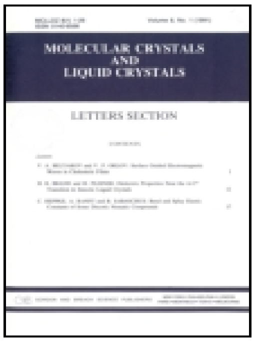

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Study of mesomorphism and laterally substituted nitro group

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ABSTRACT

A novel thermotropically mesomorphic, meta-substituted nitro group of chalconyl ester series, RO-C_6H_4-COO-C_6H_3-(NO_2)-CO-CH=CH-$C_6H_4OC_{12}H_{25}$(n) (para) is synthesized and studied with an aim to establish the relation between molecular structure and the mesomorphism with reference to changing molecular flexibility in presence of nitro lateral group. Novel homologous series consist of thirteen homologs (C_1–C_{18}) whose mesomorphism commences from C_5 homolog as enantiotropic nematogenic with absence of smectic property, even in the monotropic condition. Transition temperatures of novel substances were determined by an optical polarizing microscope, equipped with a heating stage (POM). Textures of a nematic phase are threaded or Schlieren. N-I transition curve exhibited narrow, sharp and short odd-even effect; with deviating trend in a phase diagram. Analytical, spectral and thermal data confirmed the molecular structures of homologs. Thermal stability for nematic is 182.89°C, whose mesophase lengths minimum to maximum ranges from 17°C to 45°C and it is an upper middle ordered melting type series. Group efficiency order for nematic is series 1 > series Y > series X, as derived from comparative study of structurally similar analogous series.

KEYWORDS

Nematic; smectic; enantiotropy; liquid crystal; mesogen

Introduction

Liquid crystalline [25] substances have established their applicability and utility in the manufacture of LC devices related to thermography, display devices, etc. in the benefit of mankind [14,22,20]. Moreover the Liquid crystal (LC) chalconyl ester derivatives being bioactive, may be applied as antibacterial, antifungal, antimalarial, anticancer, anti-inflammatory, etc. [1,9,12,19,23,28] which may be applicable in the benefit of mankind in the pharmaceutical field and agricultural production to reduce the utilization of pesticides and insecticides. Therefore, present investigation is planned with a view to understand the effect of molecular structure on LC properties of chalconyl ester derivatives [10,11,13,17] through synthesis of homologous series of dual applicability and utility for mankind. Proposed investigation will consist of novel substances involving three phenyl rings, two central bridges –COO– and –CO–CH=CH–, two terminal end groups –OR and –$OC_{12}H_{25}$ (n) as well as meta substituted nitro lateral group at the middle phenyl ring. The evaluated thermometric data will be interpreted and discussed in terms of molecular rigidity and flexibility [3,15,16,21]. Several ester

