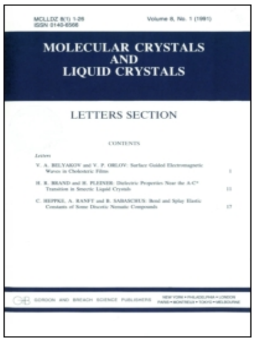

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Dependence of thermotropic mesomorphism on varying rigidity of central bridge in liquid crystals

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ABSTRACT

A novel liquid crystalline(LC) homologous series of chalconyl esters: RO-C_6H_4-COO-C_6H_4-CH = CH-CO-C_6H_4F has been synthesized and studied with a view to understanding and establishing the relationship between thermotropic LC properties and molecular structure with reference to varying molecular rigidity due to linking groups. The novel homologous series consists of eleven members (C_1 to C_{16}). C_1 and C_2 homologues are nonliquid crystals (NLC) and the rest of the homologues are enantiotropically nematic (C_3 to C_{16}). The smectogenic character, either in enantiotropic or monotropic manner is totally absent for a series. Transition temperatures and textures of nematic phase were determined by an optical polarizing microscope (POM) equipped with a heating stage. Textures of the nematic phase are threaded or Schlieren. The analytical, thermal and spectral data support the molecular structures. Cr-N/I and N-I transition curves behaved in normal manner except for the C_{14} homologue. N-I transition curve exhibits an odd- even effect with a negligible deviating effect from the C_{10} homologue. Thermal stability for the nematic is 105.2°C and mesophase lengths range from 06.0°C to 46.0°C at C_8 and C_{14} homologues respectively. The group efficiency order derived for nematic from the comparative study of present novel series with structurally similar analogous series on the basis of thermal stability as under.

KEYWORDS

Chalconyl ester; Liquid Crystal; Mesomorphism; Smectic; Nematic;
Smectic: -CO-CH = CH- > -N = N- > -CH = CH-CO-;
Nematic: -N = N > -CH = CH-CO > -CO-CH = CH-

Introduction

There is considerable scientific and technological interest in research of the liquid crystalline(LC) state [1] of both thermotropic or lyotropic type in the fields of thermographic LC devices including TV screens. Moreover their bioactivity may be utilized as antibacterial, antifungal, antimalarial, anticancer, antioxidant agents in the field of pharmaceutical preparations or in agricultural production [2–13]. The present investigation is planned with a view to understanding and establishing the effects of molecular structure on LC properties of thermotropic LC substances with reference to a central bridge linking middle and tail ended third phenyl ring of molecules consisting of three phenyl rings and two terminal units of –OR (varying) and –F (constant) polar groups [14–18]. Therefore a novel thermotropic homologous series of chalconyl esters will be synthesized, characterized and their thermometric properties will be studied by an optical polarizing microscopy (POM) equipped with a heating stage. Then the evaluated thermometric data will be compared with the structurally similar isomeric

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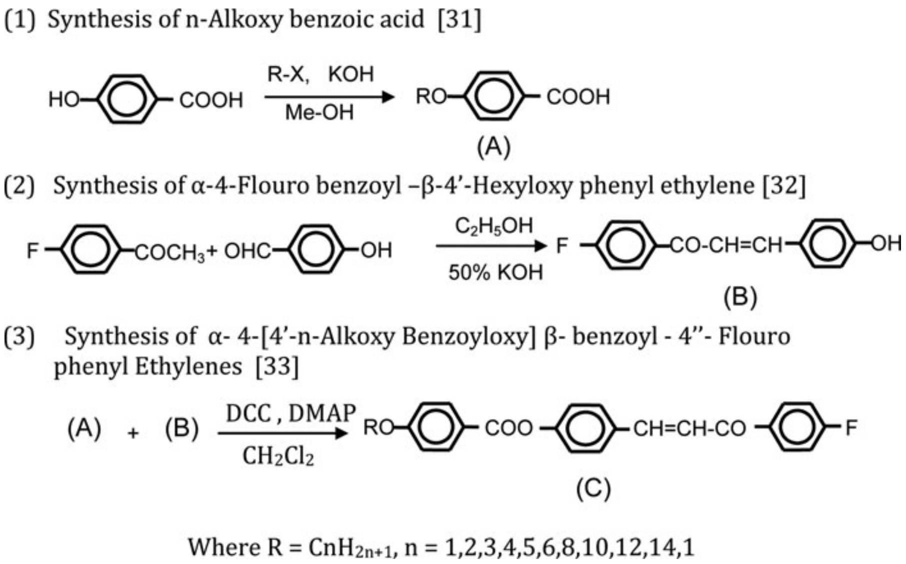
or nonisomeric analogous series. The group efficiency order will be derived on the basis of thermal stability etc. Thus, present study will include synthesis and thermotropic studies of LC substances. The experimental results will be discussed on the basis of molecular rigidity and flexibility [19–22]. Such studies are beneficial and provide scientific information to those working in other areas of liquid crystals, pharmaceuticals or agricultural purposes. Several ester homologous series of LCs have been reported to date [23–30].

