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Role of n-alkoxy terminal end groups on mesomorphism

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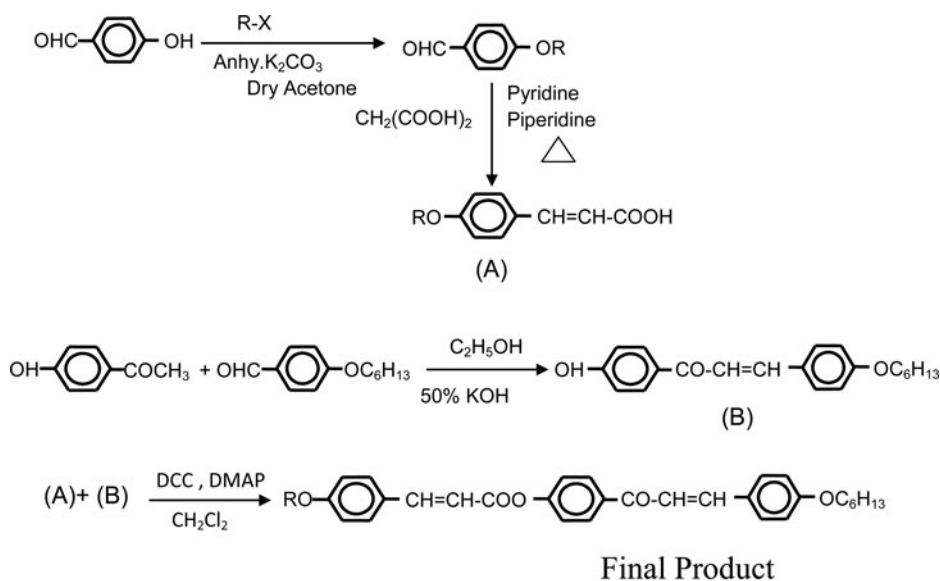
ABSTRACT

A homologous series $RO-C_6H_4-CH:CH-COO-C_6H_4-CO-CH:CH-C_6H_4-OC_6H_{13}$ (n) of novel liquid crystals (LC) has been synthesized and studied with a view to understanding and establishing the relation between molecular structure of a substance and the LC properties or behavior of thermotropic LC materials. Novel series consist of 11 homologues. C_1 and C_2 homologue derivatives are non-LCs and the rest of homologues (C_3 to C_{16}) are nematogenic without exhibition of smectic property. Transition temperatures were determined by an optical polarizing microscopy equipped with a heating stage. Transition curve Cr-N/I of a phase diagram behaved in normal manner. N/I transition curve partly deviated at C_6 and C_{10} homologues from normal descending behavior, and exhibited very narrow and sharp odd-even effects. Textures of nematic phase are threaded or Schlieren. Thermal, analytical, and spectral data confirmed the molecular structures of novel chalconyl ester derivatives. Thermal stability for nematic is 95.77°C and the upper and lower mesophase lengths vary from 35 to 16°C at C_5 and C_8 homologues respectively. Group efficiency order derived for nematic on the basis thermal stability is $-OC_{10}H_{21}$ (n) > $-OC_8H_{17}$(n) > $-OC_6H_{13}$(n).

Introduction

The study of liquid crystalline (LC) state [1] has a strong impact on the minds of scientists and technologist to the benefits of humanity [2–10]. Therefore, present investigation is planned with a view to understanding and establishing the effects of molecular structure [11–16] of LC properties with reference to tail group and terminally situated end group through synthesis of novel chalconyl ester substances. Chalconyl ester derivatives of thermotropic variety can be useful for the manufacture of LC devices to be operated at desired room temperature or as desired. The chalconyl derivatives can be useful for the manufacture of pharmaceutical preparations due to their bioactivity. Thus, the dual role of chalconyl derivatives has been attracted for the planning of present investigation of synthesizing novel thermotropic LC substances through chalconyl ester series. Thus, the proposed investigation will consist of synthesis, characterization, evaluation of thermotropic data, their interpretation, and discussion in terms of molecular rigidity and flexibility [17–20] and derivation of group efficiency order from comparative study with structurally similar analogous series. The study of biological activity and the application part of study with novel substances is left for scientific and technological researchers working on LC state with views, aims, and objects other than

Scheme 1. Synthetic route to series 1.

present view of investigation. A number of ester homologous series of LC substances have been reported till date [21–30].

