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B. B. Jain and R. B. Patel

Chemistry Department, K.K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad, Gujarat, India

ABSTRACT

A chalconyl homologous novel series of thermotropic liquid crystals (LC) have been synthesized and studied with a view to understand and establish the effects of molecular structure on LC properties in thermotropic behaviors. Homologous series RO-C_6H_4-COO-C_6H_4-CO-CH=CH-C_6H_4-$OC_{14}H_{29}$ consists of 13 homologs (C_1–C_{18}), C_1–C_6 homologs are nonliquid crystals and the rest of the homologs are enantiotropically nematogenic without exhibition of smectic property. Transition temperatures and the textures of the nematic phase were determined by an optical polarizing microscopy, equipped with a heating stage. Texture of a nematic phase are threaded or schlieren. The Spectral and analytical data confirms the molecular structures of homologs. Thermal stability for nematic is 123.0°C and its mesogenicphaselength ranges between 13°C and 34°C. Cr-N/I and N-I transition curves behaved in normal manner except C_{14} homolog which shows negligible abnormality for N-I transition temperature or curve with exhibition of odd-even effect. Some LC properties are compared with the structurally similar homologous series. Thus, present homologous series is nematogenic and middle ordered melting type.

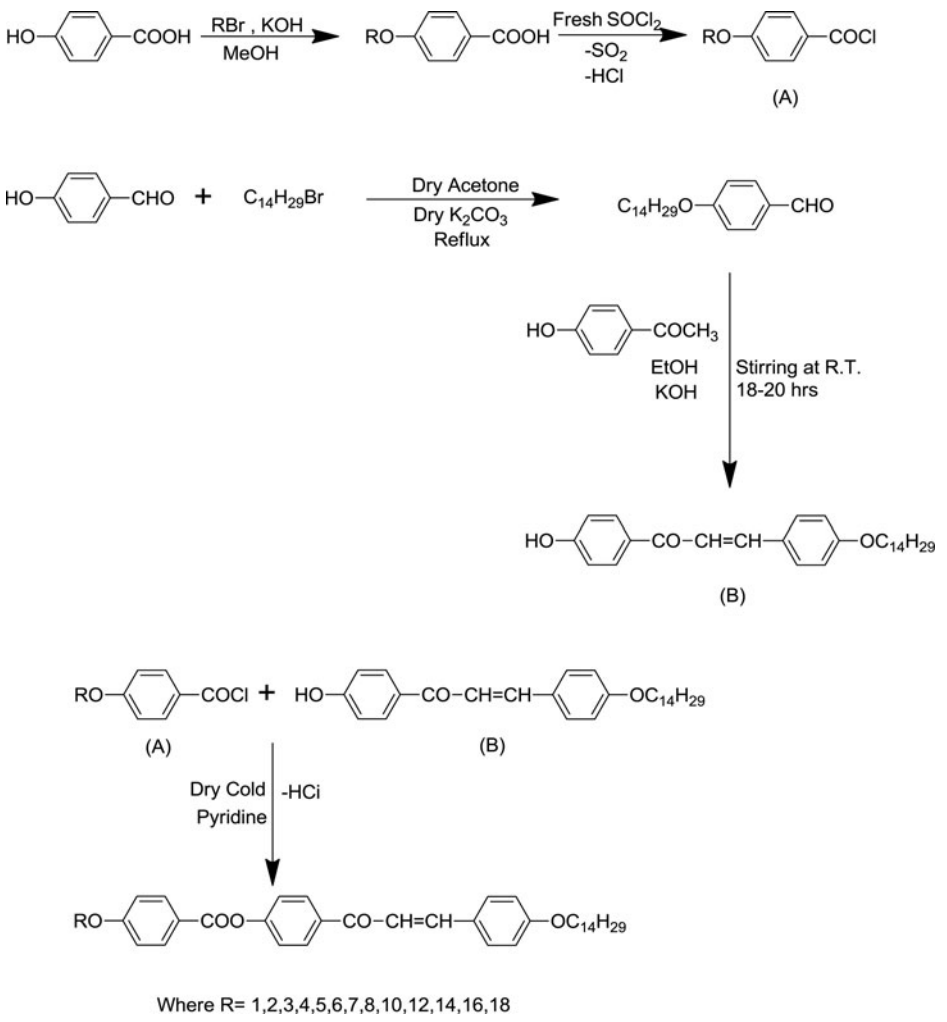
KEYWORDS

Liquid crystal; mesomorphic; mesogenic; nematic; smectic

Introduction

The interest in the study of liquid crystalline (LC) [1] state of matter has attracted to scientists and technologists because of its dual character as to flow like isotropic liquid and have to behave as rigid crystals by thermotropic and lyotropic LC. Thermotropic or lyotropic LCs has proved their ability in the interest of mankind. Some LCs like chalconyl esters derivatives are thermotropically and biologically active materials which are useful for the manufacture of LC devices or pharmaceutical preparation useful for curing of various physical disorder of human or animal bodies [2–10]. Present investigation is planned to synthesize novel LC material through homologous series with a view to understand and establish the effects of molecular structure on thermotropic LC properties, with reference to changing the tail group and its flexibility [11–14]. Thermotropic LC series of compounds of chalconyl ester derivatives is selected for synthesis, which may be biologically active and the present investigation is targeted to study their thermotropic behaviors through an optical polarizing microscopy after their due characterization. Such thermotropic behaviors of novel LC compounds will be compared with the structurally similar homologous series to derive group efficiency order,

