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To cite this article: Ravindra Solanki, Vinay Sharma & Roshan Patel (2016) Dependence of thermotropic mesomorphism on molecular flexibility of changing tail group, *Molecular Crystals and Liquid Crystals*, 631:1, 107-115, DOI: [10.1080/15421406.2016.1159786](https://doi.org/10.1080/15421406.2016.1159786)

To link to this article: <http://dx.doi.org/10.1080/15421406.2016.1159786>



Published online: 12 Jul 2016.



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Dependence of thermotropic mesomorphism on molecular flexibility of changing tail group

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ABSTRACT

A novel chalconyl ester homologous series of liquid crystals has been synthesized and studied with a view to understanding and establishing the effect of molecular structure on liquid crystalline properties. Novel series consisted of 13 members (C_1 – C_{18}) of a series. C_1 – C_4 member of a series is nonliquid crystals and, the rest of the homolog members (C_5 – C_{18}) are enantiotropically nematogenic with absence of smectogenic property. None of the homolog is monotropically mesomorphic. Transition and melting temperatures were determined by an optical microscope equipped with a heating stage. Textures of nematic phase are threaded or schlieren. Spectral and analytical data of selected members of a series confirms the molecular structures of homologues. Cr-N and N-I transition curves of a phase diagram behaved in normal manner with exhibition of odd-even effect of very short range as observed for N-I transition curve. Thermal stability for nematic is 122.0°C and the nematogenic mesophase ranges from 7.0°C to 38.0°C. Liquid crystal properties of a present series are compared with the structurally similar known homologous series.

KEYWORDS

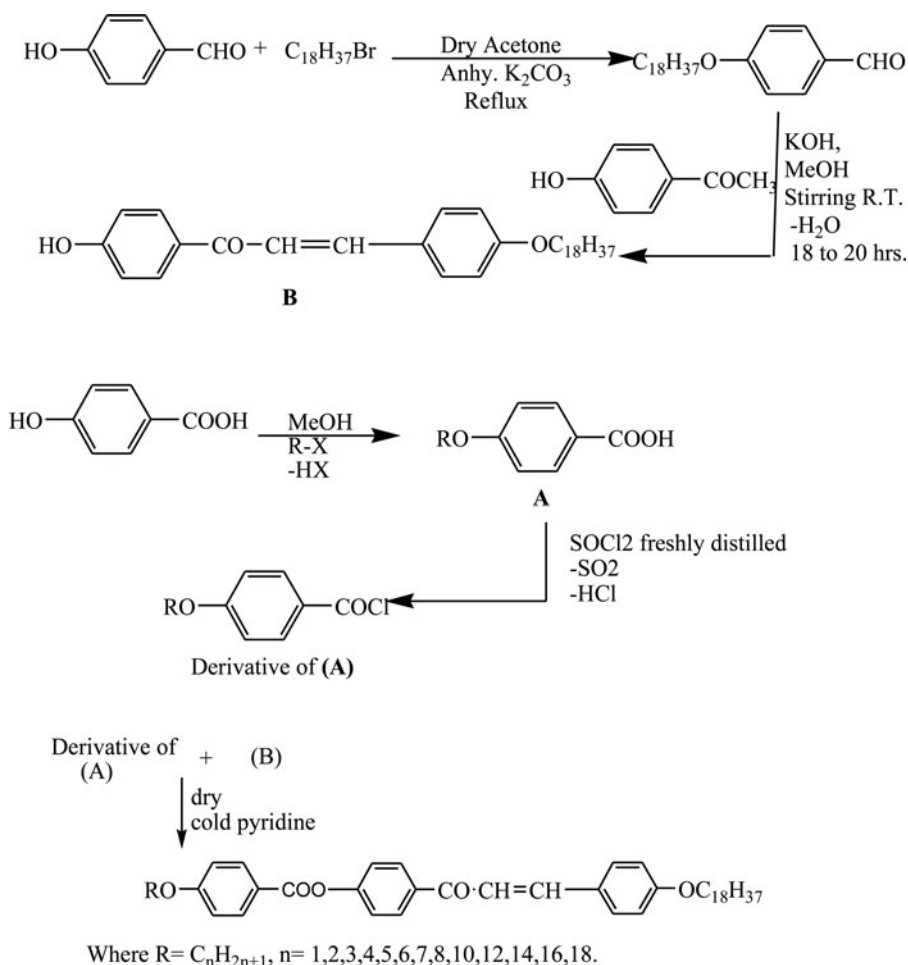
Liquid crystal;
mesomorphism; nematic;
odd-even effect; smectic

