assigned the term even–even effect with difference of four homologue, i.e. phase behaviors in present series alternates with every two higher even numbered homologues and repeats behavior at every four homologues. Thus, N–I transition curve like electromagnetic wave appearance does not match with the normal behavior, as observed in the most of the homologous series. The N–I transition as observed abnormally in higher homologue C_8–C_{16} instead of in the lower homologues as odd–even effect. The consistency of transition temperatures of homologues of present investigation were repeatedly confirmed on an optical

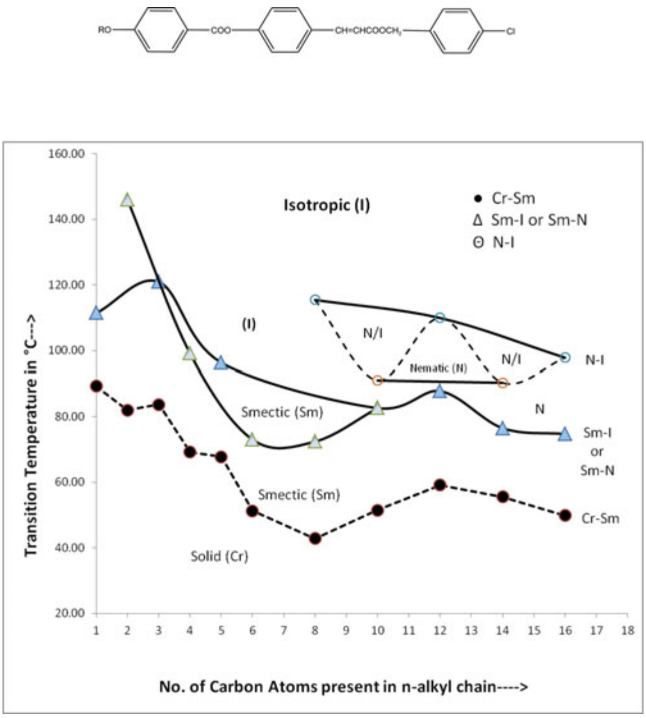


Figure 1a. Phase behavior of Series-1.

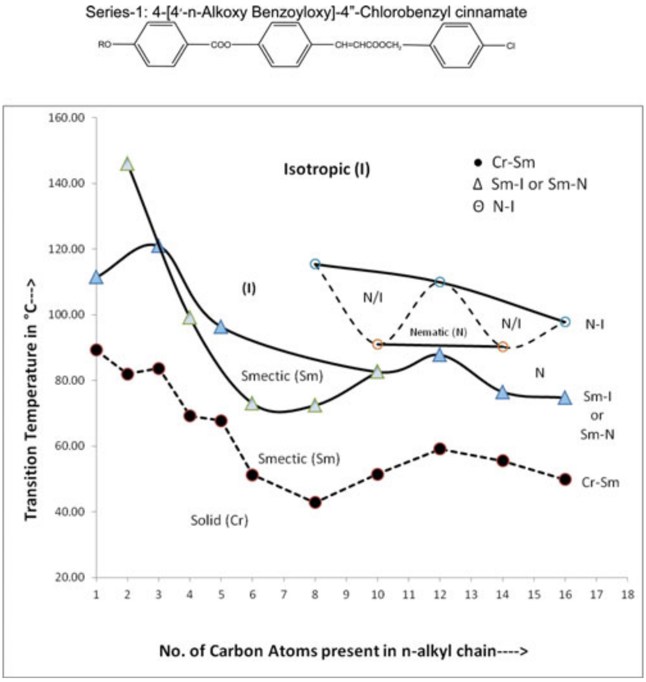

Series-1: 4-[4′-n-Alkoxy Benzoyloxy]-4"-Chlorobenzyl cinnamate

Figure 1b. Phase behavior of Series-X.