Experimental

Synthesis

4-Hydroxy benzaldehyde was alkylated by an established method [31a]. 4-N-alkoxy benzaldehydes were treated with malonic acid to convert them into trans 4-n-alkoxy cinnamic acids (A) [31b]. N-alkoxycinnamic acids were condensed with α-hydroxy benzoyl β-4' hexyloxy phenyl ethylene [32] [B] (m.p. = 103°C) by usually established method. Components A and B were condensed [33] to give final products. Synthetic route to series is mentioned below as Scheme 1. Final products were individually decomposed, filtered, washed, dried, and purified till the constant transition temperatures were obtained.

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

The chemicals 4-hydroxyl benzaldehyde, malonic acid, alkyl halides, 4-hydroxyacetophenone, 4-hexyloxybenzaldehyde, 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}H NMR spectra, and IR spectra. Textures of mesophases were characterized by the miscibility method. Microanalysis for CHN elements was performed on Perkin Elmer PE 2400 analyzer (Table 1). ^{1}H NMR spectra were obtained on Bruker spectrometer using CDCl$_3$ as solvent. IR spectra

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

Molecular formula	Elemental percentage found (compared with percentage calculated)	
	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)

were recorded on a Perkin Elmer spectrum GX. Transition temperatures and LC properties were investigated using an optical polarizing microscope with heating stage.

Analytical data

H^1 NMR: in ppm. For octyloxy homologue.

Ethylenes: (200 MHz) δ (CDCl$_3$) (ppm) 0.75 (-CH$_3$-CH$_2$ of -C$_8$H$_{17}$), 1.20 (long -CH$_2$-chain), 3.2 OCH$_2$ of (-OCH$_2$ of C$_8$H$_{17}$), 6.81 and 6.80, 8.20 and 8.05 (p-sub. benzene rings).

H^1 NMR: in ppm. For decyloxy homologue.

Ethylenes: (200 MHz) δ (CDCl$_3$) (ppm) 0.90 (-CH$_3$-CH$_2$ of -C$_8$H$_{17}$), 1.19 (long -CH$_2$-chain), 3.86 -OCH$_2$ of (-OCH$_2$ of C$_8$H$_{17}$), 6.69 and 6.89, 8.16 and 8.21 (p-sub. benzene rings).

IR in cm^{-1}

IR Spectrum: For octyloxy homologue

Ethylenes: (v_{max}/cm^{-1}): 2928, 2835, 1456, and 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 homologue

Ethylenes: (v_{max}/cm^{-1}): 2920, 2839.1, 1432, and 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, and 1463 (aromatic ring).

Results and discussion

Trans 4-n-alkoxy dimeric cinnamic acids on condensation with α-4-hydroxy benzoyl β-4′-hexyloxy phenyl ethelene yielded enantiotropic nematogenic thermotropic chalconyl ester homologues without exhibition of smectic properties. The C$_1$ and C$_2$ homologues are non-LC homologues and the rest of the nine homologues (C$_3$ to C$_{16}$) are nematogenic. Transition and melting temperatures were determined through an optical polarizing microscopy (POM) equipped with a heating stage. Textures of a nematic phase are threaded or Schlieren. Transition temperatures (Table 2) are plotted against the number of carbon atoms present in n-alkyl chain "R" of -OR group, and then Cr-N/I and N-I transition curves are obtained by linking similar or related points as depicted in a phase diagram (Figure 1). Cr-N/I transition curve adopted zigzag path of rising and falling with overall descending tendency and behaved in normal manner. The N-I transition curve initially rises and descends at C$_6$ homologue and then it again rises and descends at C$_8$ and C$_{10}$ homologues, and finally rises at C$_{12}$ derivative and descends up to C$_{16}$ homologue with exhibition of very sharp and narrow odd-even effect. Thus, the N-I transition curve partly deviates from the normal descending tendency at C$_6$ and C$_{10}$ homologues. The odd-even effect diminishes from and beyond

Table 2. Transition temperatures in °C.