Introduction

The whole world has accepted the liquid crystalline (LC) state of a substance [1] in the benefit of the mankind in various fields of applications [2–12] in thermotropic or lyotropic conditions. The present investigation is planned with a view to

- (i) Synthesize novel substances, which can be useful for the applications as thermotropic LC or Lyotropic LC, which possess biological activity, toward prevention or curing diseases;
- (ii) to understand and establish the effects of molecular structure on LC properties of thermotropic LCs;
- (iii) to evaluate some LC data and to be compared with structurally similar homologous series of novel substances; and
- (iv) to provide the source of novel substances to the researchers working using LC materials to continue and extend their research activities [13–15].

However, our present investigation will be limited to novel thermotropic LC materials only. Number of homologous series have been reported till the date [16–22] by various groups of researchers. Present novel thermotropic LCs consisted of three phenyl rings linked through two central bridges $-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ and two flexible terminal end groups, viz.,



Scheme 1. Synthetic route of the series.

varying $-\text{OR}$ and fixed $-\text{OC}_{18}\text{H}_{37}$ (C_1 – C_{18}) and their LC behaviors are discussed and interpreted in terms of molecular rigidity and flexibility [23–26].

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 [27], α -4-Hydroxy benzoyl β -4'-octadecyloxy phenyl ethylene (B) was prepared by usual established method [28]. Acid chloride component of each 4- n -alkoxy benzoic acids (A) were condensed with 4-hydroxy derivative of chalcone (B) in dry cold pyridine by usual established method [29] carefully. Thus, chalconyl ester homologue derivatives were finally decomposed, filtered, washed, dried, and purified till constant transition temperatures obtained using an optical polarizing microscope equipped with a heating stage. 4-Hydroxy benzoic acid, alkyl halides, thionyl chloride, MeOH, EtOH, KOH, H_2SO_4 , acetone, pyridine, 4-hydroxy acetophenone, 4-hydroxy benzaldehyde, octadecyl halide, etc., required for synthesis were used as received except solvents

Table 1. Elemental analysis for methoxy, pentyloxy, decyloxy, octadecyloxy derivatives.

Sr. no.	Molecular formula	Elements found%		Elements calculated%	
		C	H	C	H
1	C ₄₁ H ₅₄ O ₅	78.59	8.62	77.99	8.61
2	C ₄₅ H ₆₂ O ₅	79.17	9.09	79.00	8.80
3	C ₅₀ H ₇₂ O ₅	80.00	9.60	79.50	9.20
4	C ₅₈ H ₈₈ O ₅	80.74	10.20	79.80	9.80

which were dried and distilled prior to use. The synthetic route to the series is shown below as Sch. 1.

Characterization

Representative homologs of a series were characterized by elemental analysis, mass spectrography, Infrared spectroscopy, ¹H NMR spectra, IR spectra were recorded by Perkin-Elmer spectrum GX, ¹H NMR spectra were recorded on Bruker using CDCl₃ as solvent. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyzer (Table 1). Transition temperature and LC properties (Textures) were determined using an optical polarizing microscopy equipped with heating stage. Textures of nematic phase determined by a miscibility method (Table 2).

Analytical data

IR Spectra in cm⁻¹ for decyloxy, Hexadecyloxy, and octadecyloxy derivatives

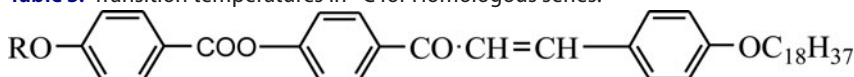
Decyloxy: 717 Polymethylene (–CH₂–)_n of –OC₁₀H₂₁, 840(–C–H– def. m di-substituted-Para), 771 Polymethylene (–CH₂–) of –OC₁₈H₃₇, 941 (–C–H– def. hydrocarbon), 1056 and 1018(–C–O–) Str, 1373 and 1303 and 1249, 1165 (–C–O str in (–CH₂)_n chain, 1427 and 1465 (–C–H– def. in CH₂), 1512 (–C=C–)str, 1604 and 1681 (–C=O group), 1735 (–COO– ester group), 2854 and 2916 (–C–H str in CH₃).