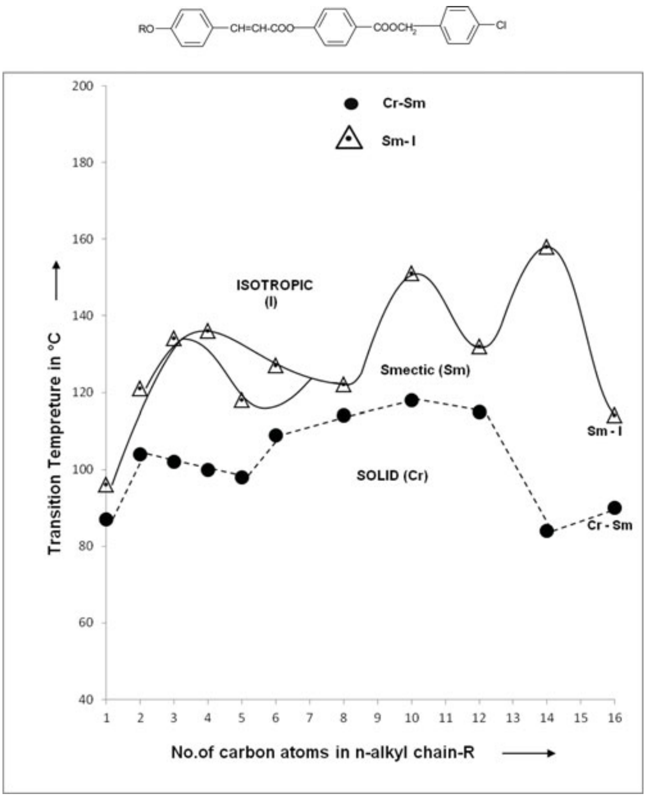


Figure 1c. Phase behavior of Series-Y.

polarizing microscopy equipped with a heating stage (POM) and the same values were experimentally noted. Thus, mesomorphic properties of thermotropic liquid crystals depending upon transition temperature which varies from homologue to homologue in the same present series. Hence, present series is fully smectogenic and partly nematogenic whose Sm–I or N–I transition temperatures vary between 90.3°C and 145.9°C. Cr–Sm transition temperatures vary between 42.8°C and 89.3°C and corresponding Sm–I, Sm–N, N–I, and total (Sm + N) mesophase length ranges between 21.7 (C_6) and 63.9 (C_2), 21.0 (C_{14}) and 31.1 (C_{10}), 8.4 (C_{10}) and 42.6 (C_8), 21.7 (C_6) and 72.2 (C_8), respectively.

Disappearance of dimerization of *n*-alkoxy acids is attributed to the breaking of hydrogen bonding by the process of esterification, between two acid molecules. Alternation of transition temperatures is due to the even and odd number of methylene unit or units present in *n*-alkyl chain bonded to first phenyl ring through oxygen atom. The disappearance of dimerization reduces the rigidity of aromatic acid molecule and hence the transition temperatures of final esterified compounds are lowered as compared to the corresponding *n*-alkoxy acids. Moreover, the non-mesomorphicity of 4-methoxy benzoic acid and 4-ethoxy benzoic acids disappears due to linking of non-mesogenic component 4-hydroxy-4′-chlorobenzyl cinnamate with methoxy and ethoxy benzoic acids by increasing molecular length, polarity, and polarizability as a consequence of favorable molecular rigidity and flexibility, the magnitudes of which results into lamellar packing of molecules in the crystal lattices of all members of a novel series including methoxy and ethoxy benzoic acids derivatives which provides an environment to induce smectogenic property. The exhibition of only smectogenic property from

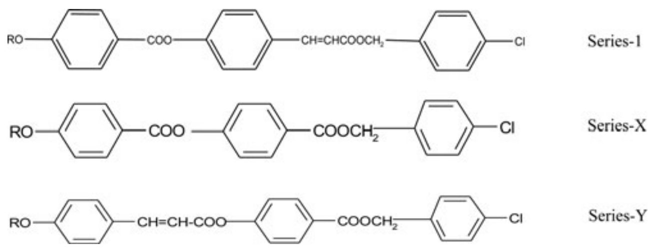


Figure 2. Structurally similar homologous series.