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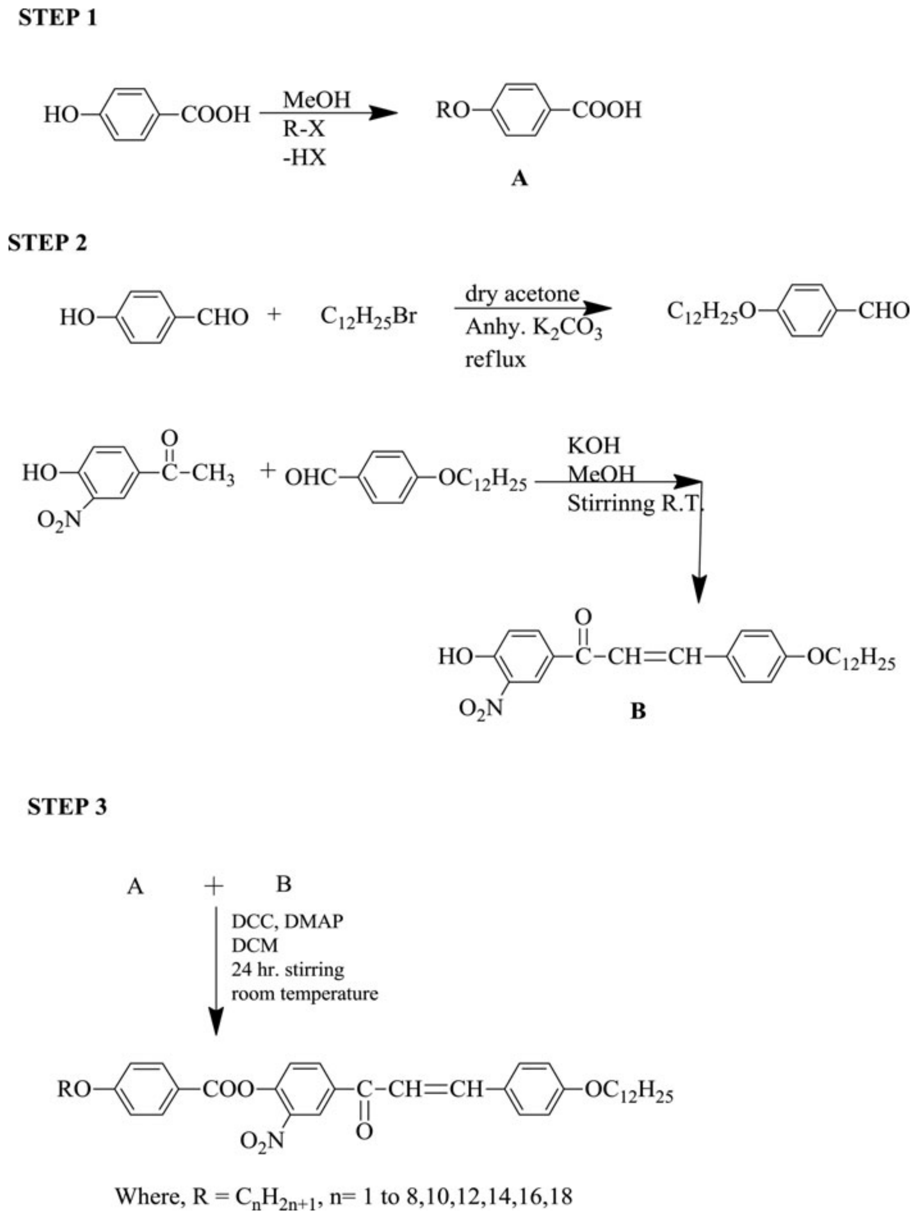
homologous series are reported to date [5–8,18,24,26]. The effect of laterally substituted nitro group efficiency order will be derived for smectic and nematic from comparative study of structurally analogous series.

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated using suitable alkylating Agent (R-X) to convert it into 4-*n* alkoxy benzoic acids by a modified method of Dave and Vora [4].



Scheme 1. Synthetic route to the series 1.

α-3-Nitro-4-hydroxy benzoyl β-4′-dodecyloxy phenyl ethylene (B) was prepared by usual established method [30]. Chalconyl esters were synthesized by a literature method [29]. 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). 4-Hydroxy benzoic acid, alkyl halides, 4-hydroxy benzaldehyde, 3-nitro 4-hydroxy acetophenone, dicyclohexyl carbodimide, 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 in Scheme 1.

Characterization

Some selected representative homologs of the series were characterized by infrared [IR], ^{1}HNMR technique and elemental analysis. IR spectra were recorded on Perkin Elmer spectrum GX. ^{1}HNMR spectra were recorded 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 microscope with heating stage. Textures of the novel homologs were determined by miscibility method.

Analytical data

Table 1. Elemental Analysis for heptyloxy, octyloxy, decyloxy, and tetradecyloxy.