Hexadecyloxy: 740 Polymethylene (–CH₂–)_n of –OC₁₈H₃₇, 648 polymethylene (–CH₂–)_n of C₁₆H₃₃ 817(–C–H– def. m di-substituted-Para), 972 (–C–H– def. hydrocarbon), 1064 (–C–O–) Str, 1365 and 1249, 1165 (–C–O str in (–CH₂)_n chain, 1365 and 1427 (–C–H– def. in CH₂), 1504 (–C=C–)str, 1604 and 1681 (–C=O group), 1735 (–COO– ester group), 2854 and 2924(–C–H str in CH₃).

Octadecyloxy: 763 Polymethylene (–CH₂–)_n of –OC₁₈H₃₇, 833(–C–H– def. m di-substituted-Para), 941 (–C–H– def. hydrocarbon), 1056 (–C–O–) Str, 1373 and 1303 and 1249, 1165 (–C–O str in (–CH₂)_n chain, 1388 and 1468 (–C–H– def. in CH₂), 1512 (–C=C–)str, 1604 and 1681 (–C=O group), 1735 (–COO– ester group), 2854 and 2916 (–C–H str in CH₃).

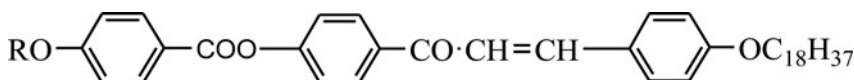
Table 2. Textures of nematic phase by miscibility method for C₅, C₈, C₁₂, and C₁₈.

Sr. no.	Homolog	Texture
1	C ₅	Threaded
2	C ₈	Threaded
3	C ₁₂	Schlieren
4	C ₁₈	Schlieren

Table 3. Transition temperatures in °C for Homologous series:

α -4-(4'-n-alkoxybenzoyloxy)benzoyl- β -4''-octadecyloxyphenyl ethylenes.

Compound no.	n-Alkyl chain $\text{C}_n\text{H}_{2n+1}$	Transition temperatures (°C)		
		Smectic	Nematic	Isotropic
1	C_1	—	—	130.0
2	C_2	—	—	139.0
3	C_3	—	—	128.0
4	C_4	—	—	132.0
5	C_5	—	125.0	134.0
6	C_6	—	112.0	125.0
7	C_7	—	115.0	122.0
8	C_8	—	110.0	124.0
9	C_{10}	—	112.0	128.0
10	C_{12}	—	89.0	127.0
11	C_{14}	—	84.0	110.0
12	C_{16}	—	92.0	109.0
13	C_{18}	—	101.0	119.0



^1H NMR spectra in CDCl_3 in δ ppm for heptyloxy and tetradecyloxy derivative: heptyloxy: 0.88(t, $-\text{CH}_3$ of $-\text{C}_7\text{H}_{15}$), 1.25-1.20(m, n-poly methylene groups of $-\text{OC}_7\text{H}_{15}$), 1.50 (m, n-poly methylene groups of $-\text{OC}_{18}\text{H}_{37}$), 3.4-3.8(s, $-\text{OCH}_2-\text{CH}_2-$ of $\text{OC}_{18}\text{H}_{37}$), 4.0-4.2(s, $-\text{OCH}_2-\text{CH}_2-$ of OC_7H_{15}), 7.2-7.3(s, $-\text{CO}-\text{CH}=\text{CH}$), 8.8-8.9 (s, p-disubstituted phenyl ring). **Tetradecyloxy:** 0.87(t, $-\text{CH}_3$ of $-\text{C}_{18}\text{H}_{37}$), 0.98 (t, $-\text{CH}_3$ of $-\text{OC}_{14}\text{H}_{29}$), 1.2-1.4 (m, n-poly methylene groups of $-\text{OC}_{18}\text{H}_{37}$), 1.5-1.8 (m, n-poly methylene groups of $-\text{OC}_{14}\text{H}_{29}$), 2.6 (s, $-\text{OCH}_2$), 3.4 (s, $-\text{OCH}_2-\text{CH}_2-$ of $\text{OC}_{14}\text{H}_{29}$), 4.0-4.2(s, $-\text{OCH}_2-\text{CH}_2-$ of $\text{OC}_{18}\text{H}_{37}$), 6.9-7.2(s, $-\text{CO}-\text{CH}=\text{CH}$), 7.5-7.7(s, p-substituted phenyl ring).

