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Mesomorphism and flexibility of alkyl chains in chalcone esters

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ABSTRACT

A novel homologous series of chalconyl ester liquid crystals (LCs): RO–C_6H_4–CH:CH–COO–C_6H_4–CO–CH:CH–C_6H_4–$OC_{10}H_{21}$ (*n*) (para) has been synthesized and studied with a view to understanding and establishing the relationship between molecular structure and LC properties with reference to flexibility of the terminal chain. The novel series consists of eleven homologs (C_1–C_{16}). The C_1 and C_2 homologs are nonliquid crystals and the rest of the homologs (C_3–C_{16}) are enantiotropic nematic without exhibition of smectic mesophase. Transition and melting temperatures were determined by an optical polarizing microscope equipped with a heating stage. Textures of nematic phases are threaded or Schlieren. Cr-N/I transition curve adopts a zigzag path in a normal manner with overall descending behaviors. The N-I transition curve exhibits a sharp and shorter odd-even effect from C_3 to C_6 and it diminishes from and beyond C_6 for higher homologs of longer *n*-alkyl chain (R) in more or less or negligible deviating manner from normal descending tendency. Thermal stability for the nematic is 116.4°C and mesophase length ranges from 19°C to 67°C at the C_3 and C_{12} homolog respectively. The LC properties of present novel series are compared with structurally similar analogous series to derive group efficiency order.

KEYWORDS

Degree of mesomor; enantiotropy; phismnematic; smectic

Introduction

Chalconyl ester thermotropic liquid crystalline [1] substances are useful to mankind in LC devices and the pharmaceutical preparations through their bioactive properties [2–7]. The present investigation is aimed to study the relationship between molecular structure [8–12] and liquid crystal properties with special reference to the molecular flexibility of *n*-alkoxy groups of longer *n*-alkyl chain [13–16]. The proposed investigation involves synthesis, characterization of novel substances, and study of thermometric behaviors using optical polarizing microscope (OPM) to provide information on thermal stability, commencement of mesophase, degree of mesomorphism, and derivation of group efficiency order. Several homologous series of esters, azoesters, and chalconyl esters have been reported to date [17–23].

Experimental

Synthesis

4-Hydroxy benzaldehyde was alkylated by a usual established method [24a]. *n*-Alkoxy benzaldehydes were treated with malonic acid to convert them into 4-*n*-alkoxy cinnamic acids

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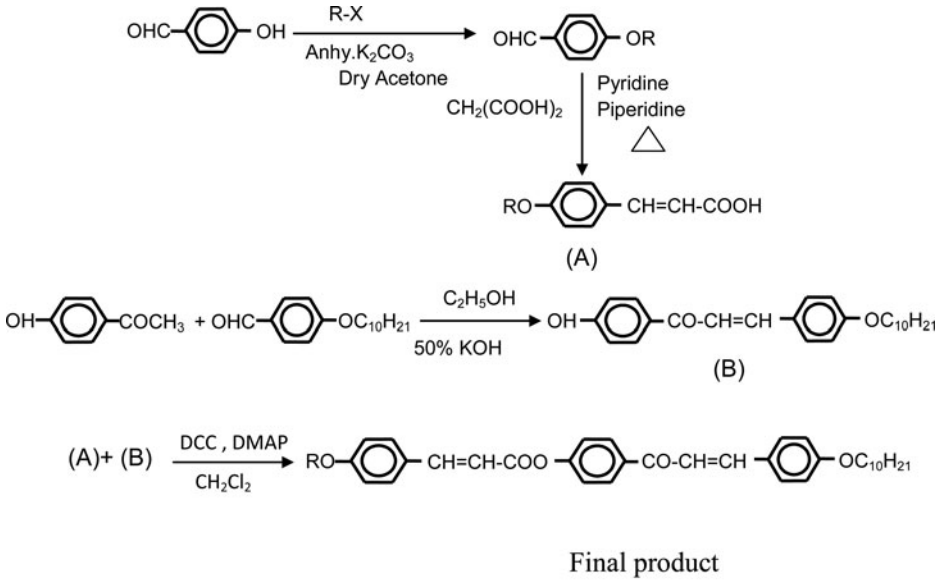
(A) [24b]. *n*-Alkoxy cinnamic acids were condensed with α-4hydroxy benzoyl-4′ decyloxy phenyl ethylene [25] [B] (m.p. 130°C) by a usual established method. Components A and B were condensed [26] to give final products. The synthetic route to the series is shown below in scheme 1. Final products were individually decomposed, filtered, washed, dried, and purified until the constant transition temperatures obtained.