CONTACT R. B. Patel roshanpatel770@gmail.com Chemistry Department, K.K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad, Gujarat, India.



Scheme 1. Synthetic route of series.

etc., and results will be interpreted in terms of molecular rigidity and flexibility [15–19]. Number of ester homologous series have been reported till the date [20–27].

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated using suitable alkylating agent (*R-X*) to convert it into 4-*n*-alkoxy benzoic acids by modified method of Dave and Vora [27]. α-4-hydroxyl benzoyl β-4$^{/}$-tetradecyloxy phenyl ethylene (B) was prepared by usual established method [28]. Acid chlorides component of each 4-*n*-alkoxy benzoic acid (A) were condensed with α-4$^{/}$-hydroxyl benzoyl β-4-tetradecyloxy phenyl ethylene (B) in dry cold pyridine by usual established method [29] carefully. Thus, chalconyl ester homolog derivatives were finally decomposed, filtered, washed, dried, and purified till constant transition temperature obtained using an optical polarizing microscope equipped with a heating stage.4-Hydroxy benzoic acid, alkyl halides, thionyl chloride, MeOH, EtOH, KOH, acetone, pyridine, 4-hydroxy acetophenone,

4-hydroxy benzaldehyde, tetradecyl halide, etc., required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below as Scheme 1.

Characterization

Selected members of the novel homologous series were characterized by elemental analysis, infrared spectroscopy, ^{1}H NMR spectra (Table 1). IR spectra were recorded by Perkin-Elmer spectrum GX, ^{1}H 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.

Analytical data

IR spectra in cm^{-1} for heptyloxy and tetradecyloxy derivatives

Heptyloxy: 686 Polymethylene (-CH_2-)n of –OC_7H_{15}, 840(–C-H- def. m di-substituted-para), 771 polymethylene (-CH_2-) of –$OC_{14}H_{29}$, 948 (–C-H- def. hydrocarbon), 1056 and 1010 (-C-O-) Str, 1165,1249 and 1303 (-C-O str in –(CH_2)n chain, 1427 and 1465 (-C-H- def. in CH_2),1512 (-C = C-)str, 1604,1681 and 1735 (-C = O group) and (-COO- ester group), 2854 and 2916 (-C-H str in CH_3).
Tetradecyloxy: 717 polymethylene (-CH_2-)n of –$OC_{14}H_{29}$, 840(–C-H- def. m di-substituted-para), 771 polymethylene (-CH_2-) of –$OC_{14}H_{29}$, 948 (–C-H- def. hydrocarbon), 1056 and 1018 (-C-O-) Str, 1396, 1303 and 1165, 1249 (-C-O str in –(CH_2)n chain, 1427 and 1465 (-C-H- def. in CH_2),1512 (-C = C-)str, 1604,1681 and 1728 (-C = O group) and (-COO- ester group), 2854 and 2924 (-C-H str in CH_3).

