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Synthesis and mesomorphic behavior of liquid crystal chalconyl esters

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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 consists of 13 homologs (C_1–C_{18}), C_1–C_4 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 *(POM)*. Texture of a nematic phase are threaded or Schlieren. The Spectral and analytical data confirms the molecular structures of homologs. Cr-N/I and N-I transition curves behaved in normal manner except C_7 homolog which shows negligible abnormality for N-I transition temperature or curve with exhibition of odd-even effect.

KEYWORDS

Liquid crystal; mesomorphic; mesogenic; nematic; smectic

Introduction

The interest in the study of liquid crystalline (LC) [1] state of matter has attracted 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. Chalconyl derivatives are well-known for their biological activity as antibacterial, antifungal, antimalarial, anticancer [2–8], etc., and its involvement in many other biological processes in solution or lyotropic state. Present investigation is planned with a view to understand and establish the relation between thermotropic mesomorphism and the molecular structure of a substance. The object of the study is also aimed to provide novel LC material of chalconyl derivatives for study to scientists and technologists working with multidisciplinary LC state in the benefit of mankind or living entities including to the biologists and pharmacists. Novel chalconyl derivatives will consists of three phenyl rings bonded through -COO- and -CO-CH=CH- central bridges and two terminal flexible end groups -OR and -$OC_{14}H_{29}$. 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

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group efficiency order, etc., and results will be interpreted in terms of molecular rigidity and flexibility [9–12]. Number of ester homologous series have been reported till the date [13–21].

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 [22]. α- 4- hydroxyl benzoyl β-4$^{/}$- heptyloxy phenyl ethylene (B) was prepared by usual established method [23]. Esters were synthesized by a literature method[30]. Thus, the Chalconyl - ester homolog derivatives were filtered and washed with sodium bicarbonate and sodium hydroxide solution and dried and purified till constant transition temperatures using an optical polarizing microscope equipped with a heating stage. 4-hydroxy benzoic acid, Alkyl halides, 4-hydroxy benzaldehyde, 4-hydroxy acetophenone, dicyclohexyl carbodimide, dimethyl amino pyridine, DCM, MeOH, acetone required for synthesis were used as received except solvents which was dried and distilled prior to use. The synthetic route to a series is mentioned in Schemes 1.

Characterization

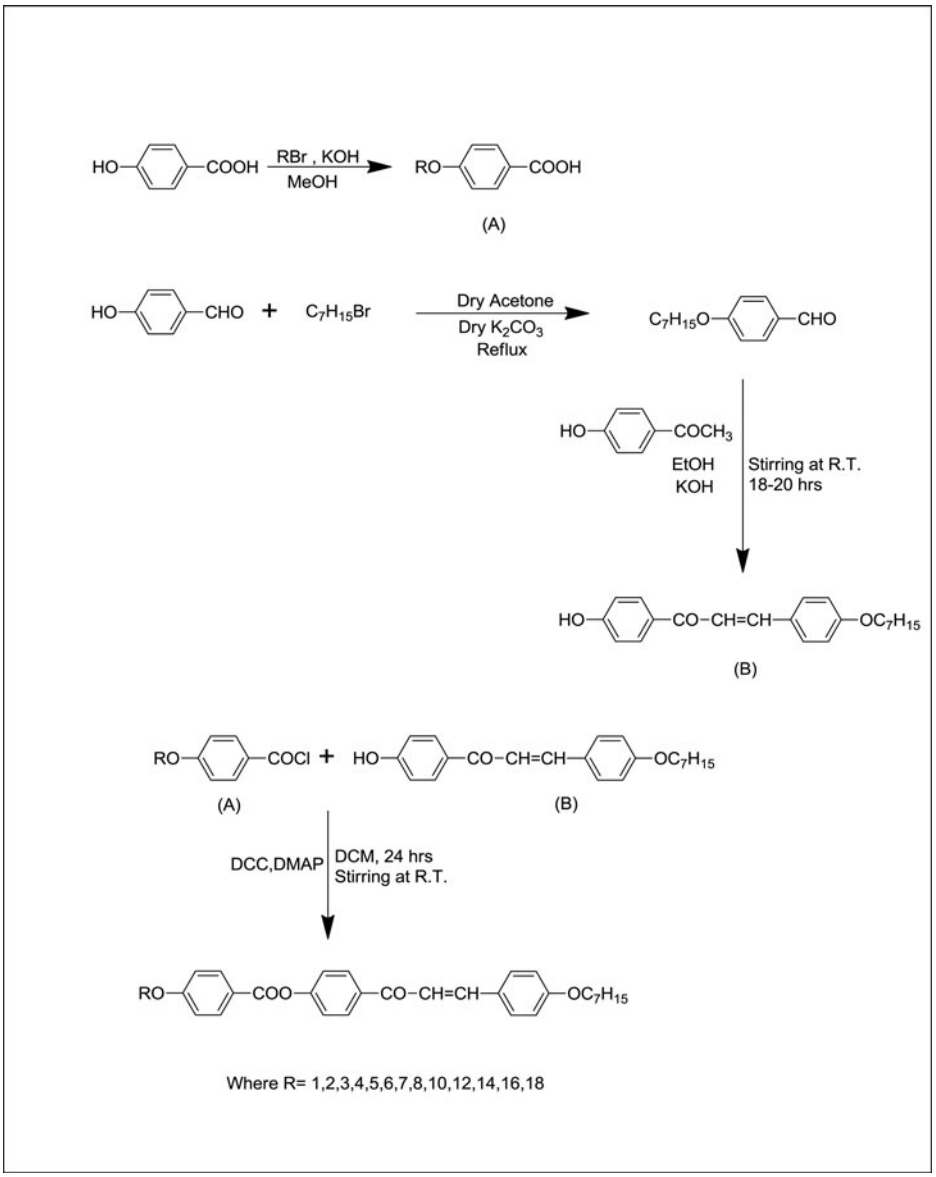
Selected members of the novel homologous series were characterized by elemental analysis (Table 1), infrared spectroscopy, ^{1}H NMR spectra. IR spectra were recorded by Perkin-Elmer spectrum GX, ^{1}H NMR spectra were recorded on Bruker using $CDCl_3$ as solvent. Microanalysis was performed on a Perkin-Elmer 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 (Table 2).

