Study of Thermotropic Mesomorphism in Nonlinear and Linear Isomeric and Nonisomeric Series

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ABSTRACT. Chalconyl homologous series: RO-C₆H₄-COO-C₆H₄(m)-CO-CH=CH-OC₁₄H₂₉(n) para has been synthesized and studied with a view to establish the relation between the molecular structure and thermotropic Liquid crystalline (LC) properties. Novel nonlinear series consists of thirteen members (C₁ to C₁₈) of a series. C₆ to C₁₈ members are enantiotropically nematogenic and the rest of the homologues (C₁ to C₅) are nonliquid crystals (NLC). Smectogenic character is totally absent. Transition temperatures and the textures of the novel homologues were determined by an optical polarizing microscopy (POM) equipped with a heating stage. Textures of a nematic phase are threaded or schlieren. Transition curves Cr-N/I and N-I behaved in normal manner. N-I transition curve exhibited odd-even effect. Analytical and spectral data confirmed the molecular structures of homologues. Thermal stability is 107.0 and mesomorphic nematogenic degree of mesomorphism vary minimum to maximum are 17.0°C to 35.0°C at the C₁₄ and C₈ homologues respectively. Some mesogenic properties of presently investigated homologous series are compared with structurally similar isomeric and nonisomeric homologous series, and their group efficiency order derived. Thus, present novel series is nematogenic with absence of smectogenic character whose nematogenic transition temperatures vary from 74.0°C to 117.0°C.

1. INTRODUCTION

The Combination of thermotropic LC Property [1] and biological activity possessing property have been matched in chalconyl derivatives. Such combination of dual character has inspired for the study of novel substances which may be potentially capable and important for LC devices [2,3,4] and for the pharmaceutically antibacterial, antimalarial, anticancer, etc. etc... [5,6,7,8,9,10]. Therefore present investigation is planned with a view to understand and establish the relation between thermotropic LC properties and the molecular structure of a substance or substances [11,12,13,14,15] through synthesis of novel chalconyl ester series of homologues. Such novel homologues may be useful for extending and continuing the research activity of groups of researchers working on LC state with different aims, objects and views at different angle. Number of ester, azoester, azomethene, benzyl ester, chalconyl ester etc. are reported till the date [16,17,18,19,20,21,22,23] present investigation will consist of three phenyl rings and two central bridges with varying number of methylene unit in left n-alkoxy terminal end group and fixed – OC₁₄H₂₉ (n) group at the tail end. Evaluated results will be discussed and interpreted in terms of molecular rigidity and flexibility [24,25,26,27] and LC properties of present nonlinear series will be compared structurally similar series with derivative of group efficiency order derivation.

2. EXPERIMENTAL

Synthesis:

4-Hydroxy Benzoic acid was alkylated using suitable alkylating Agent (R-X) to convert it into 4-n alkoxy benzoic acids(A) by modified method of Dave and Vora [28]. α -3-Hydroxy benzoyl β -4-tetradecyloxy ethylene (B) was prepared by usual established method [29]. Esters were synthesized by a literature method[30]. Thus, the Chalconyl - ester homologue derivatives were decomposed filtered, washed with solution of sodium bicarbonate and sodium hydroxide followed

by water dried and purified till constant transition temperatures obtain using an optical polarising microscope equipped with a heating stage. 4-hydroxy benzoic acid, Alkyl halides, 4-hydroxybenzaldehyde, 3-hydroxy acetophenone, dicyclohexylcarbodiimide, Dimethyl amino pyridine, DCM, MeOH, Acetone required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to a series is mentioned below in Scheme-1.

Scheme 1: Synthetic route to the series

3. CHARACTERIZATION

Selected members of the novel homologous series were characterized by Elemental Analysis, infrared spectroscopy, ^1H NMR spectra. IR spectra were recorded by Perkin-Elmer spectrum GX, ^1H NMR spectra were recorded on Bruker using CDCl_3 as solvent. Microanalysis was performed on a Perkin-Elmer PE2400 CHN analyzer. Transition temperature and LC properties (Textures) were determined using an optical polarizing microscopy equipped with a heating stage. Textures of nematic phase determined by miscibility method. Thermodynamic quantity enthalpy (ΔH) and entropy (ΔH) are qualitatively discussed instead of DSC scan.