Experimental

Synthesis

4-n-Alkoxy benzoic acids (A) were synthesized from 4-hydroxy benzoic acid using the corresponding suitable alkylating agent (RX) by the modified method of Dave and Vora [31].α-4-Flouro benzoyl –β-4′-Hexyloxy phenyl ethylene (B) (Chalcone) was prepared from 4-flouro acetophenone and 4-hexyloxy benzaldehyde by a known condensation[32] method. 4-n-Alkoxy benzoic acids (A) and α-4-hydroxy benzoyl –β-4′-Hexyloxy phenyl ethylene (B) were condensed in 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) and CH$_2$Cl$_2$ [33]. The synthetic route to the series is shown below in **scheme-1**. The final products were individually filtered, washed, dried and purified until constant transition temperatures were obtained.



Scheme 1. Synthetic route to the series-1.

Characterization

Some selected members of the novel series were characterized by elemental analysis, ^{1}HNMR spectra and IR spectra, Textures of mesophases were characterized by a miscibility method. Microanalysis for C,H,N, elements was performed on Perkin Elmer PE 2400 analyzer (Table 1). ^{1}HNMR spectra were obtained on a Bruker spectrometer using CDCl$_3$ as solvent. IR spectra were recorded on a Perkin- Elmer spectrum GX. Transition temperatures and

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

	Elemental % found (Compared with % calculated)	
Molecular formula	C	H
$C_{26}H_{27}O_4F$	72.12 (72.22)	6.30 (6.25)
$C_{30}H_{31}O_4F$	74.28 (74.38)	6.21 (6.40)
$C_{32}H_{35}O_4F$	90.25 (91.64)	8.49 (8.35)

liquid crystal properties were investigated using an optical polarizing microscope with a heating stage [POM].

Analytical Data

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

Ethylenes: (200 MHZ) δ ($CDCl_3$) (ppm) 0.98 (-CH_3-CH_2 of –C_8H_{17}), 1.40 (long-CH_2-chain), 3.8 -OCH_2 of (—OCH_2 of C_8H_{17}), 6.58& 6.45, 8.40 & 8.30 (p-sub. benzene rings)

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

Ethylenes: (200 MHZ) δ ($CDCl_3$) (ppm) 1.02 (-CH_3-CH_2 of –C_8H_{17}), 1.52 (long-CH_2-chain), 3.25 -OCH_2 of (—OCH_2 of C_8H_{17}), 6.69 & 6.45, 8.35 & 8.28(p-sub. benzene rings) IR in Cm^{-1},

IR Spectrum For Hexyloxy homologue

Ethylenes: (vmax/cm^{-1}):2982, 2878, 1475, 1338 (-C-H, aliphatic), 1728, 1256(ester group), 1740 (>C=O group), 1558 (-C=C-, aromatic), 1031, 1235 (ether group), 855.0 (p- sub. benzene ring), 1622, 1475, 1464 (Aromatic ring).