1HNMR spectra in $CDCl_3$ in δ ppm for decyloxy and hexadecyloxy derivative

Decyloxy: 0.82(t, -CH_3 of –$C_{10}H_{21}$), 1.2–1.4(*m*, *n*-poly methylene groups of-$OC_{10}H_{21}$), 1.70 (*m*, *n*-poly methylene groups of -$OC_{14}H_{29}$),3.9(s,-OCH_2-CH_2-of$OC_{14}H_{29}$), 6.9–7.2(s,-CO-CH = CH), 8.0 (s, p-disubstituted phenyl ring).
Hexadecyloxy: 0.88 (t,-CH_3 of –$C_{16}H_{33}$), 1.2–1.4(*m*, *n*-poly methylene groups of-$OC_{16}H_{33}$), 1.80 (*m*, *n*-poly methylene groups of -$OC_{14}H_{29}$), 3.5–3.6(s,-OCH_2-CH_2-of$OC_{16}H_{33}$), 4.0(s,-OCH_2-CH_2-of $OC_{16}H_{33}$), 6.9–7.3(s,-CO-CH = CH),8.1 (s, p-disubstituted phenyl ring).

Results and discussion

4-*n*-Alkoxy benzoic acids are dimeric and on linking them with nonmesogenic α - 4 – hydroxy benzoyl β-4′-*n*-tetradecyloxy phenyl ethylene (m.p.—80°C), which added chalconyl ester derivatives whose LC property as enantiotropicnematic commences from heptyloxy (C_7) homolog derivative and continued uptooctadecyloxy (C_{18}) homolog with absence of smectogenic property. Transition temperatures (Table 3) as determined from an optical polarizing microscopy, were plotted versus the number of carbon atoms present in *n*-alkyl chain of the left *n*-alkoxy terminal end group. Transition curves Cr-N/I and N-I are obtained by linking like or related points as depicted in a phase diagram (Fig. 1) showing the phase behaviors of a novel series. Cr-N/I transition curve adopts a zigzag path of rising and falling with

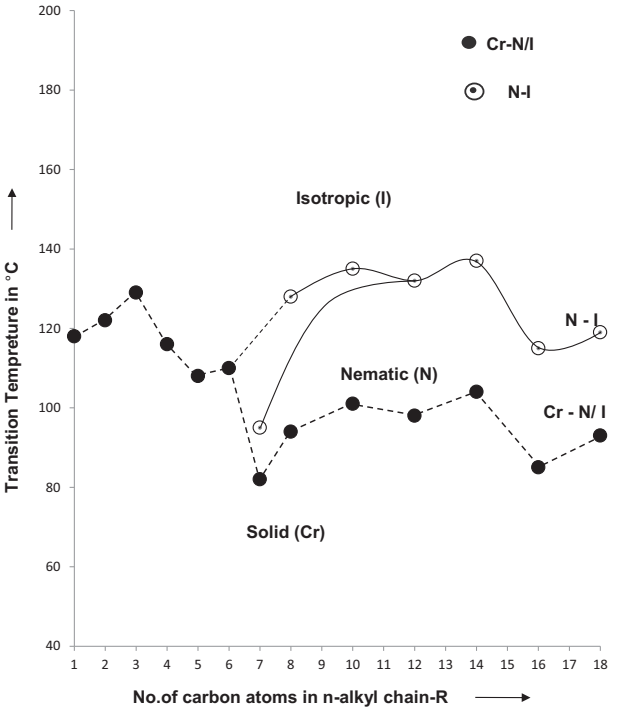


Figure 1. Phase behaviors of series.