Compound No.	n-Alkyl (C_nH_{2n+1}) group	Smectic	Nematic	Isotropic
1	C_1	–	–	105.0
2	C_2	–	–	112.0
3	C_3	–	72.0	89.0
4	C_4	–	67.0	98.0
5	C_5	–	66.0	100.0
6	C_6	–	70.0	92.0
7	C_8	–	92.0	108.0
8	C_{10}	–	70.0	93.0
9	C_{12}	–	82.0	106.0
10	C_{14}	–	74.0	96.0
11	C_{16}	–	60.0	80.0

C_5: Threaded nematic
C_8: Threaded nematic
C_{16}: Schlieren nematic

nearby C_6 or C_7 homologue and then N-I transition curve prolonged as a single transition curve. Variations in mesogenic thermometric LC properties from homologue to homologue in the same series are observed, keeping right terminal -OC_6H_{13} (n) and the rest of the molecular part intact throughout the entire series. Thermal stability for nematic is 95.77 and the nematogenic mesophase lengths vary from minimum to maximum are 16.0°C to 34.0°C at the C_8 and C_5 homologues. Thus, novel series is a lower middle-ordered melting type.
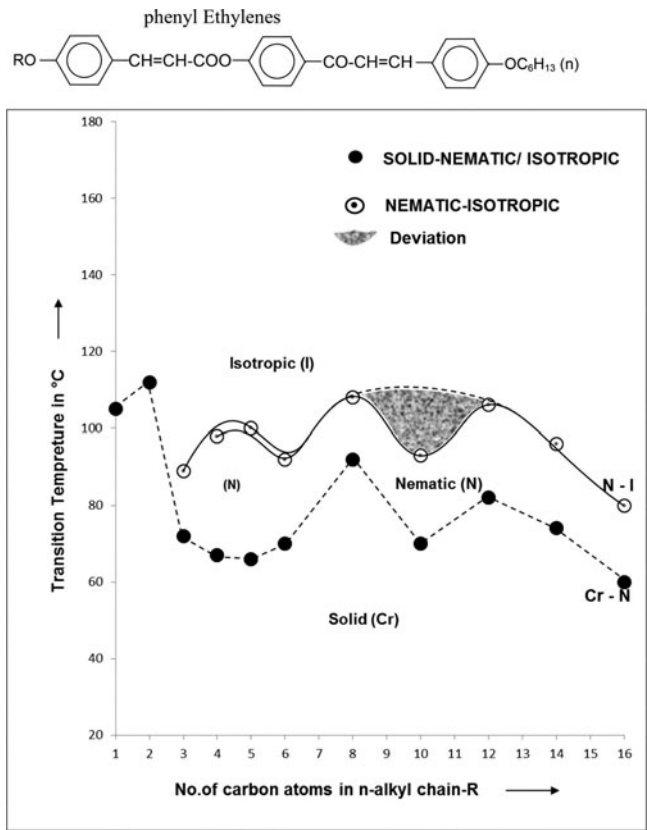

Figure 1. Homologous series: α-4-[4′-n-alkoxy cinnamoyloxy] β-benzoyl-4″-hexyloxy phenyl ethylenes.