Spectrum For Octyloxy homologue

Ethylenes:(vmax/cm^{-1}):2928, 2828, 1450, 1364 (-C-H, aliphatic), 1716, 1233(ester group), 1728 (>C=O group), 1556 (-C=C-, aromatic), 1026, 1265 (ether group), 844.2 (p- sub. benzene ring), 1632, 1470, 1478 (Aromatic ring),

Result and discussion

Novel chalconyl esters of liquid crystal materials were synthesized by condensing 4-n-alkoxy benzoic acids and α-4-hydroxy phenyl 8–4′-fluoro benzoyl ethylene (m.p.90°C, yield 85%). The transition temperatures of novel homologues are lower than corresponding dimeric 4-n-alkoxy benzoic acids. Mesomorphic property commences from C_3 homologue. Totally eleven homologue derivatives (C_1 to C_{16}) are synthesized. C_1 and C_2 homologues are nonliquid crystals and the rest of the homologues (C_3 to C_{16}) homologues are enantiotropically nematogenic without exhibition of smectic property. Transition temperatures as recorded in Table 2 were plotted versus the number of carbon atoms present in n- alkyl chain -R of –OR left terminal end group and then Cr-I/N and N-I transition curves are obtained on linking like or related transition points; as depicted in a phase diagram (Fig. 1). Cr-I/N transition curve follows its zigzag path and descended in normal manner. N-I transition curve behaved in normal manner with negligible deviation from C_{10} to C_{12} and then maximum at C_{14} homologue derivative. Odd-even effect is observed for N-I transition curve from C_3 to C_8 homologue and then negligible or considerable deviation from normal expected behavior observed between C_{10} to C_{14} homologue. Odd-even effect diminishes from C_3 to C_8 and both curves merge into each other at the C_8 homologue. N-I transition curve propagates as a single transition curve from and beyond the C_8 derivative. The textures of nematic phase are threaded or Schlieren. Thermal

Table 2. Transition temperatures in °C.

Compound No	n-alkyl (C_nH_{2n+1}) group	Smectic	Nematic	Isotropic
1	C_1	—	—	135.0
2	C_2	—	—	123.0
3	C_3	—	94.0	132.0
4	C_4	—	87.0	128.0
5	C_5	—	81.0	105.0
6	C_6	—	90.0	112.0
7	C_8	—	78.0	84.0
8	C_{10}	—	50.0	88.0
9	C_{12}	—	50.0	95.0
10	C_{14}	—	65.0	110.0
11	C_{16}	—	47.0	93.0

stability in average for nematic is 105.2°C and total mesophase length is ranging from 6.0°C to 46.0°C at C_8 and C_{14} homologue respectively. Analytical, thermal and spectral data support molecular structures of novel homologues. The thermotropic LC properties vary from homologue to homologue in the same novel series.

Lowering of transition temperatures of novel homologues as compared to corresponding dimeric n-Alkoxy benzoic acids are attributed to the breaking of hydrogen bonding between two molecules of aromatic acids by esterification process. The condensation of two unlike molecules of 4-n-alkoxy benzoic acid and a 4-hydroxy derivative of chalcone increases molecular length, length to breadth ratio, ratio of the molecular polarity to polarizability, permanent dipole moment across the long molecular axis, favorable magnitudes of dispersion forces and dipole-dipole interactions, favorable combined effect of molecular rigidity and flexibility etc. which emerges the suitable magnitudes of anisotropic forces of intermolecular end

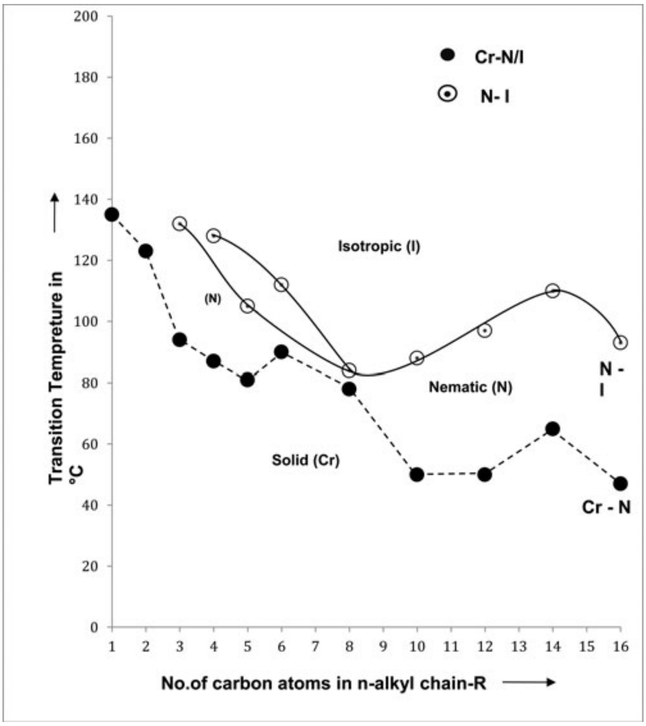


Figure 1. Phase behavior of series.