Analytical Data:

Table 1: Elemental Analysis for octyloxy, decyloxy, tetradecyloxy and octadecyloxy derivatives

Sr. No.	Molecular formula	%Elements found		%Elements Theoretical	
		C	H	C	H
1	$\text{C}_{44}\text{H}_{60}\text{O}_5$	79.13	9.05	79.04	8.98
2	$\text{C}_{48}\text{H}_{68}\text{O}_5$	79.64	9.46	79.77	9.39
3	$\text{C}_{52}\text{H}_{76}\text{O}_5$	80.27	9.84	80.20	9.74
4	$\text{C}_{54}\text{H}_{80}\text{O}_5$	80.48	9.98	80.57	9.90

IR Spectra in cm^{-1} for Octyloxy & Dodecyloxy Derivatives:

Octyloxy: 719 Polymethylene ($-\text{CH}_2-$) $_n$ of $-\text{OC}_8\text{H}_{17}$, 831 ($-\text{C}-\text{H}-$ def. m di-substituted), 761 Polymethylene ($-\text{CH}_2-$) of $-\text{OC}_{14}\text{H}_{29}$, 952 ($-\text{C}-\text{H}-$ def. hydrocarbon), 1114 ($-\text{C}-\text{O}-$) Str, 1165, 1249 and 1379 ($-\text{C}-\text{O}$ str in $-(\text{CH}_2)_n$ chain), 1456 ($-\text{C}-\text{H}-$ def. in CH_2), 1510 ($-\text{C}=\text{C}-$) str, 1604 ($-\text{C}=\text{O}$ and $-\text{COO}-$ ester group), 2850 and 2920 ($-\text{C}-\text{H}$ str in CH_3).

Dodecyloxy: 719 Polymethylene ($-\text{CH}_2-$) $_n$ of $-\text{OC}_{12}\text{H}_{25}$, 817 ($-\text{C}-\text{H}-$ def. m di-substituted), 769 Polymethylene ($-\text{CH}_2-$) of $-\text{OC}_{12}\text{H}_{25}$, 952 ($-\text{C}-\text{H}-$ def. hydrocarbon), 1114 ($-\text{C}-\text{O}-$) Str, 1379, 1163 and 1251 ($-\text{C}-\text{O}$ str in $-(\text{CH}_2)_n$ chain), 1462 ($-\text{C}-\text{H}-$ def. in CH_2), 1510 ($-\text{C}=\text{C}-$) str, 1602 ($-\text{C}=\text{O}$ and $-\text{COO}-$ ester group), 2848 and 2918 ($-\text{C}-\text{H}$ str in CH_3).

^1H NMR spectra in CDCl_3 in δ ppm for Hexyloxy & Decyloxy Derivative:

Hexyloxy: 0.87 (t, $-\text{CH}_3$ of $-\text{C}_6\text{H}_{13}$), 1.1-1.4 (m, n-poly methylene groups of $-\text{OC}_6\text{H}_{13}$), 1.73 (m, n-poly methylene groups of $-\text{OC}_{14}\text{H}_{29}$), 3.2-3.3 (s, $-\text{OCH}_2-\text{CH}_2-$ of $-\text{OC}_{14}\text{H}_{29}$), 4.01 (s, $-\text{OCH}_2-\text{CH}_2-$ of $-\text{OC}_6\text{H}_{13}$), 6.48 (d, $-\text{CH}=\text{CH}-$) 6.8-7.4 (s, $-\text{CO}-\text{CH}=\text{CH}-$), 8.13 (s, p-disubstituted phenyl ring).

Decyloxy: 0.84 (t, $-\text{CH}_3$ of $-\text{C}_{10}\text{H}_{25}$), 1.2-1.6 (m, n-poly methylene groups of $-\text{OC}_{10}\text{H}_{25}$), 1.78 (m, n-poly methylene groups of $-\text{OC}_{14}\text{H}_{29}$), 3.3-3.6 (s, $-\text{OCH}_2-\text{CH}_2-$ of $-\text{OC}_{14}\text{H}_{29}$), 4.13 (s, $-\text{OCH}_2-\text{CH}_2-$ of $-\text{OC}_{12}\text{H}_{25}$), 6.72 (d, $-\text{CH}=\text{CH}-$) 6.9-7.6 (s, $-\text{CO}-\text{CH}=\text{CH}-$), 8.3 (s, p-disubstituted phenyl ring).

Table 2: Texture of Nematic Phase of C_6 , C_{10} , C_{12} , C_{16} by miscibility method.