Lowering of transition temperatures of novel chalconyl esters as compared to corresponding trans n-alkoxycinnamic acids is attributed to the breaking of hydrogen bonding between two molecules by esterification process. The nematic mesophase formation is exhibited after disappearance of dimerization of corresponding n-alkoxycinnamic acid. The molecules of novel nematogenic esters are attributed to suitable magnitudes of anisotropic forces of intermolecular end-to-end cohesion and closeness because of favorable molecular rigidity and flexibility. This molecular rigidity and flexibility resist the exposed thermal vibrations to stabilize, maintain, and facilitate the molecules of C_3 to C_{16} homologues to float on the surface with statistically parallel orientational order to induce nematic mesophase. However, the magnitude of intermolecular forces of attractions and closeness is insufficient to facilitate and organize any of the molecules to float with sliding layered arrangement to exhibit smectogenic mesophase formation even in the monotropic condition. The non-mesomorphicity of C_1 and C_2 homologues is attributed to their high crystallizing tendency. On cooling the C_1 and C_2 homologues, no mesophase is generated. However, the nematogenic mesophase formation for C_3 and C_{16} homologues reappears exactly at a temperature at which it had appeared reversibly on heating. The exhibition of odd-even effect in N-I transition curve is due to the sequentially added methylene unit at the n-alkyl chain "R" of "-OR." The disappearance of odd-even effect from and beyond merging of N-I transition curves for higher homologues of longer alkyl chain is attributed to the coiling or bending or flexing, or coupling of longer n-alkyl chain "R" of "-OR" and -OC_6H_{13} (n) terminals with the principal axis of core structure. Thus, unusual and uncertainty in the status of longer n-alkyl chains "R" of "-OR" induces deviating trend in N-I transition curve, affecting molecular length, length-to-breadth ratio, permanent dipole moment across long molecular axis, magnitudes of intermolecular dispersion forces, molecular rigidity and flexibility, and molecular polarity and polarizability from homologue to homologue in the same series. Thus, mesomorphic (LC) properties vary from homologue to homologue in the same series by changing number of carbon atoms in n-alkyl chain "R" of "-OR" group keeping rest of the molecular part uncharged. The thermotropic properties of presently investigated novel series 1 is compared with structurally similar analogous series X [33] and Y [34] as shown below in Figure 2.

Homologous series 1 of the present investigation and series X and Y chosen for comparison are identically similar with respect to three phenyl rings and two central bridges -CH=CH-COO- and -CO-CH=CH- contributing to total molecular rigidity. The left n-alkoxy -OR groups are identically the same for the same homologue from series to series, contributing partly to total flexibility, but its magnitude differs from homologue to homologue in the same series. Moreover, the flexible nature of right-sided end groups -OC_6H_{13}(n), -OC_8H_{17}, and -$OC_{10}H_{21}$(n), which partly contributes to the total flexibility, differs from series to series. Thus, changing trend in mesogenic properties and the degree of mesomorphism from series to series for the same homologue or from homologue to homologue in the same series depend upon the differing features of molecular structure from series to series or from homologue to homologue in the same series based on differing magnitudes of combined effects of molecular
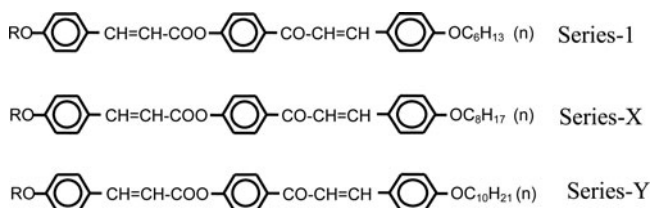

Figure 2. Structurally similar analogous series.

Table 3. Thermal stability in °C.

→ Series	Series 1 [-OC$_6$H$_{13}$ (n)]	Series 2 [-OC$_8$H$_{17}$(n)]	Series 3 [-OC$_{10}$H$_{21}$(n)]
Sm-I or Sm-N		_____	_____
Commencement of smectic phase	–	–	–
N-I	95.77	112.66	116.4
Commencement of nematic phase	(C$_3$–C$_{16}$) C$_3$	(C$_3$–C$_{16}$) C$_3$	(C$_3$–C$_{16}$) C$_3$
Total mesophase lengths in °C	16.0 to 34.0	5.0 to 44.0	19.0 to 67.0
	C$_8$C$_5$	C$_{12}$C$_4$	C$_3$C$_{12}$

rigidity plus molecular flexibility. Table 3 represents some thermotropic evaluated data for series 1, X, and Y under comparative study.