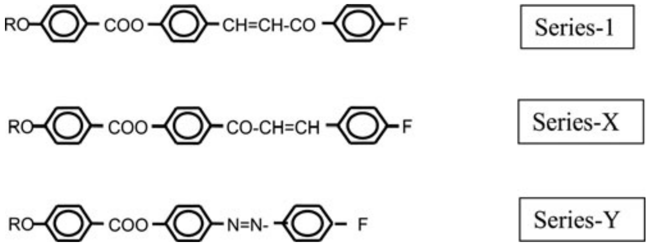


Figure 2. Structurally similar homologous series.

to end attractions and closeness commencing from C_3 homologue to disalign and arrange their molecules at an angle less than ninety degree on the plane of floating surface with statistically parallel orientational order of molecules, resisting exposed thermal vibrations of proper rate of heating and of proper intensity of radiation. Thus, molecules of novel chalconyl ester derivatives(C_3 to C_{16}) facilitate the formation of nematic phase for definite range of temperature in enantiotropic manner with total absence of smectogenic character even in the monotropic condition. The absence of either smectic and/or nematic mesophase formation in either reversible or irreversible manner in C_1 and C_2 homologues is attributed to low magnitudes of intermolecular dispersion forces and the low magnitudes of dipole dipole interactions, leading to high crystallizing tendency. The exhibition of odd-even effect observed for C_3 to C_8 homologue is due to the sequentially added methylene unit at the n-alkyl chain 'R' of –OR group. The diminishing of odd-even effect from and beyond C_8 homologue for higher homologues of longer n-alkyl chain 'R' is attributed to the n-alkyl chain 'R' which may coil or bend or flex or couple to lie with major axis of core structure of a molecule. The variations in LC properties from homologue to homologue in the same series is due to the varying number of carbon atoms present in n-alkyl chain R; which vary molecular flexibility in combination with molecular rigidity from homologue to homologue as depended upon either its usual expected or unusual unpredicted status, affecting suitable magnitudes of anisotropic forces of intermolecular cohesions and closeness. The LC properties of presently investigated homologous series-1 are compared with structurally isomeric or similar analogous series-X[34] and Y[35] selected for comparative study as shown below in Fig. 2.

Figure 2 shows that, homologous series-1 and X are isomeric with respect to each other, whereas series-1 and Y are structurally analogous or similar to each other. Thus, homologous series-1, X and Y are identical with respect to three phenyl rings and a central bridge linking first and middle phenyl rings –COO-, which partly contributes to the total molecular rigidity. Left n-alkoxy group –OR and tail ended flexible group –F are same for the same homologue from series to series, which contributes equally to the total molecular flexibility for same homologue but differ with respect to molecular rigidity. However, the homologous series 1,

Table 3. Relative thermal stability in °C.

Series	Series-1	Series-X	Series-Y
Sm-N or Sm-I Commencement of smectic phase	—	158.55 $(C_1 – C_{16})$ C_1	116.80 $(C_8 – C_{16})$ C_8
N-I Commencement of nematic phase	95.89 $(C_3 - C_{16})$ C_3	—	189.70 $(C_1 – C_{10})$ C_1
Total mesophase lengths from t°C to t_2°C	06.0 to 46.0 C_8C_{14}	5.1 to 74.5 $C_{12}C_{14}$	15.0 to 103.0 $C_{16}C_6$

X and Y differ with respect to a second central bridges–CH=CH-CO-, -CO-CH=CH- and –N=N- linking middle and third phenyl rings which contributes partly to the total molecular rigidity. Thus, variations in Thermotropic LC properties, behaviors or degree of mesomorphism will depend upon the varying features of series 1, X and Y for the same homologue from series to series and from homologue to homologue in the same series. The molecular flexibility for the same homologue from series to series are same but their molecular rigidity differs for the same homologue from series to series. The phenomena of mesomorphism are operated by combined effect of molecular rigidity plus molecular flexibility. Therefore combined effect of molecular rigidity plus molecular flexibility varies from homologue to homologue in the same series and for the same homologue from series to series depending on individual molecular structure of each, homologue of each series. Table 3 shows some thermotropic properties of the series under comparative study.