Results and discussion

Dimerization of 4-n-alkoxy benzoic acid disappears on esterification process by linking it with 4-hydroxy chalconyl derivative (m.p. is 74°C and yield is 69%). Mesomorphism commences from C_5 homologue as enantiotropic nematic phase with absence of smectogenic mesophase, that is, C_5 – C_{18} homolog derivatives are only nematogenic whose melting and/or transition temperatures vary between 84.0°C and 139.0°C . Thus, lowering of transition temperatures as compared to corresponding n-alkoxy benzoic acids, in spite of increasing length or size of the novel molecules with alternation of transition temperatures. The phase transition temperatures (Table 3) of the homologs are plotted versus the number of carbon atom present in n-alkoxy chain bonded to phenyl ring through oxygen atom. Smooth curves are drawn through the like or related points (N-I and Cr-N) in a phase diagram showing phase behaviors of series (Fig. 1).

The Cr-N transition curve adopts a zigzag path of rising and falling with overall descending tendency as series is ascended. N-I transition curve exhibit very narrow ranged odd-even effect between C_5 and C_{10} homologs. It descends from C_5 to C_8 and then rises for 6 to 8.0°C at C_{10} and C_{12} and finally descended up to C_{16} , but abnormally ascended by 10°C at C_{18} homolog. N-I transition curves for odd and even members are extrapolated to