	Element % found			Element % calculated		
Molecular formula	C	H	N	C	H	N
$C_{41}H_{53}O_7N$	72.20%	6.89%	2.00%	73.32%	7.89%	2.08%
$C_{42}H_{55}O_7N$	71.09%	7.79%	1.95%	73.57%	8.02%	2.04%
$C_{44}H_{59}O_7N$	73.24%	7.43%	1.77%	74.05%	8.27%	1.96%
$C_{48}H_{67}O_7N$	73.00%	7.91%	1.37%	74.90%	8.71%	1.82%

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

Pentyloxy: 648.08 & 690.52(m-substituted phenyl ring), 786.96(polymethylenes ($-CH_2$) of $-OC_5H_{11}$), 833.25(-OH deferences in m-disubstituted para), 968(-CH deferences hydrocarbon), 1163.08(C-O of alkoxy $-OC_5H_{11}$), 1244 & 1309.67(C-O stretching in$(-CH2)_n$ chain), 1344.28($-NO_2$ group), 1467.83(-C-H deferences in $-CH_2$), 1606.70($-C = O$ group), 2850.79 & 2922.16(-CH stretching in $-CH_3$). IR supports the structure.

Dodecyloxy: 646.15(m-substituted phenyl ring), 717.52(polymethylene $(-CH2)_n$ of $-OC_{12}H_{25}$), 921(-CH deferences hydrocarbon), 1060(-CO stretching), 1150 & 1241.48(-CO deferences in $-CH_2$), 1276.88(-COO group), 1465.90(-CH deferences in $-CH_2$), 1537.27($-NO_2$ group), 1606.70($-C = O$ group), 2852.72 & 2922.16(-CH stretching in $-CH_3$). IR supports the structure.

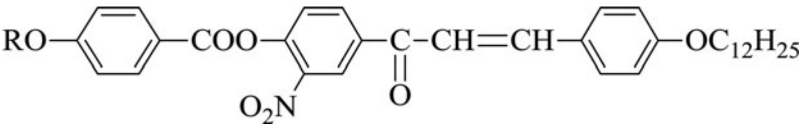
^{1}HNMR Spectra in $CDCl_3$ in δ ppm for hexyloxy and hexadecyloxy derivatives:

Hexyloxy: 1.19($-CH_2$ of $-OC_6H_{13}$), 2.00 to 2.19(m, n-polymethylene group of $-OC_6H_{13}$), 2.90 to 3.09(s, $-OCH_2-CH_2$ of $-OC_6H_{13}$), 4.20 to 4.99(t, $-OCH_2-CH_2$ of $-OC_6H_{13}$), 6.1(s, $-CO-CH = CH$), 7.1(s, p-disubstituted phenyl ring). NMR supports the structure.

Hexadecyloxy: 1.14 to 1.26(-CH_2 of $–OC_{16}H_{33}$), 1.98 to 2.70(m, n-polymethylene group of -$OC_{16}H_{33}$), 3 to 3.9(s, -OCH_2-CH_2 of $–OC_{16}H_{33}$), 6.3(s, -CO-CH = CH). NMR supports the structure.

Table 2. Texture of nematic phase of C_6, C_{10}, C_{12}, and C_{16} by miscibility method.

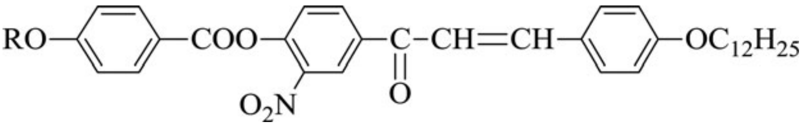
Sr. No.	Homolog	Texture
1	C_6	Threaded
2	C_8	Threaded
3	C_{12}	Threaded
4	C_{16}	Schlieren



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

Table 3. Transition temperature in°C.