Table 3 indicates that,

- Presently investigated novel series-1 is only nematogenic, series-X is only smectogenic, and series-Y is smectogenic plus nematogenic.
- Smectogenic thermal stabilities decreases from series-X to Y to 1 or it increases from series-1 to Y to X.
- Smectic mesophase commences from very first(C_1) member of a series-X and it commences late from C_8 member of a series-Y whereas it does not commence until the last member(C_{16}) of series-1.
- Nematic mesophase commences from very first(C_1) member of a series-Y and it commences from C_3 member of a series-1, but it does not commence until the last C_{16} homologue of a series-X.
- Upper total mesophase length increases from series-1 to X to Y whereas it decreases from series-Y to 1 to X.

A novel homologous series-1 and a series-X are isomeric to each of each other with differing place of linking carbonyl group of a chalconyl central bridge attached directly to third or tail ended last phenyl ring (-CH=CH-CO-C_6H_5F-Series-1) or attached to middle phenyl ring as (-C_6H_4-CO-CH=CH-Series-X). Therefore, the positional placement of carbonyl unit of chalconyl central group, linking directly either with middle or third phenyl ring causes variations in molecular rigidity and the combined effect of molecular rigidity plus molecular flexibility and of differing magnitudes of its induced effectivity on respective flexibility of series-1 and X, in terms of differing thermodynamic quantity ΔH or heat of formation for the same homologue from series to series. Thus, suitable magnitudes of anisotropic forces of intermolecular cohesions and closeness are strong enough to arrange the molecules of presently investigated series-1 in only statically parallel orientational order without facilitating the formation of lamellar packing of molecules in their crystal lattices under floating condition under differing degree of molecular noncoplanarity which maintain only formation of nematic phase commencing from C_3 homologue to last C_{16} homologue with absence of smectogenic character for definite range of temperature. However, the positional status of carbonyl unit of central chalconyl group (series-X) attached directly with middle phenyl ring induces suitable magnitudes of anisotropic forces of intermolecular attraction which is being stronger than intermolecular attraction between two molecules of series-1, which facilitate the formation lamellar packing of molecules in the crystal lattices of molecules of series-X to disalign the molecules of series, perpendicular to the plane of a floating surface and subsequently layered structure of crystal lattices facilitate the floating of ordered molecular organization, with sliding layered molecular arrangement favoring the extent of molecular coplanarity under exposed thermal vibrations for definite range of temperature; excluding formation and facilitation of subsequent nematic phase. Thus, the direct attachment of carbonyl unit of chalconyl central bridge with middle or third phenyl ring of a substance containing three phenyl rings and two central bridge; leads the facilitation and formation of only smectic or only nematic phase formation respectively. The geometrical shape, size, the extent of molecular planarity, polarity and polarizability, combined effect of molecular rigidity and flexibility, intermolecular dispersive forces and favorable or suitable magnitudes of dipole-dipole interactions and resulting molecular rigidity and flexibility due to planner –N=N- in trans configuration of the molecules of a series-Y are strong enough and of suitable magnitudes which facilitated the formation of nematic phase from very first member C_1 homologue of a series to C_{10} homologue and the smectic mesophase formation from C_8 to C_{16} homologue. Thus, -N=N- (series-Y) central bridge is smectogenic plus nematogenic, -(-ph-)-CO-CH=CH-(series-X) central bridge is only smectogenic and –CH=CH-CO-(-ph) (Series-1) central bridge is only nematogenic. Thermal resistivity and mesophase lengths and the commencement of mesophase (smectic or nematic) depends upon only suitable magnitudes of anisotropic forces of intermolecular cohesions and closeness as well as the extent of molecular noncoplanarity which may cause early or late mesophase formation for the definite time period or for the temperature range which are related to intensity of exposed thermal vibrations. Thermal stabilities in average of LC substances are depended upon the resistivity offered by the individual molecules against exposed thermal vibrations through energy stored by them, which vary from one molecular structure to another molecular structure for the same homologue from series to series or from homologue to homologue in the same series.