Sr. No.	Homologue	Texture
1	C_6	Threaded
2	C_{10}	Schlieren
3	C_{12}	Threaded
4	C_{16}	Schlieren

α -3-(4'-n-alkoxybenzoyloxy)benzoyl- β -4''-tetradecyloxyphenyl ethylenes

Figure 1: Structurally similar series

Table 3: Transition Temperature of Homologous series

Sr.no	R= n-alkyl group	Transition temperatures in $^{\circ}\text{C}$		
		Smectic	Nematic	Isotropic
1	C1	-	-	131.0
2	C2	-	-	136.0
3	C3	-	-	140.0
4	C4	-	-	127.0
5	C5	-	-	124.0
6	C6	-	81.0	113.0
7	C7	-	75.0	103.0
8	C8	-	82.0	117.0
9	C10	-	88.0	108.0
10	C12	-	80.0	113.0
11	C14	-	83.0	100.0
12	C16	-	74.0	99.0
13	C18	-	76.0	103.0

Figure 2: Phase behaviours of series

4. RESULT AND DISCUSSION

α -3-Hydroxy benzoyl β -4-tetradecyloxy ethylene (m.p.-72.0°C, yield 66.54%) is a nonliquid crystal component but on condensation with dimeric n-alkoxy benzoic acids, yielded chalconyl ester derivatives of lower transitions than the corresponding n-alkoxy benzoic acids. Alternations of transition temperatures in mesogenic homologues are observed. Transition temperatures (table-3) of homologues were plotted against the number of carbon atoms present in n-alkyl chain -R of -OR terminal end group and on linking them i.e. like or related transition point, Cr-N/I and N-I transition curves are obtained , showing phase behaviours of a novel series as depicted in a phase diagram of figure-1. Cr-N/I transition curve adopted a zigzag path of rising and falling tendency as series is ascended till C_{18} homologue and behaves in normal manner. N-I transition curves for odd and even number are merging into each other at the decyloxy C_{10} homologue and then from and beyond C_{10} . It prolonged as a single transition curve passing through maxima at C_{12} and descended as series is ascended with negligible rise at C_{18} homologue, and negligible abnormality from descending tendency at C_{14} homologue. Thus, N-I transition curve behaved in almost normal manner. N-I

transition curve for even numbers occupies higher position than curve (N-I) for odd members. The mesophase (nematic) commences from hexyloxy (C_6) homologue and continued upto octadecyloxy homologue (C_{18}) as enantiotropically nematogenic. C_1 to C_5 homologues are nonmesogenic (NLC). Smectogenic LC Phase is missing throughout the nonlinear novel chalconyl series. The LC behaviours from homologue to homologue in the same series undergoes variations. Thermal stability for nematic is 107.0°C whose LC phase length vary from 17.0°C to 35.0°C at the C_{14} and C_8 homologue respectively. Thus, it is a middle ordered melting type series of medium ranged liquid crystallinity. Lowering of transition temperatures of present novel homologues as compared to corresponding n-alkoxy benzoic acids is attributed to the breaking of hydrogen bonding between two molecules of aromatic acid by esterification process. Alterations of transition points are attributed to odd and even number of carbon atoms in alkyl chain (R) of $-\text{OR}$ group. Thenonmesomorphism of C_1 to C_5 homologues is attributed to low magnitudes of intermolecular dispersion forces and low dipole-dipole interactions as a consequence of unfavourable molecular rigidity and flexibility, which induces unsuitable magnitudes of intermolecular end to end and/or lateral cohesion and closeness as well as high crystallising tendency. As a result of this, the molecules of C_1 to C_5 are unable to resist exposed thermal vibrations and melt sharply to the isotropic state without passing through LC state. The inexistence of smectogenic character throughout a novel series is due to absence of lamellar packing of molecules in their preoccupied rigid crystal lattices, which fails to build up three dimensional networking layers. Therefore, the inadequate intermolecular lateral cohesion fails to form sliding layered molecular arrangement, under the influence of exposed thermal vibrations in floating condition. Thus, smectogenic character is missing prior to nematogenic mesophase formation. However residual intermolecular anisotropic forces of end to end attractions and closeness are strong enough to disalign the molecules of C_6 to C_{18} at an angle less than ninety degree on floating surface and resists the exposed thermal vibrations for some temperature difference and maintained the molecular arrangement in statistically parallel orientational order to show the formation of nematic phase as a consequence of end to end favourable magnitudes of cohesion and closeness. The molecules of homologue either from rigid crystalline state or nematogenic mesophase, transform into isotropic state, at an isotropic temperature, at which the molecules are randomly orient in all possible direction with high order of disorder or randomness or high entropy ($\Delta S = \Delta H$). But on cooling the isotropic mass from and below isotropic temperature, the nematic mesophase formation reappears in reversible manner exactly at a temperature at which, it had appeared. Thus, it is enantiotropic transitions. None of the homologues could undergo monotropic transition. Odd-even effect observed for N-I transition curve is due to the sequentially and progressively added methylene unit or units at the left $-\text{OR}$ group. The odd-even effect disappears from and beyond C_{10} homologue and N-I transition curve prolonged as a single transition curve for the higher homologues of longer n-alkyl chain 'R' of left $-\text{OR}$ group, because, longer n-alkyl chain may coil or bend or flex or couple to lie with major axis of the core structure and hence, the alteration diminishes as series is ascended from and beyond C_{10} homologue. The negligible abnormality from normal descending tendency at C_{14} homologue and rising tendency of deviation of N-I transition curve at the C_{18} homologues are attributed to the uncertainty in the status of n-alkyl chain R of $-\text{OR}$ and n-alkyl chain of common longer tail end group $-\text{OC}_{14}\text{H}_{29}(\text{n})$ (Para) of nonlinear shaped molecules of homologues. Moreover an unique homologue of $-\text{OR}$ equal to $-\text{OC}_{14}\text{H}_{29}(\text{n})$ and tail end $-\text{OC}_{14}\text{H}_{29}(\text{n})$ i.e. in case of a homologue in which terminal end groups are identically same, the vector sum of all bonds of $-\text{OC}_{14}\text{H}_{29}$ group will be exactly equal in magnitudes and opposite in directions which contributes to ZERO polarity. Therefore the effectiveness of molecular polarity and polarizability may reflect to molecular flexibility showing more or less or negligible deviation at an unique homologue involving identically same n-alkoxy terminal end groups in chalconyl ester derivatives. In case of the rest of the homologues other than C_{14} the group polarity difference between $-\text{OR}$ and $-\text{OC}_{14}\text{H}_{29}(\text{n})$ reflects the molecular flexibility, descending tendency and nondeviating behaviour of each homologue of a present novel series [31]. The variations in mesogenic(LC) properties from homologue to homologue in the same novel series is attributed to