		Transition temperatures in°C		
Compound No.	Homolog (*n*-alkyl chain)	Smectic	Nematic	Isotropic
1	C_1	—	—	223.0
2	C_2	—	—	227.0
3	C_3	—	—	220.0
4	C_4	—	—	210.0
5	C_5	—	148.0	193.0
6	C_6	—	172.0	196.0
7	C_7	—	144.0	186.0
8	C_8	—	138.0	171.0
9	C_{10}	—	136.0	180.0
10	C_{12}	—	142.0	164.0
11	C_{14}	—	160.0	177.0
12	C_{16}	—	168.0	191.0
13	C_{18}	—	162.0	188.0



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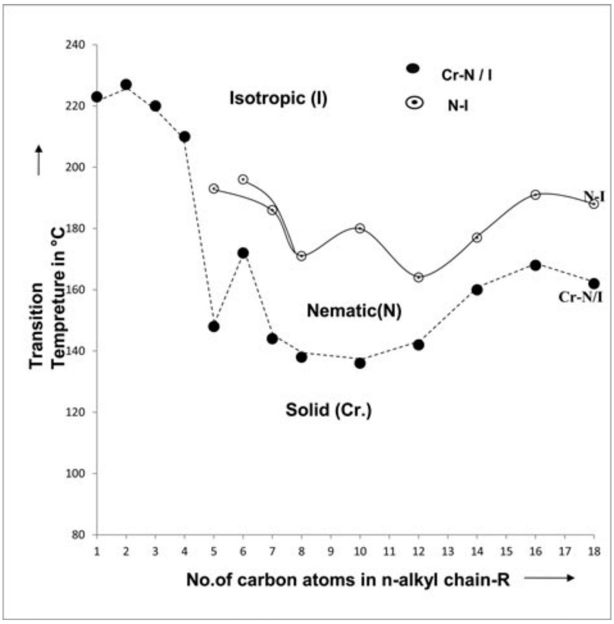
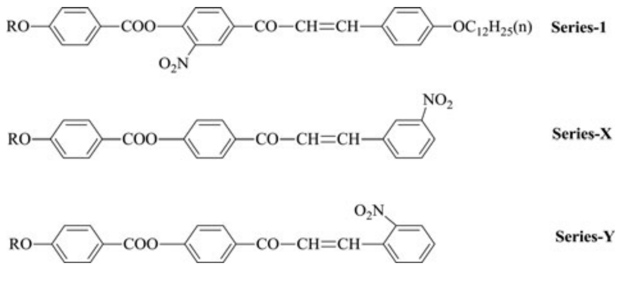


Figure 1. Phase behavior of series.

Results and discussion

Though the dimerization of 4-*n*-alkoxy benzoic acids disappears by the process of esterification, the transition temperatures of novel chalconyl ester derivatives are not lowered to the expected extent. The C_5–C_{18} homologs of a present series are enantiotropically nematogenic with absence of smectogenic character. C_1–C_5 homologs are nonliquid crystals. Transition temperatures (Table 2) as determined by an optical polarizing microscopy (POM) equipped with a heating stage were plotted versus the number of carbon atoms present in *n*-alkyl chain 'R' of –OR flexible group and the Cr-N and N-I transition curves were plotted by linking like or related points as depicted in a phase diagram (Figure 1), showing phase behaviors of a novel series. Cr-N/I transition curve rises and falls in zigzag manner with overall descending tendency and behaved in normal manner. N-I transition curve deviated from normal behavior from C_8–C_{18} homolog with exhibition of odd-even effect. Thermal stability for nematic is 182.89°C and the mesophase length ranges minimum to maximum which is 17°C–45°C at the C_{14} and C_5 homologs, respectively. The odd-even effect diminishes from and beyond C_8 homolog for higher homologs of longer *n*-alkyl chain. The textures of nematic phase are threaded or schlieren. The evaluated analytical, spectral, and thermal data confirm the molecular structure of homologs. The mesogenic properties from homolog to homolog in present series undergo variations. The mesomorphic transition temperatures varied between 136.0°C and 196.0°C.