Table 1. Elemental analysis for hexyloxy, decyloxy, dodecyloxy, and hexadecyloxy derivatives.

		%Elements found		%Elements theoretical	
Sr. No.	Molecular formula	C	H	C	H
1	$C_{42}H_{58}O_5$	81.08	9.37	81.03	9.32
2	$C_{46}H_{66}O_5$	81.36	9.79	81.41	9.73
3	$C_{48}H_{70}O_5$	81.87	9.96	81.58	9.91
4	$C_{52}H_{78}O_5$	81.96	10.31	81.89	10.24

Table 2. Texture of nematic phase of C7, C12, C14, C16 by miscibility method.

Sr. No.	Homolog	Texture
1	C_7	Threaded
2	C_{12}	Threaded
3	C_{14}	Schlieren
4	C_{18}	Schlieren



Scheme 1. The preparation of $[Et_3N\text{-}SO_3H]Cl$.

Analytical data

IR Spectra in cm^{-1} for octyloxy & dodecyloxy derivatives

Octyloxy: 721Polymethylene (–CH_2–)n of –OC_8H_{17}, 831(–C–H– def. m di-substituted), 759 Polymethylene (–CH_2–) of –OC_7H_{15}, 952 (–C–H– def. hydrocarbon), 1112(–C–O–) Str, 1165, 1251 and 1379 (–C–O str in –(CH_2)n chain), 1458 (–C–H– def. in CH_2), 1518 (–C=C–)str, 1604 (–C=O group) 1710(–COO– ester group), 2848 and 2922 (–C–H str in CH_3).

Dodecyloxy: 718Polymethylene (–CH_2–)n of –$OC_{12}H_{25}$, 815(–C–H– def. m di-substituted), 767 Polymethylene (–CH_2–) of –OC_7H_{15}, 952 (–C–H– def. hydrocarbon), 1110(–C–O–) Str, 1377, 1165 and 1254(–C–O str in –(CH_2)n chain, 1465(–C–H– def. in

CH_2), 1516 (–C=C–)str, 1602 (–C=O group) 1712 (–COO– ester group), 2848 and 2920 (–C–H str in CH_3).

1HNMR spectra in $CDCl_3$ in δ ppm for Hexyloxy & Decyloxy Derivative

Hexyloxy: 0.86(t, $-CH_3$ of $-C_6H_{13}$), 1.1–1.5 (m, n-poly methylene groups of-OC_6H_{13}),1.75(m, n-poly methylene groups of $-OC_7H_{15}$), 3.2–3.4 (s,$-OCH_2$-CH_2-ofOC_7H_{15}), 4.03 (s,$-OCH_2$-CH_2-of OC_6H_{13}), 6.8–7.2 (s,–CO–CH=CH), 8.12 (s, p-disubstituted phenyl ring).