Where, R= C_nH_{2n+1}, n = 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16.

Scheme 1. Synthetic route to the series-1.

Final product

The chemicals 4-hydroxyl benzaldehyde, malonic acid, alkyl halides, 4- hydroxy acetophenone, 4-decyloxy benzaldehyde, potassium Hydroxide, hydrochloric acid, etc. required for synthesis were used as received except solvents which were dried and distilled prior to use.

Characterization

Some selected members of the titled series were characterized by elemental analysis, ^{1}HNMR spectra, and IR spectra, Textures of mesophases were characterized by miscibility method. Microanalysis for C,H,N, elements was performed on Perkin Elmer PE 2400 analyzer (Table 1). ^{1}HNMR spectra were obtained on Bruker spectrometer using $CDCl_3$ as solvent. IR spectra were recorded on a Perkin-Elmer spectrum GX. Transition temperatures and liquid crystal properties were investigated using an OPM with a heating stage.

Analytical data

H^{1}NMR: in ppm. For Octyloxy homolog.

Ethylenes: (200 MHZ) δ ($CDCl_3$) (ppm) 0.75 (−CH_3–CH_2 of –C_8H_{17}), 1.20 (long–CH_2–chain), 3.2 –OCH_2 of (–OCH_2 of C_8H_{17}), 6.81 & 6.80, 8.20 & 8.05 (p-sub. benzene rings)

Table 1. Elemental analysis for the hexyloxy, octyloxy, and decyloxy derivatives.

	Elemental % found (compared with % calculated)	
Molecular formula	C	H
$C_{44}H_{58}O_5$	79.89 (78.68)	8.33 (8.19)
$C_{46}H_{62}O_5$	79.96(78.99)	8.42 (8.46)
$C_{48}H_{66}O_5$	79.52 (79.27)	8.89 (8.70)

H^1NMR: in ppm. For Decyloxy homolog.

Ethylenes: (200 MHZ) δ ($CDCl_3$) (ppm) 0.90 (−CH_3–CH_2 of –C_8H_{17}), 1.19 (long–CH_2–chain), 3.86 –OCH_2 of (–OCH_2 of C_8H_{17}), 6.69 & 6.89, 8.16 & 8.21 (p-sub. benzene rings)

IR in Cm^{-1},

IR Spectrum. For Octyloxy homolog

Ethylenes: (vmax/cm^{-1}): 2928, 2835, 1456, 1389 (–C–H, aliphatic), 1739, 1260 (ester group), 1720 (>C=O group), 1561 (–C=C–, aromatic), 1059, 1253 (ether group), 846.2 (p-sub. benzene ring), 1620, 1498, 1456 (Aromatic ring).

IR Spectrum. For Decyloxy homolog

Ethylenes: (v_{max}/cm^{-1}): 2920, 2839.1, 1432, 1382 (–C–H, aliphatic), 1736, 1239 (ester group), 1730 (>C=O group), 1523 (–C=C–, aromatic), 1063, 1253 (ether group), 849 (p-sub. benzene ring), 1622, 1483.2, 1463 (Aromatic ring).

Textures by miscibility method

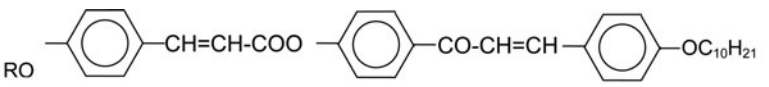
C_5 … … … …..Threaded nematic
C_8 … … … … …Threaded nematic
C_{16} … … … …Schlieren nematic

Result and discussion

Transition temperatures of novel homologs are relatively lower than corresponding *n*-alkoxy aromatic acids. Eleven homologs were synthesized by condensing dimeric 4-*n*-alkoxy cinnamic acids and α-4-hydroxy benzoyl β-4′-*n*-decyloxy phenyl ethylene [m.p. 130 yield 76.0%]. Transition temperatures (Table 2) as determined by OPM are plotted against the number of carbon atoms present in *n*-alkyl chain 'R' of –OR of left terminal end group. A phase diagram (Fig. 1) is obtained by linking like or related points to form Cr-N/I and N-I transition

Table 2. Transition temperatures in °C.