Homologous series 1, X and Y under comparative study are as follows:

- Only nematogenic with absence of smectic property.
- Nematic thermal stability is in increasing order.
- Upper mesophase, lengths are in increasing order.
- Lower mesophase lengths are in decreasing order from series Y to 1 to series X.
- Commencement of nematic phase identically occurs from C$_3$ homologue.

All the molecules of three analogous series have identical molecular rigidity by three phenyl rings and the same two central bridges containing conjugated double bonds. However, the total molecular flexibilities vary from homologue to homologue in the same series and for the same homologue from series to series. Thus, variations in observed mesogenic behaviors from series to series and homologue to homologue in the same series can be linked with the changing magnitudes of molecular flexibility. The exhibition of only nematogenic character by series 1, X, and Y is attributed to the suitable magnitude of anisotropic forces of intermolecular cohesion and closeness as occurred in molecules through end-to-end attractions because of favorable constant molecular rigidity and changing molecular flexibility. However, intermolecular cohesion by lateral attraction through individual varying molecular polarity and polarizability causes unsuitable magnitudes of forces of intermolecular attractions, which disallow the formation of sliding layered molecular arrangement prior to appearance of nematic phase in floating condition under the influence of exposed thermal vibrations. The increasing order of thermal stability from series 1 to X to Y is attributed to the increasing number of two methylene units from -OC$_6$H$_{13}$ (n) to -OC$_8$H$_{17}$ (n) to -OC$_{10}$H$_{21}$ (n) tail ends of series under comparative study. Thus, increasing number of methylene unit or units sequentially increases molecular polarity and polarizability as well as length to breadth ratio for the same homologue from series to series. Thus, stabilization of nematogenic mesophase formation is favored by adding two methylene units at the tailed n-alkoxy terminal end group in a sequential manner. As tailed n-alkoxy end group is gradually lengthened, the resistivity toward exposed thermal vibration also gradually raises, and hence the upper nematogenic mesophase lengths acquire increasing order from series 1 to X to Y irrespective of order of lower mesophase lengths. The commencement of nematogenic mesophase identically takes place from C$_3$ homologue for all the series of the present comparative study because the extent of molecular non-coplanarity of analogous series remains almost equivalent with very negligible difference in magnitude, which maintains mesophase commencement in equal order.

Conclusions

- Novel homologous series of vinyl carboxychalconyl derivatives are only nematogenic with absence of smectogenic property whose mesophase lengths are relatively shorter and low-order melting-type series.

- Group efficiency order derived for nematic based on (a) thermal stability, (b) commencement of mesophase, and (c) upper mesophase lengths are as under.
    - (a) Nematic

        -$OC_{10}H_{21}$ (n) > -OC_8H_{17}(n) > -OC_6H_{13}(n)
    - (b) Nematic

        -OC_6H_{13} (n) = -OC_8H_{17}(n) = -$OC_{10}H_{21}$(n)
    - (c) Nematic

        Upper: -$OC_{10}H_{21}$ (n) > -OC_8H_{17}(n) > -OC_6H_{13}(n)

        Lower: -$OC_{10}H_{21}$ (n) > -OC_6H_{13}(n) > -OC_8H_{17}(n)
- Present study may be useful for the study of binary systems and bioactivity of novel compounds.
- Mesomorphism is very sensitive and susceptible to molecular structure.
- Chalconyl group is generally nematogenic like vinyl carboxy group.
- Present investigation supports and raises credibility to the conclusions drawn earlier.

Acknowledgments

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