overall falling tendency and behaves with normal manner. N-I transition curve is ascended from C_7 homolog, then it descended from C_{10} homolog to C_{16} homologs with negligible rise of 1 or 2°C temperature of C_{14} and C_{18} derivatives, than normal expected path of propagation with exhibition of odd-even effect. Odd-even effect diminishes as series is ascended for higher homologs from and beyond merging of N-I curves for odd and even members nearby about C_{12} homolog. N-I transition curves for odd members occupy lower position than even member's curve. The N-I transition curve for even members is extrapolated to C_6 homolog to predict the N-I transition temperature and its exhibition of nematic mesophase formation. The changing trend in mesomorphic behaviors from homolog to homolog observed for present novel series in usual manner. Thermal stability for nematic is 123.0°C, and the total mesophase length ranges from 13.0°C to 34.0°C. Thus, present novel chalconyl ester homologous series is middle ordered melting type whose melting transition temperatures vary between 82°C and 137°C.

The lowering of transition temperatures of present chalconyl novel ester homologous as compared to corresponding dimeric 4-*n*-alkoxy benzoic acids is attributed to breaking of hydrogen bonding between two aromatic acid molecules by esterification process. Alterations of transition or melting temperatures are due to odd and even number of carbon atoms present in *n*-alkyl chain of the left *n*-alkoxy group. The nonmesomorphicity of C_1–C_6 homologs is attributed to their inability to resist exposed thermal vibrations which, abruptly breaks the crystal lattices and sharply transform into isotropic liquid without exhibition of smectic or nematic phase due to their high crystallization tendency. High crystallization tendency of a substances (C_1–C_6) rises from unfavorable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions as a consequence of resultant rigidity and flexibility due to low dipole-dipole interactions and the low magnitudes of dispersion

forces through interactions between instantaneous dipoles produced by the oscillation of the electron clouds of the molecules. Thus, C_1–C_6 homolog molecules are randomly oriented in all possible directions without any ordered molecular arrangement under floating condition. Hence, they neither shows mesophase on heating nor they exhibit monotropic mesophase formation on cooling the same. However, nematogenic mesophase formation commences late from C_7 homolog and continues up to last C_{18} homolog in enantiotropic manners. The increasing length of *n*-alkyl chain by $-CH_2-$ unit, the corresponding permanent dipole moment across the long molecular axis and dispersion forces as a consequences of favorable molecular rigidity and flexibility, causes occurrence of suitable magnitudes of anisotropic forces of intermolecular cohesion and closeness by end-to-end attractions only, which manages to float the molecules on the surface through statistically parallel orientational order only from C_7 to C_{18} homologs. Thus, only nematic mesophase formation induced for C_7–C_{18}. The absence of smectogenic character throughout the novel series is due to the unsuitable magnitudes of lateral attractions which fails to induce lamellar packing of molecules in the crystal lattices from any stage of a novel series. Therefore, molecular polarizability being less effective to form lamellar packing of molecules in their rigid crystals which fails to adopt the sliding layered molecular arrangement in floating condition, to exhibit smectogenic property, under exposed thermal vibrations. The exhibition of odd-even effect of N-I transition curve is attributed to sequentially added methylene unit or units at the *n*-alkyl chain bonded to phenyl ring through oxygen atom. Diminishing of odd-even effect from and beyond C_{12} homolog is due to coiling or bending or flexing or coupling with major axes of a core structure of a molecule for longer *n*-alkyl chains. The extrapolation [30–33] of N-I transition curve to nonmesogenic C_6 homolog merges into its isotropic temperature, which indicates that there is no temperature difference for appearance of nematic phase above or below its isotropic temperature. The negligible abnormality in N-I transition temperature of C_{14} homolog may be due to the bonding of $-OC_{14}H_{29}$ end groups on both the terminals, whose vector sum of bond polarities contributed by $-OC_{14}H_{29}$ on both ends of a molecule being equal in magnitudes and opposite in directions, which nullifies the effects due to each other toward total molecular polarities and polarizability. Thus, intermolecular dispersion forces of cohesion are disturbed and induce abnormality. Abnormality observed for C_{18} homolog may be attributed to the uncertainty in the status of the longest C_{18} *n*-alkyl chain of left *n*-alkoxy group. The variations in mesogenic behaviors from homolog to homolog in the same series is due to the sequential addition of methylene unit or units, which varies suitable or unsuitable magnitudes of molecular rigidity or/and flexibility responsible to induce mesophase formation. Some mesogenic properties of present novel series 1 are compared with structurally similar series-*X* [34] and -*Y* [35] as shown below in Fig. 2