Compound no.	*n*-Alkyl (C_nH_{2n+1}) group	Smectic	Nematic	Isotropic
1	C_1	—	—	124.0
2	C_2	—	—	128.0
3	C_3	—	102.0	121.0
4	C_4	—	76.0	103.0
5	C_5	—	49.0	112.0
6	C_6	—	80.0	120.0
7	C_8	—	92.0	132.0
8	C_{10}	—	89.0	118.0
9	C_{12}	—	63.0	130.0
10	C_{14}	—	60.0	92.0
11	C_{16}	—	81.0	120.0



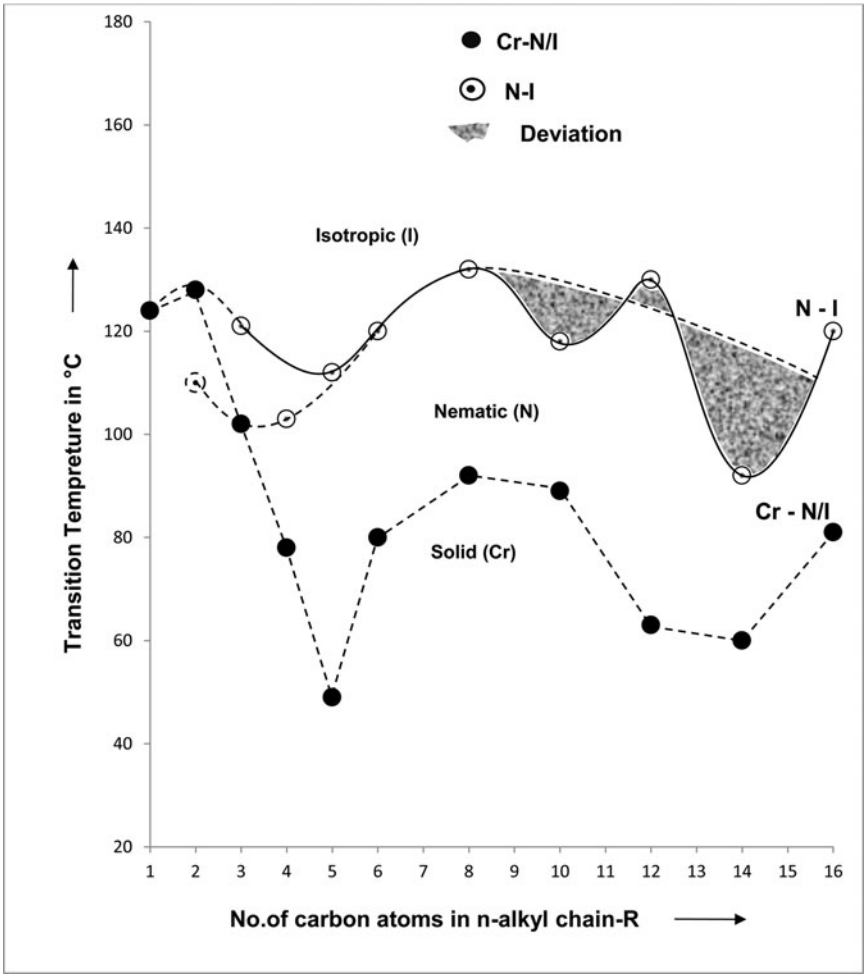


Figure 1. Homologous Series: α- 4-[4′-*n*-Alkoxy Cinnamoyloxy] β-benzoyl - 4″- Decyloky phenyl Ethylenes.

curves showing phase behaviors of novel series. Cr-N/I transition curve adopted zigzag path of rising and falling tendency in a usual established normal manner. The N-I transition curve exhibits an odd-even effect from C_3 to C_6 which merges into a single curve from and beyond the C_8 homolog. The N-I transition curves for odd and even members are extrapolated to nonliquid crystal homologs C_1 and C_2 to predict their hypothetical latent transition temperatures. Transition curve for odd members occupies a higher position for the N-I curve than even members. The variations in mesomorphic (LC) properties from homolog to homolog in the same series are observed with changing number of carbon atoms present in n-alkyl chain 'R' of –OR keeping $-OC_{10}H_{21}$ (*n*) flexible tail end unchanged throughout entire novel series. Analytical and spectral data support the molecular structures of homologs with threaded or Schlieren textures of nematic phase.