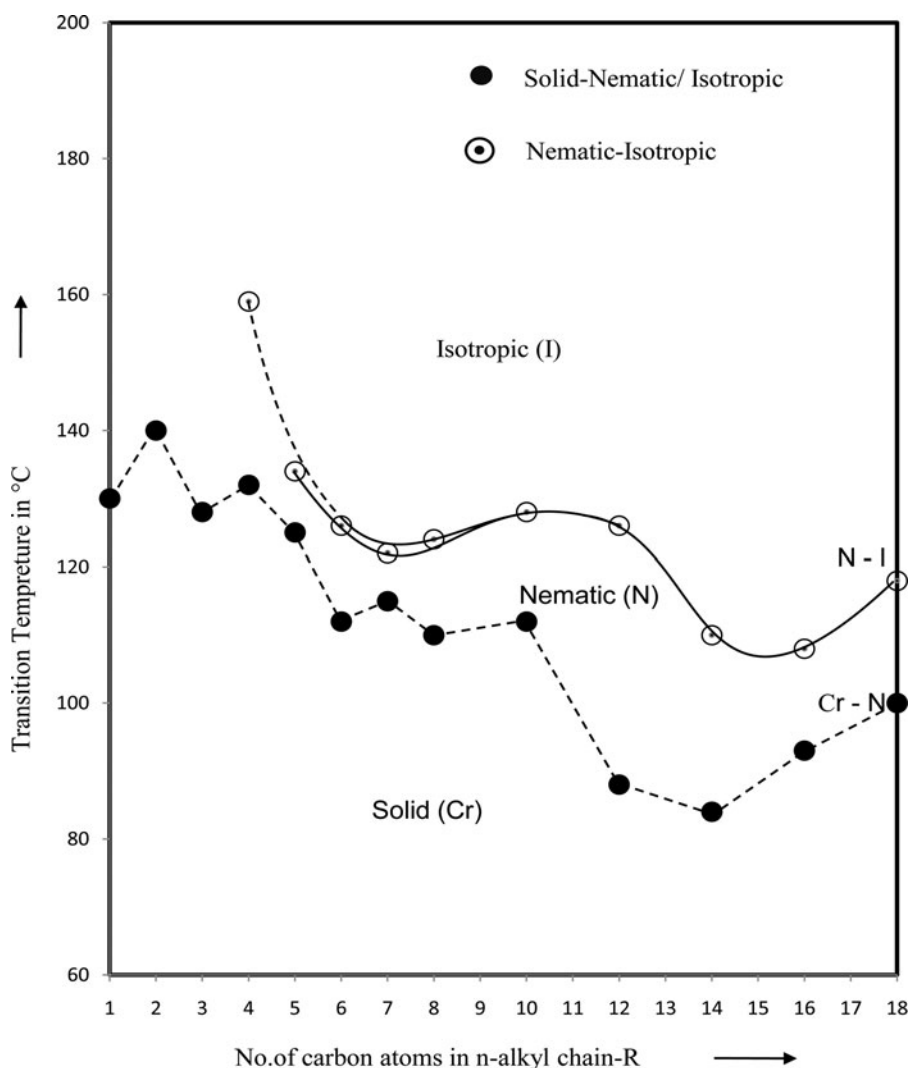


Figure 1. Phase behavior of series.

C_3 and C_4 homolog to intensify the odd-even effect, following the trend of N-I transition curve by extrapolation method [30, 31, 32]. Thus, Cr-N/I transition curve behaved in normal manner, but N-I transition curve behaved predominantly in normal manner with partly negligible abnormal manner. The thermal and mesomorphic properties from homolog to homolog vary in the same series. Thermal stability for nematic in average is 122.0°C with total mesophase length range 7.0–38.0°C. Hence, the presently investigated novel homologous series is predominantly nematogenic and partly nonmesogenic and middle ordered melting type.

Disappearance of dimerization and the lowering of transition temperatures of novel homologues as compared to corresponding 4-n-alkoxy benzoic acids are attributed to breaking of hydrogen bonding between two molecules of acid and subsequent esterification process. The nonmesogenic property of C_1 – C_4 homologs is attributed to their high crystallizing tendency which arises as a result of unsuitable magnitude of combined effect of molecular rigidity and flexibility induced by low dipole–dipole interactions and low magnitudes of dispersion forces

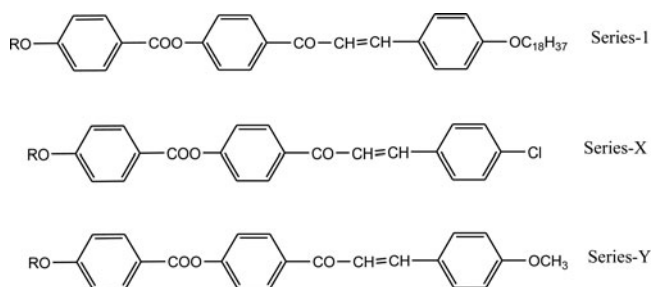


Figure 2. Structurally similar series.

by the interactions between instantaneous dipoles produced by the spontaneous oscillations of electron clouds of the molecules inducing high crystallizing tendency, which causes inability to resist or withstand exposed thermal vibrations. Hence, the molecules of C_1 – C_4 homologs sharply transform into isotropic liquid prior to exhibition of liquid crystal state.

The absence of lamellar packing of molecules in their crystal lattices (C_1 – C_{18}) due to unsuitable magnitudes of intermolecular anisotropic forces of lateral attractions which hinders to maintain sliding layered arrangement of molecules in floating condition on the surface under exposed thermal vibrations. The exhibition of only nematic mesophase formation for definite range of temperature by C_5 – C_{18} homolog is attributed to the suitable magnitudes of anisotropic forces of intermolecular attractions due to fittest magnitudes of molecular polarity and polarizability, permanent dipole-moment across long molecular axis, dispersion forces, etc. as a consequence of favorable molecular rigidity and flexibility which facilitated statistically parallel orientational order of molecules in floating condition on the surface to cause nematic mesophase formation under thermal energy. The negligible abnormality shown by few homologues is due to the unexpected status of the *n*-alkyl chains (C_{10} , C_{12} , and C_{18}) causing hindrance in the magnitudes of molecular flexibility. Variations observed in transition temperatures from homolog to homolog in the same series are attributed to the sequential addition of methylene ($-\text{CH}_2-$) unit or units in a left *n*-alkoxy terminal end group keeping right-sided end group unchanged. Odd-even effect in N-I transition curve disappears from and beyond C_{10} homolog because longer *n*-alkoxy chain from C_{10} to C_{18} may coil or bend or flex or couple to lie with major axis of the core structure. Thus, N-I transition curve adopt a path of single transition curve or with the missing of odd-even effect. Some mesomorphic properties of presently investigated homologous series are compared with the structurally similar known homologous series-X [33] and Y [34] in the following Fig. 2.