C_1 to C_6 suggest that, the magnitudes of intermolecular anisotropic forces of end to end attractions and closeness are unsuitable as a consequence of unfavorable magnitudes of molecular rigidity and flexibility which hinders the statistically parallel orientational order of molecules in floating condition on the surface; but the same molecules of pre-occupied lamellar packing of molecules in their crystal lattices which exhibited smectic phase and now directly transform into the isotropic liquid, in which molecules are randomly oriented in all possible directions with high order of disorder or high entropy from and beyond isotropic temperatures, by missing of formation of nematic mesophase. The predominancy of intermolecular lateral attractions caused more as compared to end to end attractions which arranges molecules to float with sliding layered arrangement to show ordered molecular arrangement on heating and subsequent cooling, respectively. Thus, molecules of C_1 to C_6 are unable to resist exposed thermal vibrations beyond temperature of maintaining smectic phase formation because of the low dipole–dipole interactions and the low magnitudes of dispersion forces by the interactions between instantaneous dipoles produced by the spontaneous oscillations of electron clouds of molecules. The exhibition of nematic mesophase between C_8 and C_{16} of the even numbered homologues is due to the suitable magnitudes of anisotropic forces of end to end cohesion of the molecules. The intermolecular residual forces of end to end attractions is now from and beyond C_8 homologue is sufficient to maintain statically parallel orientational molecular order in floating condition on the surface to exhibit nematogenic character, i.e. isotropic mesophase appears via nematic mesophase from smectic phase. Odd–even effect observed for Sm-I/Sm-N transition curve is due to the sequentially added methylene unit or units present in *n*-alkyl chain of left *n*-alkoxy terminal end group. The absence of odd–even effect in N–I transition curve is attributed to the late commencement of nematic phase from C_8 homologue and it continues for higher homologues of longer (C_8, C_{10}, C_{12}, C_{14}, C_{16}) *n*-alkyl chain with only even numbered methylene units in *n*-alkyl chain. Abnormal behavior of Sm-N transition curve is attributed to the uncertainty in the status of the *n*-alkyl chain which may coil or bend or flex or couple to lye with the principle axis of the core structure affecting molecular rigidity and flexibility, due to the variations in the length, size, polarity and polarizability, permanent dipole moment across the long molecular axis etc. Sm−I/Sm−N transition curve for odd members of the present series occupies partly lower position (C_1 and C_3) and vice versa than a curve for even members in unusual manner. The molecular polarizability is attributed to the size of the mono-atomic —Cl tail group bonded to sp^2 carbon of third phenyl ring and $-CH{=}CH-$ unit of vinyl carboxy group involving $-CH_2-$ unit. The mesogenic properties of present novel series-1 are compared with structurally similar other known series-X [29] and Y [30], as shown in following Fig. 2:

Homologous series-1 of present investigation and the Series-X and Y chosen for comparison are structurally similar. Homologous series-1 and X are identical with respect to three phenyl rings and a central bridge –COO– linking first and middle phenyl rings which partly

Table 3. Thermal stability in °C.

Series→	1	X	Y
Smectic–Isotropic	92.78	124.53	128.09
Or			
Smectic–Nematic	(C_1–C_{16})	(C_1–C_{16})	(C_1–C_{16})
Commencement of Smectic phase	C_1	C_1	C_1
Nematic–Isotropic	100.8	–	–
Commencement of	(C_8–C_{16})		
Nematic phase	C_8		
Mesophaselength range in °C	Sm:- 21 to 31.1		
Sm-	Nm:- 8.4 to 42.6	Total: 6.5 to 52.0	Total: 8.6 to 73.2
Nm-	Total: 21.7–72.2		
Total-	C_6 C_8		