Homologous series-1 of present investigation and the series-*X* and -Y chosen for comparison are structurally identical with respect to three phenyl rings, central bridges –COO- and –CO-CH=CH- and the left *n*-alkoxy terminal end group –OR for the same homolog from series to series. However, they differ with respect to right-sided terminal tail end group viz. $-OC_{14}H_{29}$, -Cl, $-OC_{18}H_{37}$, respectively, from series to series. Thus, the changing mesogenic behaviors and the degree of mesomorphism depend upon the varying features of the combined effects of molecular rigidity and flexibility, which induces, due to differing molecular polarity and polarizability for the same homolog from series to series by changing right-sided terminal end groups. Following Table 2 represents some mesogenic properties in comparative manner for series-1, -*X* and -*Y*.

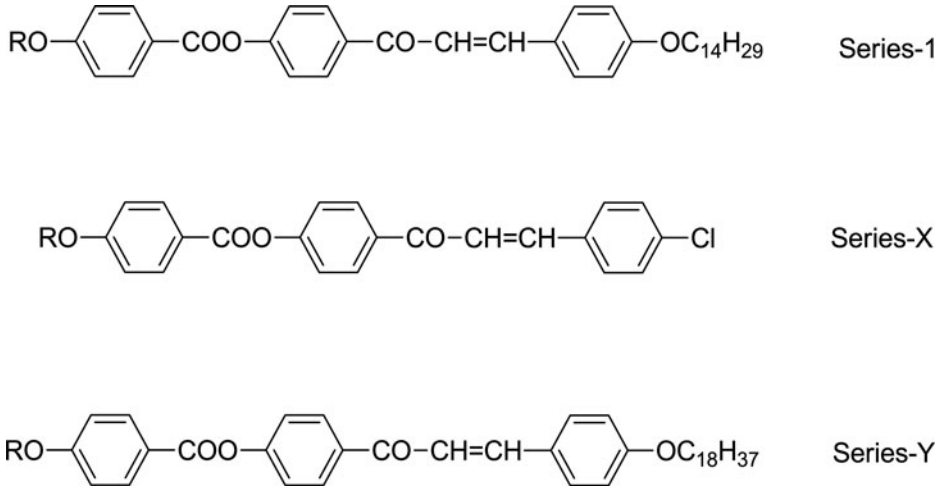


Figure 2. Structurally similar series.

Table 1. Elemental analysis for heptyloxy, decyloxy, tetradecyloxy, and hexadecyloxy derivatives.

Sr. no.	Molecular formula	%Elements found		%Elements theoretical	
		C	H	C	H
1	$C_{43}H_{58}O_5$	78.89	8.87	78.48	8.54
2	$C_{46}H_{64}O_5$	79.31	9.19	78.87	8.76
3	$C_{50}H_{72}O_5$	79.78	9.57	79.45	9.30
4	$C_{52}H_{80}O_5$	80.00	9.74	79.46	9.34

Table 2. Texture of nematic phase of C_7, C_{10}, C_{14}, C_{16} by miscibility method.

Sr. No.	Homolog	Texture
1	C_7	Threaded
2	C_{10}	Threaded
3	C_{14}	Threaded
4	C_{16}	Schlieren

α-4-(4′-n-alkoxybenzoyloxy)benzoyl-β-4″-tetradecyloxyphenylethylenes

Table 3. Transition temperature of homologous series.