the sequentially added methylene unit or units to n-alkoxy group (-OR) which alters molecular lengths, permanent dipole moment across the long molecular axis, length to breadth ratio, ratio of the polarity to polarizability, intermolecular cohesion and closeness due to varied dispersion forces, dipole-dipole interactions etc. etc. . . Thus, variation in LC properties of presently investigated homologous series are altered due to changing intermolecular attractions and of changing molecular flexibility, keeping unaltered molecular rigidity throughout the same series. The LC properties of novel series-1 are compared with the structurally analogous or similar series-X [32] and Y [33] as shown below in figure-2.

Homologous series-1 and Y are geometrically nonlinear and a series-X is a linear in shape. Series-1 and X are isomeric to each other containing three phenyl rings linked through identical central bridges -COO- and -CO-CH=CH- and the left n-alkoxy-OR and -OC₁₄H₂₉ end groups for the same homologue from series to series, but the combined effect of molecules rigidity plus flexibility may differ due to varied geometrical molecular shape, size, molecular polarity and polarizability etc. Homologous series-1 and Y are identical in all respect except right sided tail end groups -OC₁₄H₂₉(n) and -OC₁₆H₃₃(n) respectively, for the same homologue from series to series in which variations in molecular flexibility differs by -CH₂-CH₂- unit. Thus, the variations in LC properties and the degree of mesomorphism can be attributed to the changing features amongst the series 1, X, Y. Some LC properties are tabulated in following table-4 for their comparative study.

Table 4: Thermal Stability in °C

Series →	1	X	Y
Sm-I or Sm-N Commencement of Smectic phase	—	—	—
N-I Commencement of Nematic phase	107.0 (C ₆ -C ₁₈) C ₆	123.0 (C ₇ -C ₁₄) C ₇	104.5 (C ₆ -C ₁₈) C ₆
Total mesophase length range in °C (Sm to N)	17.0 to 35.0 C ₁₄ C ₈	13.0 to 34.0 C ₇ C ₈ C ₁₀ C ₁₂	13.0 to 37.0 C ₁₀ C ₆

Table-4 represent that,

- All the three series 1, X and Y under comparative study are nematogenic only without exhibition of Smectic property.
- Mesomorphism commences from C₆ homologue in case of nonlinear series 1 and Y, but it commences late from C₇ homologue of a linear but isomeric homologue series-X.
- Thermal stability of a linear series-X is higher than the nonlinear series 1 and Y.
- The degree of mesomorphism of all the series are almost nearer or in increasing order from series 1 to X to Y.