contributes to molecular rigidity and flexible –Cl tail end group common for the homologues of same series. The left *n*-alkoxy terminal end group which vary from homologue to homologue for same series but remain unaltered for the same homologue from series to series. However, a central bridge $-CH{=}CH-COO-CH_2-$ and $-COO-CH_2-$ linking middle and third phenyl ring differs from series-1 to series-X, which contributes to the total molecular rigidity. Thus, combined effect of molecular rigidity and flexibility which operates the phenomenon of mesomorphism can vary accordingly. Homologous series-1 and Y are isomeric to each other. They are identical with respect to three phenyl rings which partly contributes to total molecular rigidity and two flexible terminal end groups –OR and –Cl which contribute to total molecular flexibility for the same homologue from series to series but differs from homologue to homologue in same series. However the central bridge –COO– of series-1 linking first and middle phenyl rings is replaced by –CH=CH–COO– in series-Y. Similarly a central bridge linking middle and third phenyl ring $-CH{=}CH-COO-CH_2-$ of series-1 is replaced by $-COO-CH_2-$ in series-Y. The replacement of central bridges in case of isomeric series-1 and Y causes difference due to –CH=CH– unit which displaces its place nearer or away from tailed –Cl common terminal end group. –CH=CH– unit in case of series-1 and Y contributes equally to the total molecular rigidity. But the difference in molecular rigidity arises due to the difference in the distance of its place from tailed end group –Cl, (or –OR), as affected by induced electronic environmental change on –CH=CH– unit. Thus, molecular flexibility of flexible units –Cl and –OR for the same homologue from series to series remains all almost unaltered by the replacement of central bridges but the magnitudes of molecular rigidity between isomeric series-1 and Y differs from each other. The terminal end groups –Cl and –OR being commonly present in all the three series under comparative study, the molecular flexibility for the same homologue from series to series remains unchanged but differs in molecular rigidity for the same homologue from series-1 to series-X to series-Y due to their part of dissimilarity. Thus, the variations in mesomorphic properties and the degree of mesomorphism observed amongst the molecules of homologues in the same series or for the same homologue from series to series depend upon changing molecular rigidity (ΔH), keeping molecular flexibility almost unchanged. The phenomenon of mesomorphism occurs by the combined effect of molecular rigidity and flexibility, but in case of present comparative study, the variations in the mesomorphism will arise by varied molecular rigidity by replacement of –CH=CH– unit difference (series-1 and X) and the displacement of place (series-1 and Y) of –CH=CH– unit. Hence, the mesomorphism dependence of molecular rigidity plays an important role in present comparative study. Following Table 3 represents some mesomorphic properties for the series under comparison.

From the Table 3, it is clear that,

- Homologous series of present investigation-1 is fully or predominantly smectogenic and partly nematogenic whereas; homologous series-X and y chosen for comparison are only smectogenic without exhibition of nematogenic property.
- Thermal stability for smectic and nematic for series-1 are 92.78 and 100.8, respectively, whereas, smectic thermal stability of series-X and Y are 124.53 and 128.09, respectively, i.e. smectic thermal stability is in increasing order from series-1 to X to Y.
- Smectic mesophase commences from very first (C_1) member of series-1, X and Y under comparative study and it continues till the last member (C_{16}) member of each series.
- Nematic mesophase commences from octyloxy homologue (C_8) of a series-1 and continue till hexadecyloxy homologue (C_{16}) of the series. But nematic mesophase does not commence till the last member (C_{16}) of the series-X and Y.
- Total mesophase length range is lowest and highest for the series-X and Y whereas, it is an intermediate valued for present series-1.
- Phase diagrams of series under comparison (series-1, X, Y) differ from each other as shown in Figs. 1a–c.

Exhibition of only smectic property in absence of nematic property in series-X and Y indicate that, the forces holding the planes of the layers together in the pre-occupied lamellar packing of molecule in the rigid crystal lattices are weaken relatively to the intermolecular attractions among the molecules within a given layer at solid-mesomorphic transition temperature and the layers may become free to slide and rotate over one another inducing smectic phase. Then on heating the smectic mesophase to a higher temperature, the intermolecular forces between the sides of the molecules further weakened to such an extent that, resultant intermolecular forces do not permit molecules to slide out of the layer and statistically parallel orientational molecular order in floating condition does not maintain at all. Thus, absence of nematic property and the exhibition of only smectic property for series-X and Y become feasible. However, exhibition of nematic phase in addition to smectic phase become feasible in series-1 by suitable magnitudes of residual anisotropic forces which resists exposed thermal vibrations to maintain statistically parallel orientational order of molecules to induce nematic phase after the smectic phase in series-1 as a consequence of added molecular rigidity through –CH=CH– unit which situated nearest to flexible –Cl tail end group in presently investigated series-1, but it is either absent in series-X or it is far away from –Cl tail end group in series-Y the causes hindrance of the possibility of inducing nematic property. The commencement of smectic phase of series-1, X and Y occurs from the very first member (C_1) of each series. Early or late commencement smectic phase of series is related to the extent of non-coplanarity of molecules. The early commencement of smectic phase is related with less molecular non-coplanarity. Thus, planarity of the molecules of all the series under comparison are reduced by common —Cl mono-atomic tailed end group for the same homologue from series to series as well as due to the presence of multiple bond in –CH=CH– unit. The extent of non-coplanarity and lateral attractions due to the central bridge being almost the same for the molecules of all the series under comparative study, the added polarizability due to tailed end group in present comparison is almost zero, because all the series have common flexible –Cl tail. Moreover, the added polarizability due to –CH=CH– unit of central bridge increases intermolecular attractions as a consequence of differing molecular rigidity related to energy stored in unit mass and characteristics at constant pressure (ΔH). Therefore, the resistivity towards exposed thermal vibrations varies for the same homologue from series to series and from homologue to homologue in the same series. Thus, varying thermal resistivity results into variations in the degree of mesomorphism of smectic/nematic or total mesophase length range and thermal stabilities for smectic and/or nematic. Hence, increasing order of smectic thermal stability is observed for the series-1, X and Y. Missing of facilitating nematic mesophase in series X and Y operates higher values of their smectic thermal stability and the lowest value of smectic thermal stability of series-1 attributed to occurred at the cost of the exhibition of added nematic mesophase formation. Now looking to the phase diagrams of isomeric series-1 and Y both series resembles to each other with respect to abnormal transition curves obtained for C_8, C_{10}, C_{12}, C_{14}, C_{16} homologues, which appears like an electromagnetic wave and the positions of curves for odd and even members of the series-1 and Y. Thus, exchange of central bridge involving –CH=CH– unit facilitated to induce nematic phase in present series-1, but the same –CH=CH– nearer to same tail group facilitated and induce smectic phase for C_8, C_{10}, C_{12}, C_{14} and C_{16} homologues. In case of homologous series-X, the transition curves for odd-even members, resemble to series-1, but shapes of curves from C_8 to C_{16} differs abnormal behaviors due to absence of –CH=CH– unit.