The exhibition of nonmesomorphic behavior of C_1–C_4 homologs is attributed to the low magnitudes of dispersion forces and low magnitudes of dipole-dipole interactions, which induces high crystallizing tendency in a substances and inability to resist exposed thermal vibrations. Hence, the facilitation of mesophase formation is hindered and abruptly breaks the crystal lattices to melt sharply and directly transformation to isotropic state or from isotropic state to crystalline state with high crystallizing tendency on cooling the same. The molecules of C_5–C_{18} homologs resists exposed thermal vibrations and dis-aligned at an angle less than ninety degree and maintain floating of the molecules on the surface with only statistically parallel orientational order for definite temperature gradient to induce nematic phase and then continued excessive, heating results into random orientation of molecules with high order of disorder from and beyond isotropic temperature. However on cooling the same from and below isotropic temperature, the same energized randomly oriented molecules de-energies by loosing energy and exhibit to reappear nematic mesophase formation in reversible manner at a same temperature at which nematic mesophase was appeared on heating. Thus, mesophase appearance in reversible manner for the same sample is termed as enantiotropic transition. The odd-even effect observed for the N-I transition temperature is due to sequential addition of methylene unit at the *n*-alkyl chain 'R' of —OR group. The lowering of transition temperatures by esterification process of present novel homologs is not as low as it is expected, because the highly polar meta substituted lateral nitro group increases molecular width but induces molecular polarizability to such an extent that, suitable magnitudes of anisotropic forces of intermolecular end to end attractions raised to increase mesophase lengths and transition temperatures above 200°C. The disappearance of odd-even effect from and beyond C_8 homolog for higher homologs of longer *n*-alkyl chain 'R' of —OR and $-C_{12}H_{25}$ of $-OC_{12}H_{25}$ group is attributed to the coiling or bending or flexing or coupling of *n*-alkyl chains with principal axes of core structure of molecules. Therefore, uncertainty and its magnitudes in the status of *n*-alkyl chain may vary from homolog to homolog which may modify the morphological appearance of molecule and the magnitudes of molecular rigidity and/or flexibility as depended upon magnitudes of uncertainty and its type which induces deviation in the mesogenic behaviors in the transition curve or curves; of a phase diagram. The variations of mesomorphic properties, behaviors, and the degree of mesomorphism from homolog to homolog in the same series is attributed to the net intermolecular end-to-end cohesion and closeness as a result of changing molecular length, permanent dipole moment across the long molecular axes, dispersion forces, effective and favorable molecular rigidity and flexibility, etc., which vary with the number of carbon atoms present in *n*-alkyl chain 'R' of —OR group, keeping rest of the molecular part intact. The changing trends in mesomorphic properties of presently investigated novel series-1 and the structurally similar analogous series X [27] and Y [2] chosen for comparative study are mentioned below in Figure 2.



Above homologous series involving three phenyl rings and two central bridges contributing to total molecular rigidity are identically same and —OR flexible group at the left end are also identically same contributing partly to the total molecular flexibility for the same homolog from series to series. The ortho- or meta-substituted nitro group with respect to —CO–CH = CH- central group at the middle or last phenyl rings differs partly to the total flexibility irrespective of same highly polar and polarizable nitro group due to their varied positional difference and their substitution at different phenyl rings for the same homolog from series to series. Moreover they differ with respect to different terminal end groups –$OC_{12}H_{25}$(n), -H and –H which alters the magnitudes of total molecular flexibility. Thus, variations in mesomorphic properties, behaviors and the degrees of mesomorphism for the same homolog from series to series can be linked to the differing features of series 1, X, and Y, respectively, under comparative study. Following Table 3 represents some thermotropic properties and evaluated data in comparative manner are as under.

Table 4. Relative thermal stability in °C.