Homologous series of present investigation-1 and the homologous series selected for comparison purpose are identical with respect to three phenyl rings and the two central bridges $-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ contributing to the total molecular rigidity and the left *n*-alkoxy terminally situated varying end group ($-\text{OR}$) for the same homolog from series to series, But they [series-1,X,Y] differ with respect to terminally situated fixed right-handed flexible tail or end groups, viz., $-\text{OC}_{18}\text{H}_{37}$, $-\text{Cl}$, and $-\text{OCH}_3$ contributing partly to the total molecular flexibility, which added to the common part of the flexibility contributed by left *n*-alkoxy [$-\text{OR}$] end group. Thus suitable or unsuitable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions occurred as a consequence of combined effect of molecular rigidity and flexibility from homolog to homolog in the same series or for the same homolog from series to series vary with the changing magnitudes of permanent dipole-moment across the long molecular axis, dipole–dipole interactions and dispersion forces, etc.

Table 4. Average thermal stabilities in °C.

Series→	1(−OC ₁₈ H ₃₇)	X(−Cl)	Y(−OCH ₃)
Smectic-isotropicSmectic-nematicCommencement of smectic phase	–	–	118.0(C ₇ –C ₁₄)C ₇
Nematic-isotropicCommencement of nematic phase	122.0(C ₅ –C ₁₈)C ₅	149.4(C ₅ –C ₁₄)C ₅	157.0(C ₅ –C ₁₆)C ₅
Total mesophase (Sm+N) length in °CFrom C _i to C _j	7–38C ₇ –C ₁₂	14–25C ₇ –C ₁₂ C ₈	28–66C ₅ –C ₈

Thus, the mesomorphic properties and the degree of mesomorphism vary with the changing part of molecule, that is, in present novel series variations in LC behaviors will depend upon polarity of changing tail group −OC₁₈H₃₇, −Cl, and −OCH₃, which remains unchanged for same individual series. Some LC properties of present series like, thermal stabilities, commencement of mesophase or mesophase length range, odd-even effect, etc. are recorded in the following (Table 4) as shown below.

From Table 4, it is seen that

- Presently investigated a series-1 of chalcone derivatives is thermotropically nematogenic and the structurally similar homologous series-X and Y are only nematogenic as well as nematogenic in addition to smectogenic, respectively.
- Smectic phase for series-Y commences from C₇ homolog, whereas it does not commence till the last homolog of the series-X and 1.
- Nematic mesophase commences from C₅ homolog of the series 1, X, and Y.
- Smectic thermal stability of series-Y is 118.0, whereas smectic mesophase destabilized in series 1 and X, till the last member.
- Nematic thermal stabilities of series 1, X, and Y are in increasing order (122, 149.4, 157.0) respectively.
- Total mesophase length range is the highest for a series-Y and the lowest for a series-X, whereas it is intermittent for present series-1, between the series-X and series-Y.
- Odd-even effect is exhibited by N-I and/or Sm-N transition curves in the respective phase diagram.

The observed difference among the series under comparative study of series 1, X, and Y for the mesogenic properties and the degree of mesomorphism, which depend, upon the tail groups, −OC₁₈H₃₇, −Cl, and −OCH₃ for the same homolog from series to series. The individual group polarity of tail groups is different. The group polarity of any group is a vector sum of all bond polarities in a functional group.

Similarly, molecular polarity of a molecule is the vector sum of all bonds. Therefore, molecular polarity of series-1, X, and Y vary with the changing tail groups −OC₁₈H₃₇, −Cl, and −OCH₃.

The changing molecular polarity causes variations in permanent dipole moment across the long molecular axis, dipole–dipole interactions, dispersion forces, related to end to end, and lateral attractions for the same homolog from series to series as a consequence of changing molecular rigidity and flexibility. Internal stored energy of any thermodynamic system of a substance depends upon the quantity (mass) of the substance and its characteristics or thermodynamically heat of formation (Δ*H*) at constant pressure and at a given temperature as a consequence of molecular rigidity, which varies from homolog to homolog in the same series and for the same homolog from series to series. Therefore, energy associated (Δ*H*) with a molecule, depending upon molecular rigidity and flexibility induces thermal resistivity or thermal stability towards exposed thermal vibrations to facilitate the ordered molecular arrangement in floating condition either as sliding layers or/and statistically parallel orientational order for definite range of temperature to induce either smectic or/and