Lowering of transition temperatures of novel homologs as compared to corresponding dimerized *n*-alkoxy cinnamic acids are attributed to the breaking of hydrogen bonding by way of esterification process. The exhibition of only nematic property with absence of

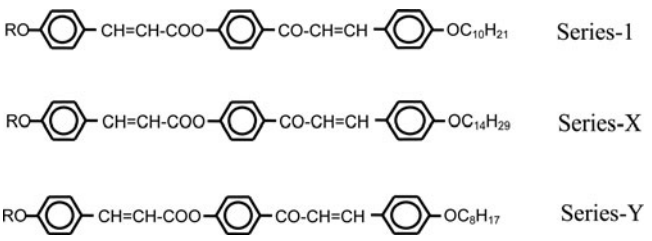


Figure 2. Structurally similar series.

smectic property by C_3–C_{16} homologs is attributed to the favorable and suitable magnitudes of anisotropic forces of end to end attractions to cause a statistically parallel orientational order of the molecules. The absence of lamellar packing of molecules due to insufficient intermolecular adhesion precludes the generation of a smectic phase. The lack of any mesomorphism in the C_1 and C_2 homologs is attributed to the low magnitudes of intermolecular dispersion forces and low magnitudes of dipole–dipole interactions leading to their high crystallizing tendency. The exhibition of odd-even effect in N-I transition curve is attributed to the odd and even number of carbon atoms in *n*-alkyl chain 'R' of –OR terminal group from C_3 to C_6 homolog. Then the deviating behavior of N-I transition curve from C_8 to C_{16} homologs is attributed to the uncertainty and unusual status of longer *n*-alkyl chain 'R' of –OR of higher homologs from and beyond C_6 or C_8 homologs, from normal descending tendency. The disappearance of odd even effect from C_6 homolog is attributed to the coiling or bending of the longer *n*-alkyl chain. The extrapolated [27–30] N-I transition curve to C_1 from C_3 homolog matches with the isotropic temperature of C_1 which precludes the possibility of the nematic phase even in the monotropic condition. The predicted L.T.T. for C_2 from extrapolation is 110°C, but it is actually not realizable because of its high crystallizing tendency. The changing trend in mesomorphic or LC properties from homolog to homolog in the same present series is attributed to the sequentially and progressively added methylene unit or units at the *n*-alkyl chain 'R' or –OR, left terminal end group which alters the intermolecular forces of cohesion by varying magnitudes of molecular length and other related cohesive forces of end to end attraction as a result of altering molecular flexibility from homolog to homolog in the same series. The thermotropic behavior of present series such as thermal stability, commencement of mesophase, and upper and lower mesophase lengths are compared with the structurally similar analogous series X[31] and Y[32] as shown in Fig. 2.

It is clear from Fig. 2, that a homologous series-1 of present investigation and analogous series-X and Y chosen for comparative study are identical with respect to three phenyl rings and two central bridges vinyl carboxylate and –CO–CH=CH–contributing to total molecular rigidity and *n*-alkoxy group for the same homolog from series to series, but they differ from homolog to homolog in the same series and for the same homolog from series to series with respect to tailed end groups $-OC_{10}H_{21}(n)$, $-OC_{14}H_{29}(n)$, and $-OC_8H_{17}(n)$ which partially contributes to total molecular flexibilities. Therefore, thermotropic properties and the degree of mesomorphism, etc. depend upon the changing features of homologous series-1, X, and Y. Thus, the changing magnitudes of molecular flexibility from series to series for the same homolog and from homolog to homolog in the same series can be linked with changing trend of LC properties of series-1, X, and Y under comparison. Some LC properties of series-1, X, and Y are recorded in following Table 3 as under.

It is clear from Table 3 that,

- The homologous series-1, X, and Y are enantiotropic nematic without exhibition of smectic property.

Table 3. Thermal stability in °C.