The suitable magnitudes of anisotropic forces of end to end intermolecular cohesion and closeness as a consequence of favourable molecular rigidity and flexibility which arranges molecules of all the homologous series (1,X and Y) to float on the surface with statistically parallel orientational order for different degree of mesomorphism, depending upon individual varying magnitudes of molecular polarities and polarizability. Thus, only nematic mesophase formation occurs with absence of focal conic Smectic phase, due to absence of inadequate magnitudes of environmental situation and forces of cohesion as required for exhibition of smectogenic character. The intermolecular end to end cohesive forces are depended upon intermolecular distances or closeness. The intermolecular forces of cohesion and distance in case of linear molecule (series-X) are relatively more and closer as compared to nonlinearity shaped molecules of series-1 and Y. However, the intermolecular cohesive forces of cohesion depends upon polarisability of a molecule related to broadening of a molecule. Thus, two opposing effects, viz.(a) one which increases intermolecular cohesion with decreasing intermolecular distance (more closer or linear series-x) and

(b) other one which increases intermolecular cohesion with increasing intermolecular (i.e. broadening of a molecule) cohesion with increasing intermolecular distance in the nonlinear series-1 and Y due to more polarizability which increases the intermolecular cohesion. Thus, two opposing effects (a) and (b) are operated at a same time for the same reason. The resultant effect depends upon the predominating factor (a) or (b) mentioned above. Now looking to the values of thermal stability of a linear shaped isomeric series-X as compared to corresponding thermal stabilities of nonlinear shaped series 1 and Y, it is clear that, the thermal stability values depress for nonlinear isomeric series-1 or any other nonlinear series i.e. thermal stability undergo reduction by introducing branching or nonlinearity in a molecule which is facilitated by the predominancy of the factor related to reduction in the suitable magnitudes of intermolecular anisotropic forces of cohesion. Simultaneously the resistivity towards exposed thermal vibrations and an angle of disalignment of molecules in floating condition decides the degree of mesomorphism. It is clear from table-4 that, the difference of degree of mesomorphism is very very short. Therefore, though thermal stabilities among the series under comparative study may differ between linear and nonlinear series; but, the resistivity against exposed thermal vibrations is independent of the molecular shape linear or nonlinear. Moreover, the commencement of Nematic phase in case of nonlinear series 1 and Y which take place identically from C₆ homologues of the series 1 and Y of nearly equal thermal stability, but it commences late by one homologue from C₇ homologue. i.e. the extent of molecular noncoplanarity is enhanced for a linear series-X as compared to nonlinear series 1 and X. The extension of n-alkyl chain length (-OC₁₆H₃₃(n) instead of -OC₁₄H₂₉(n)) in nonlinear series by two methylene units does not work much against the thermal stability, degree of mesomorphism and the commencement of nematic phase.

5. CONCLUSION

- The chalconyl ester nonlinear derivatives consisting three phenyl rings and n-alkoxy group as a tail group of higher homologues (greater than C₁₀) are nematogenic only and do not differ much with respect to their thermal stabilities, commencement of mesophase and the degree of mesomorphism.
- The group efficiency order derived on the basis of (a) thermal stability (b) commencement of mesophase and (c) the degree of mesomorphism for nematic is as under.

(a) Nematic

Linear -OC₁₄H₂₉ > nonlinear -OC₁₄H₂₉ > nonlinear -OC₁₆H₃₃

(b) Nematic

Nonlinear -OC₁₄H₂₉ = Nonlinear -OC₁₆H₃₃ > Linear -OC₁₄H₂₉

(c) Nematic

Nonlinear -OC₁₆H₃₃ > Linear -OC₁₄H₂₉ > nonlinear -OC₁₄H₂₉

- An unique homologue of chalconyl ester series whose two end groups are same shows more or less or negligible deviation from normal descending tendency of a mesomorphic-isotropic transition curve.
- Combined effect of molecular rigidity and flexibility operates a phenomena of mesomorphism.
- A phenomena of mesomorphism is very sensitive and susceptible to the molecular structure.
- LC derivatives of present investigation are useful for the study of binary systems to operate display devices at room temperature or at a desired temperature as well as for the researchers working on LC state with aims and objects other than present object.
- Chalconyl derivatives are biologically active molecules, whose bioactivity can be exploited and studied for pharmaceutical preparation purposes.
- Present investigation may be useful for the agricultural quality production in the growth of fruits, flowers etc.
- Present investigation supports and raises the credibility to conclusion drawn about earlier.

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