Decyloxy: 0.83 (t,$-CH_3$ of $-C_{10}H_{25}$), 1.3–1.6(m, n-poly methylene groups of-$OC_{10}H_{25}$), 1.77 (m, n-poly methylene groups of $-OC_7H_{15}$), 3.4–3.6(s,$-OCH_2$-CH_2-ofOC_7H_{15}), 4.12(s,$-OCH_2$-CH_2-of $OC_{10}H_{21}$), 6.9–7.4 (s,–CO–CH=CH),8.2 (s, p-disubstituted phenyl ring).α-;4-(4′-n-alkoxybenzoyloxy)benzoyl-β-4′′-tetradecyloxyphenyl ethylenes.

Results and discussion

4-*n*-Alkoxy benzoic acids are dimeric and on Condensation them with nonmesogenic α - 4 – Hydroxy benzoyl β-4′-*n*-heptyloxy phenyl ethylene (m.p.–), which added chalconyl ester derivatives whose LC property as enantiotropic nematic commences from heptyloxy (C_5) homolog derivative and continued upto octadecyloxy (C_{18}) homolog with absence of smectogenic property. Transition temperatures (Table 3) as determined from an optical polarizing microscopy with heating stage (POM), 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 overall falling tendency and behaves with normal manner. N-I transition curve is ascended from C_7 homolog, then it descended from C_{12} homolog to C_{18} homologs. 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_9 homolog. The changing trend in mesomorphic behaviors from homolog to homolog observed for present novel series in usual manner. Thermal stability for nematic is 102°C, and the total mesophase length ranges from 14.0°C to 32.0°C at the C_{10}-C_{16} homolog, respectively. Thus, present novel chalconyl ester homologous series is middle-ordered melting type whose melting transition temperatures vary between 67°C and 131°C. Thus, thermotropic properties vary from homolog to

Table 3. Transition temperature of homologous series in °C.

		Transition temperatures in °C		
Sr.no	R = *n*-alkyl group	Smectic	Nematic	Isotropic
1	C1	—	—	124.0
2	C2	—	—	126.0
3	C3	—	—	131.0
4	C4	—	—	119.0
5	C5	—	79.0	97.0
6	C6	—	67.0	95.0
7	C7	—	76.0	108.0
8	C8	—	72.0	101.0
9	C10	—	79.0	110.0
10	C12	—	84.0	98.0
11	C14	—	82.0	102.0
12	C16	—	76.0	108.0
13	C18	—	73.0	99.0

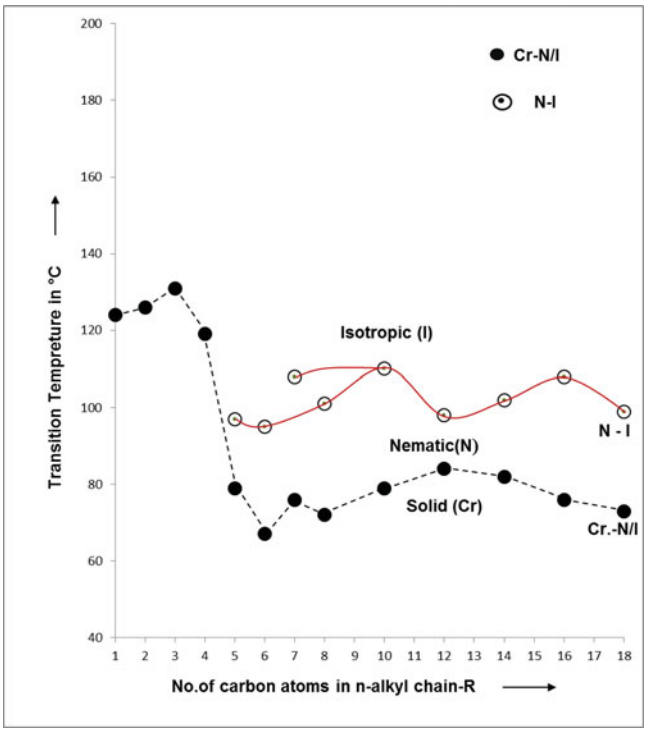


Figure 1. Phase behavior of series.

homolog in present series by changing methylene unit or units of left *n*-alkoxy terminally situated end group, keeping rest of the molecular part unchanged throughout the series. Thus, series is partly nematogenic and low melting type and relatively short ranged liquid crystallinity as well as low thermal stability.