Conclusions

- Homologous series of present investigation is fully smectic and partially nematic of low thermal stability and low melting type with considerable mesophase length.
- The group efficiency order derived for smectic and nematic on the basis of (i) thermal stability or rigidity (ii) early commencement of mesophase and (iii) mesophase length as under
  (i) Smectic
  Series-Y > Series-X > Series-1
  Nematic
  Series-1 > Series-X = Series-Y
  (ii) Smectic
  Series-1 = Series-X = Series-Y
  Nematic
  Series-1 > Series-X = Series-Y
  (iii) Mesophaselength (total)
  Series-Y > Series-1 > Series-X
- Exchange of central bridges in the isomeric series (1 and Y) bearing same tailed end group can give rise to similar abnormal behavior and shapes of transition curve, irrespective of smectic or nematic phase for higher (C_8 to C_{16}) homologues.
- Replacement of vinyl carboxy central bridge to carboxy central bridge raises smectic thermal stability but lowers mesophase length range.
- –CH=CH– unit increases molecular rigidity, thermal stability, and the mesophase length range.
- Mesomorphism and the degree of mesomorphism are very sensitive and susceptible to molecular structure.
- Study of binary system with C_6, C_8, C_{10}, and C_{16} homologue can give rise to LC mixtures workable at room temperature which may be useful to manufacture articles related to mesomorphism.
- Novel LC materials of present series may be useful to continue or extended research of researchers belonging to fields other than chemistry.
- The generalization that, sequential pattern mesophase formation in a homologous series as only nematic in initial homologue, then smectic plus nematic mesophase formation for middle homologue and finally the only smectic mesophase formation for higher homologue. “Above generalization is not universal”

Acknowledgments

Authors acknowledge thanks to the Green Circle Inc. Laboratory for providing research facilities services as and when needed. Authors acknowledge thanks to Dr. Keyur Trivedi of Solaris Industries Ltd., Vadodara, for providing the free sample of 4-chlorobenzyl bromide. Authors are also thankful to Dr. N. N. Vyas, Dr. Vipul Patel, and Dr. M. L.Chauhan, P.T. Arts and Science College, Godhara, for their valuable helping hand and microscopic facility. Also thanks are due to the Sophisticated Analytical Instrumentation Facility, Punjab University, (Chandigarh) for extending their help for analytical services.

References

[1] Reinitzer, F. (1888). *Monatsh*, *9*, 421.

[2] Narmura, S. (2001). *Displays*, *22*(1), 1

[3] Kim, W. S., Elston, S. J., & Raynes, F. P. (2008). *Displays*, *29*, 458–463.