Series→	Series 1 (meta	
-NO_2 middle ring)	Series X (meta-NO_2)	Series Y (ortho-NO_2)
Sm-N or Sm-I		
Commencement of smectic phase		
–	126.7	
(C_6-C_{12})		
C_6	138.0	
(C_3-C_{14})		
C_3		
N-I		
Commencement of nematic phase	182.89	
(C_5–C_{18})		
C_5	148.6	
(C_6–C_{16})		
C_6	163.7	
(C_3–C_{16})		
C_3		
Total mesophase lengths in°C	17.0–45.0	
C_{14} C_5	12.0–63.0	
C_{16} C_{10}	16.0–49.0	
C_{16} C_6		

From above table it is clear that,

- Homologous series 1 is only nematogenic but the series X and Y selected for comparison are smectogenic plus nematogenic.
- Mesomorphism commences from C_5 homolog of series 1 but it commences from C_6 and C_3 homolog for series-X and Y respectively.
- Thermal stabilities for smectic adopt increasing order from series 1 to X to Y.
- Thermal stabilities for nematic is in decreasing order from series 1 to series Y to series X.
- Lower mesophase length of series 1 is higher than series Y and X but upper mesophase length is in decreasing order from series X to series Y to series Y to series 1.

In exhibition of smectogenic character by homologous series 1 of present investigation as compared to analogous series-X and Y is attributed to the magnitudes of flexibility contributed by right-ended tail group –$OC_{12}H_{25}$(n) as compared to tailed end –H of series X and Y whose group polarity, polarizability, and permanent dipole moment across the long molecular axis affects the extent of molecular noncoplanarity as well as hinders the formation of lamellar packing of molecules in their preoccupied crystal lattices and then consequently sliding layered molecular arrangement in floating condition on the surface which fails to occur. Thus, smectogenic property disappears in case of series 1 and positive possibility of lamellar packing of molecules in case of series X and Y in absence of bulky group like –$OC_{12}H_{25}$(n) which does not hinder the formation of smectogenic mesophase or facilitate smectic phase formation. The presence of bulky tailed group $-OC_{12}H_{25}$(n) in presence of ortho- or meta-substituted lateral –NO_2 group at middle or third phenyl ring favorably increases intermolecular end-to-end attractions and closeness due to which energy stored in the molecules (ΔH) of series 1 resists exposed thermal vibrations to considerable extent and raises thermal stability for nematic as compared to series X and Y. The early or late commencement of mesophase or mesophases depends upon the extent of molecular non co-planarity as a consequence of changing molecular rigidity and flexibility together, which induces suitable or unsuitable magnitudes of anisotropic forces of intermolecular attractions and resistivity against exposed thermal vibration under floating condition on the surface. Thus, variations in mesogenic properties for the same homolog from series to series and homolog to homolog in the same series depend upon the difference of group polarity of terminal end groups as well as polarizability and polarity of lateral group.

Conclusions

- Homologous series of present investigation is nematogenic with absence of smectic property whose mesophase length is moderately good enough and it is a middle-ordered melting type series.
- The group efficiency order derived for smectic and nematic on the basis of (a) thermal stabilities (b) early commencement of mesophases, and (c) total mesophase lengths with respect to lateral nitro group is as under.
  a) Smectic
  Series Y > Series X > Series 1
  Nematic
  Series 1 > Series Y > Series X
  b) Smectic
  Series Y > Series X > Series 1
  Nematic
  Series Y > Series 1 > Series X
  c) Total mesophase lengths (Sm±N)
  Upper: Series X > Series Y > Series 1
  Lower: Series 1 > Series Y > Series X
- Molecular structure of a molecule is very sensitive and susceptible to a phenomenon of mesomorphism as a consequence of effective molecular rigidity and flexibility.
- Lateral Nitro group on middle phenyl ring eliminates smectic mesophase formation whereas its presence on tailed phenyl ring favors formation of smectic mesophase at ortho or meta position.
- Study of binary systems of present investigation may be useful for the electronic display devices to be operated between 120°C and 196°C.
- Biological activity of present novel substances may be useful for the preparations of pharmaceutical products.
- Present investigation supports and raises the credibility to the conclusions drawn earlier.

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