Series	Series-1 (-$OC_{10}H_{21}$)	Series-2 (-$OC_{14}H_{29}$)	Series-3 (-OC_8H_{17})
Sm-I or Sm-N Commencement of smectic phase	—	—	—
N-ICommencement of nematic phase	116.4(C_3–C_{16})C_3	99.75(C_6–C_{18})C_6	112.66(C_3–C_{16})C_3
Total upper and lower mesophase lengths in °C	19.0–67.0 C_3 C_{12}	19.0–34.0 C_6 C_8	5.0–41.0 C_{12} C_4

- Mesomorphic properties commences earliest from C_3 homolog in case of series-1 and Y, but it commences late from C_6 homolog for series-X.
- Thermal stabilities are in decreasing order from series-1 to series-Y to series-X.
- The upper mesophase length follows the same decreasing order of thermal stabilities but lower mesophase length follows increasing order from series-Y to series-X equal to series-1.
- More or less or negligible deviation from normal descending tendency exhibited by homolog of longer *n*-alkyl chain 'R' of –OR group from and beyond the merging of N-I transition curves for odd and even homologs.

The missing of smectogenic character by all the series-1, X, and Y are attributed to the absence of lamellar packing of the molecules. The exhibition of nematic property by the C_3–C_{16} or C_6–C_{18} homologs is attributed to the suitable magnitudes of anisotropic forces of intermolecular end to end attractions and closeness as a consequence of favorable molecular flexibility at constant molecular rigidity which arrange the molecules in statistically parallel orientational order in floating condition under the influence of exposed thermal vibrations, facilitating nematic mesophase formation and stabilizing for some temperature difference called as mesophase length or the degree of mesomorphism. The absence of LC state in case of nonmesogenic homologs is due to their high crystallizing tendency from low dispersion forces and low magnitudes of dipole–dipole interactions. Increasing order of thermal stability and simultaneously same increasing order of upper mesophase lengths of series-1 to Y to X is attributed to the order of thermodynamic quantity enthalpy ΔH_1, ΔH_X, and ΔH_Y for series-1, X, and Y, respectively, where $\Delta H_1 > \Delta H_Y > \Delta H_X$, that is, suitable magnitudes of energy required to commence and stabilize, or to maintain and then to resist against exposed thermal vibrations which corresponds to varying magnitudes of ΔH, the heat of formation; which vary from homolog to homolog in the same series and series to series for the same homolog as a result of changing molecular flexibility due to changing tailed end groups, $-OC_{10}H_{21}$, $-OC_{14}H_{29}$, and $-OC_8H_{17}$. The observed deviations in N-I transition curves are attributed to unusual and unexpected status of *n*-alkyl chain "R" of –OR and tailed end groups of longer *n*-alkyl chains. Early or late commencement of mesophase depends upon the extent of molecular noncoplanarity. Therefore, the extent of molecular noncoplanarity is almost equivalent for series-1 and series-Y, but it differs for series-X which restricts suitable magnitudes of anisotropic dispersion forces and the molecular arrangement as required to form nematic mesophase under floating condition.

Conclusions

- Homologous series of present investigation is enantiotropically nematogenic with absence of smectic property and of considerable degree of mesomorphism.
- Homologous series bearing longer *n*-alkoxy tail ends are of nearly equivalent thermometric properties.

- Group efficiency order derived on the basis of (a) thermal stability, (b) commencement of mesophase, and (c) mesophase lengths for nematic as are under.
  (a) Nematic: $-OC_{10}H_{21}(n) > -OC_8H_{17}(n) > -OC_{14}H_{29}(n)$
  (b) Nematic: $-OC_8H_{27}(n) = -OC_{10}H_{21}(n) > -OC_{14}H_{29}(n)$
  (C) Nematic: $-OC_{10}H_{21}(n) > -OC_8H_{17}(n) > -OC_{14}H_{29}(n)$
  $-OC_{10}H_{21}(n) = -OC_{14}H_{29}(n) > -OC_8H_{17}(n)$
- The molecular flexibility contribution towards mesomorphic properties is less effective as compared to molecular rigidity.
- Mesomorphism phenomena are very sensitive and susceptible to molecular structure of a substance.
- Chalconyl ester LC derivatives can be further studied as binary systems in the manufacture of LC devices and for pharmaceutical preparation as being bioactive molecules.
- Present investigation supports and raises credibility to the conclusions drawn earlier.

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