[4] Tadwee, I., Dr. Sahanashahi, S., Ramteke, V., & Syed, I. (2012). *IJPRAS*, ISSN 2277-36. *1*(2), 06–11.

[5] Hertz, E., Lavorel, B., & Faucher, O. (2011). *Nature Photon*, *5*, 783.

[6] Gray, G. W., & Winsor, P. A. (Eds.) *Liquid crystals and plastic crystals*, Chapter-6.2, The role of liquid crystal in life processes by G. T. Stewart, 1, pp. 308–326.

[7] Jain, U. K., Bhatia, R. K., Rao, A. R., Singh, R., Saxena, A. K., & Seha, I. (2014). *Tropical J. Pharmaceut. Res.*, *13*(1), 73–80.

[8] Gaikwad, P. P., & Desai, M. T. (2013). *Int. J. Pharma Res. Rev.*, *2*(12), 40–52.

[9] Rajesh, G., Mansi, K., Srikant, K., Babasaheb, B., Nagesh, D., Kavita, S., & Ajay, C. (2008). *Chem. Pharm. Bull.*, *56*, 897–901.

[10] Modzelewska, A., Pettit, C., Achanta, G., Davidson, N. E., Huang, P., & Khan, S. R. (2006). *Bioorg. Med. Chem.*, *14*, 3491–3495.

[11] Imrie, C. T., & Luckhrust, G. R. (1998). Liquid crystal dimers and oligomers, in Hand book of liquid crystals. In: *Law Molecular Liquid Crystals*, Vol. 2B, Demus, D., Goodby, J. W., Graw, G. W., Spiess, H. W. & Vill, V. (Eds.), Wiley-VCH: Weinheim, pp. 801–833.

[12] Henderson, P. A., Niemeyer, O., & Imrie, C. T. (2001). *Liq. Cryst.*, *28*, 463–472.

[13] Hird, M., Toyne, K. J, Gray, G. W., & Day, S. E. (1993). *Liq. Cryst.*, *14*, 741.

[14] Hird, M., Toyne, K. J., Gray, G. W, Day, S. E., & Mc Donell, D. G. (1993). *Liq. Cryst.*, *15*, 123.

[15] Collings, P. J., & Hird, M. (1997). *Introduction of Liquid Crystals Chemistry and Physics*, Taylor and Francis Ltd.: U.K.

[16] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Adv. Matter*, *4*, 285.

[17] Gray, G. W. (1962). *Molecular Structures and Properties of Liquid Crystals*, Academic Press: London.

[18] Gray, G. W., & Jones, B. (1954). *J. Chem. Soc.*, 2556–2562.

[19] Imrie, C. T. (1999). *Struct. Bond.*, *95*, 149–192.

[20] Gray, G. W. (1974). In: *Liquid Crystals and Plastic Crystals*, Gray, G. W. & Winsor, P. A. (Eds.), Chap. 4, Vol. 1, 103–153.

[21] Demus, D. (1988). *Mol. Cryst. Liq. Cryst.*, *165*, 45–84.

[22] Demus, D. (1988). *Liq. Cryst.*, *5*, 75–110.

[23] Doshi et al. (i) Suthar, D. M., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *575*, 76–83. (ii) Chauhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *570*, 92–100. (iii) Chaudhari, R. P., Chauhan, M. L., & Doshi, A. V. (2013). *575*, 88–95. (iv) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 104–110.

[24] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *527*, 51–58.

[25] Patel, B. H., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst.*, *605*(1), 23–31.

[26] Patel, B. H., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst.*, *605*(1), 42–51.

[27] (a) Pieter-Ooms, Krefeld, Bernd-Ulrich Schenke, Bottrop, ‘Process for the preparation of Hydroxybenzoic benzyl esters’ United States patent no: 2003/0053964 A1, Mar. 20, 2003. (b) European Patent EP0117502B1, Process of producing benzyl ester of aromatic hydrocarboxylic acid (Example-1), page 4, date of Publica. 19-11-1987. (c) Marathe, R. B., & Doshi, A. V. (2014). Manuscript of a research paper entitled “Mesomorphism Dependance on Terminally Substituted End groups” accepted for publication in *Mol. Cryst. Liq. Cryst.*, LCMH 281.

[28] Patel, B. H., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst.*, *605*(1), 61–69.