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. Changes in 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 nonmesomorphic property of C_1–C_4 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_4) 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_4 homolog molecules are randomly oriented in all possible directions without any ordered molecular arrangement under floating condition. Hence, they neither show mesophase on heating nor they exhibit monotropic mesophase formation on cooling the same. However, nematogenic mesophase formation commences late from C_5 homolog and continue 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

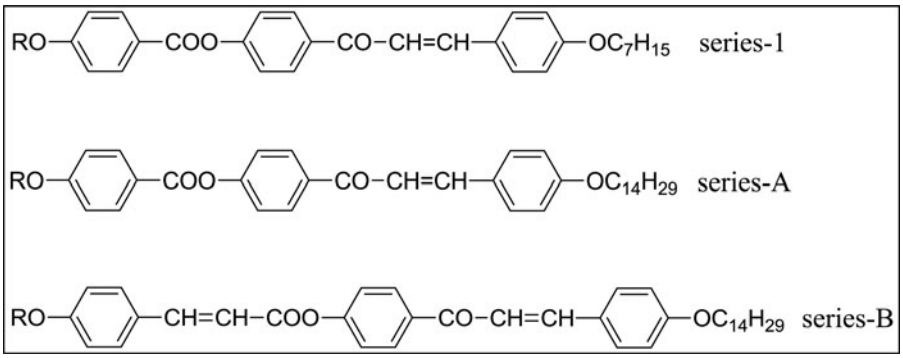


Figure 2. Structurally similar series.

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_5 to C_{18} homologs. Thus only nematic mesophase formation induced for C_5-C_{18}. The absence of smectogenic character throughout the novel series is due to the unsuitable magnitudes of lateral attractions which fail 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_9 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 negligible abnormality in N-I transition temperature of C_7homolog may be due to the bonding of $-OC_7H_{15}$ end groups on both the terminals, whose vector sum of bond polarities contributed by $-OC_7H_{15}$ on both ends of a molecule being equal in magnitudes and opposite in directions, which nullifies the effects due to each other towards 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 [25] and Y [26] as shown below in Fig. 2.

Homologous series 1 of present investigation and the series A and B chosen for comparison are structurally identical with respect to three phenyl rings, central bridges the left *n*-alkoxy terminal end group -OR for the same homolog from series to series. However, they differ with respect to Central bridges -COO, -CO-CH=CH (series 1 and A) and -CH=CH-COO, -CO-CH=CH (series B), and right-sided terminal tail end group viz. $-OC_7H_{15}$, $-OC_{14}H_{29}$, 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 4 represents some mesogenic properties in comparative manner for series 1, A, and B.

Table 4. Relative thermal stability in °C.

Series→	1	A	B
Smectic-isotropic or smectic-nematic Commencement of Smectic phase	—	—	—
Nematic-Isotropic Commencement of Nematic phase	102.0 (C_5-C_{18}) C_5	123.0 (C_7-C_{18})C_7	99.75 (C_6-C_{18}) C_6
Total upper and lower mesophase length range in °C C_i-C_j	14—32 C_{12} $C_{10}C_{16}$	13—34 C_7 C_8 C_{10} C_{12}	19—34 C_6 C_8

From above Table 4 it is clear that

- Homologous series 1, A, and B under comparative study are nematogenic with absence of smectogenic property.
- The mesogenic property commences from C_5 (series1), C_7 (series A), and C_6 (series B) homolog.
- Thermal stability for nematic of series B less than a series A and 1.
- The total mesophase length ranges from minimum to maximum in increasing order from series A to series 1 to series B.
- Thermal resistivity is poor for all the series under comparison.

Homologous series 1, A, and B are almost identical except the difference of 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, A, and X, the nonplanarity for all the series are equivalent but it slightly differs for the difference of -CH=CH-COO unit in case of series B, commencement from C_6 homolog for series B and C_5 for series 1 and C_7 for series A. The observed difference for thermal stabilities is attributed to the unusual and unexpected molecular status of *n*-alkyl chain of both ended *n*-alkoxy terminals -OR and -OC_7H_{15} depending upon resultant differing polarity difference of -OR and -OC_7H_{15} which induces thermal resistivity, degree of mesomorphism, and transition temperatures of homologs. Thus, thermal stabilities and upper and lower mesophase lengths ranges of series1, A, and B are not much differed in magnitudes.