Sr.no	*R*= *n*-alkyl group	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	C_1	—	—	118
2	C_2	—	—	122
3	C_3	—	—	129
4	C_4	—	—	116
5	C_5	—	—	108
6	C_6	—	—	110
7	C_7	—	82	95
8	C_8	—	94	128
9	C_{10}	—	101	135
10	C_{12}	—	98	132
11	C_{14}	—	104	137
12	C_{16}	—	85	115
13	C_{18}	—	93	119

Table 4. Thermal stabilities in°C.

Series→	1 (-$OC_{14}H_{29}$)	X (-Cl)	Y (-$OC_{18}H_{37}$)
Smectic-isotropicorSmectic-nematicCommencement of smectic phase	—	—	—
Nematic-Isotropiccommencement of nematic phase	123.0(C_7-C_{18})C_7	149.4(C_5–C_{14})C_5	122.0(C_5–C_{18})C_5
Total mesophase length range in°C (Sm to N)	13–34$C_7C_8C_{10}C_{12}$	14–25$C_7C_{12}C_8$	07–38C_7C_{12}

From above Table 4, it is clear that,

- homologous series-1, -*X* and -*Y* under comparative study are nematogenic with absence of smectogenic property.
- thermal stability for nematic is almost nearly equitable for series 1 and -Y, but it is less than a series-X.
- nematogenic mesophase commences from C_5 homolog of series-*X* and –*Y*, but it commences late from C_7 homolog for series-1.
- the total mesophaselength ranges from minimum to maximum in increasing order from series-*X* to series-1 to series-*Y*. Coincidently the total mesophaselength ranges from minimum to maximum by the homologs C_7–C_{12} for all the series under comparison.

Homologous series-1 and -*Y* are almost identical except the difference of four methylene units at the tail end groups at right side of the molecules. Therefore, the molecular flexibility differs to a very less extent affecting commencement of nematic phase and the intermolecular end-to-end and cohesive or dispersion forces are nearly equivalent, which facilitate and stabilize the exhibition of nematic property within definite range of temperature. Enthalpy values (ΔH) associated differs from homolog to homolog in the same series and for the same homolog from series to series which plays role in the thermometric behavior of series to series and the homolog to homolog. On comparing thermometric behaviors of series-1 and -*X*, the dipolarity of a bond between third phenyl ring and tail end groups –$OC_{14}H_{29}$ and –Cl differs because –Cl group is monoatomic and –$OC_{14}H_{29}$ is polyatomic which causes difference in the intermolecular end to end and closeness as well as the extent of molecular noncoplanarity. Thus, facilitation and stabilization of nematic mesophase is more favored in case of series-*X* as compared to series-1 and -*Y*. Thus, commencement of nematic mesophase, mesophase length range and the magnitudes of thermal stability show positive or negative variations in mesogenic behaviors, from series to series for the same homolog and homolog to homolog in the same series.

Conclusions

- Present novel chalconyl ester series is predominantly nematogenic with absence of smectic property and middle ordered melting type whose isotropic temperature varies between 108°C and 137°C.
- Group efficiency order derived for nematic on the basis of

(i) thermal stability
(ii) commencement of mesophase and

(iii) mesophaselength range are as under.

(i) Nematic

$-Cl > -OC_{18}H_{37} = -OC_{14}H_{29}$

(ii) Nematic

$-Cl = -OC_{18}H_{37} > -OC_{14}H_{29}$

(iii) Nematic

$-OC_{18}H_{37} > -Cl > -OC_{14}H_{29}$

- Molecular structure plays an important role in mesogenic behavior with reference to changing tail end group.
- Mesomorphism is very sensitive and susceptible to molecular structure.
- Novel homolog of chalconyl ester derivatives may be useful in the study of their biological activity lyotropically as antimalarial, anticancer, antibacterial …, etc.
- Present study supported early views and raised reliability and credibility to the conclusions drawn earlier.

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