nematic mesophase formation. Thus, the magnitudes of thermal stability indicates resistivity toward exposed thermal vibrations in terms of transition temperature and the mesophase length range in terms of degree of mesomorphism for the same homolog from series to series. The increasing order of thermal stability values from series-1 to X to Y are related to highly polar $-\text{OCH}_3$ tail group to compared weaker polar $-\text{Cl}$ and $-\text{OC}_{18}\text{H}_{37}$ groups. Weakening of polarity of C_{18} homolog is attributed to the cancellation of vector sum of bond polarity by two n-alkoxy ($-\text{OR}$ and $-\text{OC}_{18}\text{H}_{37}$) groups bonded to first and last phenyl ring in opposite directions.

The magnitudes of which go on reducing from C_1 to C_{16} and the molecular polarity reduced to zero by tail groups, because both tail (left and right) ends are same, that is, $-\text{OC}_{18}\text{H}_{37}$ situated in opposite directions. Moreover, phenyl rings are nonpolar. Thus, abnormality of C_{18} homolog is attributed to its molecular polarity and rigidity or thermal resistivity values which it exhibited by only two central bridges $-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ which is the lowest in present series-1 and the highest for the series-Y and intermediate for series-X as observed in Table 4. Smectic mesophase formation in series-Y indicates lamellar packing of molecules in its crystal lattices, which forms sliding layered arrangement in floating condition, but absence of preoccupied layered structure in the molecules of series-1 and X disallows smectic mesophase formation. Narrow Odd-even effect observed commonly for the series under comparative study is attributed to the sequentially added even and odd number of methylene units and the late commencements of mesophase. Hence, the variation in LC properties for the same homolog from series to series or from homologue to homologue in the same series is attributed to changing molecular rigidity or/and flexibility as immersed in form of enthalpy change (ΔH) at a given temperature at constant pressure.

Conclusions

- Chalconyl ester novel derivatives of 13 homologs (C_1 – C_8 , C_{10} , C_{12} , C_{14} , C_{16} , C_{18}) have been synthesized and their thermotropic LC properties, evaluated and compared with the structurally similar known homologous series with a view to understand the relation between LC property and molecular structure depending on changing tail groups of different polarities.
- Group efficiency order derived on the basis of (a) thermal stability, (b) commencement of mesophase, and (c) mesophase-length range for smectic and nematic are as under.
 - (a) **Smectic:** $-\text{OCH}_3 > -\text{Cl} = -\text{OC}_{18}\text{H}_{37}$
Nematic: $-\text{OCH}_3 > -\text{Cl} > -\text{OC}_{18}\text{H}_{37}$
 - (b) **Smectic:** $-\text{OCH}_3 > -\text{Cl} = -\text{OC}_{18}\text{H}_{37}$
Nematic: $-\text{OCH}_3 = -\text{Cl} = -\text{OC}_{18}\text{H}_{37}$
 - (c) **Smectic \pm Nematic:** $-\text{OCH}_3 > -\text{OC}_{18}\text{H}_{37} > -\text{Cl}$
- $-\text{OCH}_3$ tail group is a stronger and highly polar-polarizable, which induces smectic and nematic phase by suitable magnitudes of lateral and end-to-end intermolecular attractions whereas $-\text{Cl}$ and $-\text{OC}_{18}\text{H}_{37}$ are relatively less polar and polarizable, fail to induce smectic phase, but induces only nematic mesophase.
- Molecular rigidity and flexibility are the main operators of mesomorphism.
- Chalconyl ester derivatives being biologically active molecules may be useful in pharmaceutical and medicinal field, including study of binary systems.
- A phenomenon of mesomorphism is very sensitive and susceptible to molecular structure of a substance.

Acknowledgments

The authors acknowledge thanks to Dr. R. R. Shah, principal of K. K. Shah Jarodwala Maninagar Science College, Ahmedabad. The authors are also thankful to Dr. A. V. Doshi, Ex-principal of M.V.M. Science College, Rajkot for his constant support, inspirations, and help, as and when needed during the course of present investigation. The authors thank to NFDD Centre for the analytical services and spectral services.

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