Conclusions

- Present novel chalconyl ester series is predominantly nematogenic with absence of smectic property and middle-ordered melting type whose isotropic temperature vary between 95°C and 131 °C.
- Group efficiency order derived for Nematic on the basis of
  (a) Thermal stability,
  (b) Commencement of mesophase, and
  (c) Mesophaselength range are as under:
  (i) Smectic
  Series-1 = Series-X = Series-Y
  Nematic
  Series-A > Series-1 > Series-B

(ii) Nematic
Series-1 > Series-B > Series-A
(iii) Nematic
Series-A > Series-1 > Series-B

- Molecular structure plays an important role in mesogenic behavior with reference to changing tail end group and central bridges.
- Ester group of present novel investigation may be useful for the agricultural production for the growth of quality and healthy fruits and flowers, potato, and potato-like material as well as chalconyl group being biologically active and antibacterial and antifungal may reduce the consumption of pesticides and insecticides.
- 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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References

[1] Reinitzer. (1888). *Monatsh.*, *9*, 421.
[2] Jain, Upendra K., Bhatia, Rich K., Akkinepally, R., Rao, Ranjit Singh, Saxsena, Ajit K., & Seha, lrun (2014). *Trop. J. Pharm. Res.*, *13*(1), 73–80.
[3] Gaikwad, Prajkata P., & Desai, Maya, T. (2013). *Int. J. Pharm. Res. Rev.*, *2*(12), 40–52.
[4] Gray, G. W., & Winster, P. A. (Eds) Liquid crystal and plastic crystals, In: *The Role of Liquid Crystal in Life Processes* by G.T. Stewart, Chapter 6.2, Vol. 1, Ellis Harwood: Chichester, U.K., pp. 308–326.
[5] Tadwee, I., Shahi, S., Ramteke, V. & Syed, I. (2012). *IJPRAS*, *1*(2), 6–11.
[6] Rajesh, G., Mansi, K., Srikant, K., Babasaheb, B., Nageshg, D., Kavita, S., & Ajay, C. (2008). *Chem. Pharm. Bull.*, *56*, 897–901.
[7] Lee, Y. S., Lim, S. S., Shin, K. H., Kim, Y. S., Ohuchi, K., & Jung, S. H. (2006). *Biol. Pharm. Bull*, *29*, 1028–1031.
[8] Calliste, C. A., Le Bail, J. C., Trouilas, P., Poug, C., Chulia, A. J., Duroux, L. J. (2001). *Anticancer Res.*, *21* , 3949–3956.
[9] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Donell, D. G. (1993). *Liq. Cryst.*, *15*, 123.
[10] Collings, P. J., & Hird, M. (1997). *Introduction of Liquid Crystals Chemistry and Physics*, Taylor and Francis: Abingdon, U.K
[11] Macros, M., Omenat, A., Serrano, J. L., & Ezcurra A. (1992). *Adv. Matter.*, *4*, 285.
[12] Hird, M., Toyne, K. J., Gray, G. W., & Day, S. E. (1993). *Liq. Cryst.*, *14*, 741.
[13] Dermus, D. (1998). *Mol. Cryst.*, *165*, 45–84.
[14] Dermus, D. (1998). *Liq. Cryst.*, *5*, 75–100.
[15] Imrie, C. T., & Luckhrust, G. R (1998). Liquid dimers and oligomers. In: *Handbook of Liquid Crystal, Law Molecular Liquid Crystals*, Vol. 2B, Demus D., Goodby J. W., Graw G. W., Spiess H., & Vill V. (Eds.), pp. 801–833. Wiley-VCH: Weinheim, U.K.
[16] (i) Suthar, D. M., & Doshi, A. V. *Mol. Cryst. Liq. Cryst., 575*, 76–83. (ii) Chauhan, H. N., & Doshi, A.V. (2013). *Mol. Cryst. Liq. Cryst., 570*, 92–100. (iii) Chaudhari, R. P., Chauhan, M. L., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst., 575*, 88–95. (iv) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst., 552*, 104–110.
[17] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *527*, 51–58.
[18] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *582*, 79–87.

[19] Patel, B. H., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst.*, *605*, 61–69.
[20] Patel, B. H., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst.*, *607*, 78–86.
[21] Patel, B. H., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst.*, *607*, 76–86.
[22] Dave, J. S., & Vora, R. A. (1970). In: *Liquid Crystals and Ordered Fluids*, Johnson, J. F., & Porter, R. S. (Eds.), p. 447, Plenum Press: New York.
[23] Vogel, A. I. (1989). *Textbook of Practical Organic Chemistry* , 5th ed., p. 946, ELBS and Longman: London.
[24] Uhood, J. A. (2011). *International Journal of Molecular Science*., *12*, 3182–3190.
[25] Jain, B. B., & Patel, R. B. (2015). *Mol. Cryst. Liq. Cryst., 630*, 121.
[26] Jain, B. B., & Patel, R. B. (2015). *Int. Lett. Chem. Phys. Astron.*, *58*, 16–25.