Conclusion

- Novel homologous series of present investigation is enantiotropically nematogenic with absence of smectic property, whose mesophase length ranges between 6.0 and 46.0°C and it is of lower middle ordered melting type.
- Chalconyl central group containing three phenyl rings may be only smectogenic if carbonyl unit of a central chalconyl group is directly bonded to middle phenyl ring as –ph-CO-CH=CH- and it may be only nematogenic if carbonyl unit of a central chalconyl group is directly bonded to third (tailed) phenyl ring as –CH=CH-CO-ph- in case of isomeric series, but it may not be true completely for nonisomeric and nonchalconyl series.
- The group efficiency order derived for smectic and nematic on the basis of (a) thermal stability(b) early commencement of mesophase and (c) upper and lower mesophase lengths with reference to uncommon central bridges between any two phenyl rings.
  (a) Smectic
  -CO-CH=CH- > -N=N- > -CH=CH-CO-
  Nematic
  -N=N- > -CH=CH-CO- > -CO-CH=CH-
  (b) **Smectic**
  -CO-CH=CH- > -N=N- > -CH=CH-CO-
  Nematic
  -N=N- > -CH=CH-CO- > -CO-CH=CH-
  (c) **Total mesophase lengths**
  Lower: -N=N- > -CH=CH-CO- > -CO-CH=CH-
  Upper: -N=N- > -CO-CH=CH- > -CH=CH-CO-

- Mesomorphism is very sensitive and susceptible to molecular structures with reference to rigidity due to uncommon central bridges.
- Present study supports and raises the credibility to the conclusions drawn earlier and adds a conclusion for positional status of carbonyl unit of chalconyl central bridge as –ph-CO-CH=CH- and –CH=CH-CO-ph-.

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References

[1] Reinitzer, F. (1888). *Monatsh*, *9*, 421.
[2] Narmura, S. (2001). *Displays*, *22*(1), 1.
[3] Kim, W. S., Elston, S. J., & Raynes, F. P. (2008). *29*, 458–463.
[4] Hertz, E., Lavorel, B., & Faucher, O. (2011). *Nature photon*, *5*, 783.
[5] Gray, G. W., & Winsor, P. A., (Eds.) *Liquid crystals and plastic crystals*, Chapter 6.2, The role of liquid crystal in life processes by G.T. Stewart, *1*, 308–326.
[6] Tadwee, I., Sahanashahi, Ramteke V., & Syed, I. (2012). *IJPRAS*, ISSN 2277-36. *1*(2), 06–11.
[7] Calliste, C. A., Le Bail, J. C., Trouilas, P., Poug, C., Chulia, A. J., & Duroux, L. J., (2001). *Anticancer, Res.*, *21*, 3949–3956.
[8] Jain, U. K., Bhatia, R. K., Rao, A. R., Ranjit, Singh, Saxena, A. K., & Seha, I. (2014). *Tropical J. Pharmaceutical Res.*, *12*(1), 73–80.
[9] Boyd, B. J. et al. (2007). Patent No: WO2007140510A1, "Agrochemical composition comprising liquid crystal particals," Monash University.
[10] Rajan, U. (1975). *Singapore Medical Journal*, *16*(4), 297–300.
[11] (2006). Patent No. CN1246280C, "Polyhalogen-subtitled cinnamic acids and cinnamic acis derivatives and method for producing the same."
[12] Manuja, R. et al. (2013). *Int. J. Pharm. Sci. Res.*, *22*(2), 109–115.
[13] Gaikwad, P. P., & Desai, M. T. (2013). *Int. J. Pharma Res. Review*, *2*(12), 40–52.
[14] Imrie, C. T. (1999). *Struct. Bond*, *95*(1999), 149–192.
[15] Gray, G. W. (1974). In: *Liquid Crystals and Plastic Crystals*, Vol. 1, Chapter 4, Gray, G. W., & Winsor, P. A. (eds.), Ellis Horwood: Chichester, pp. 103–153.
[16] Gray, G. W. (1962). *Molecular Structures and Properties of Liquid Crystals*, Academic Press: London.
[17] Henderson, P. A., Niemeyer, O., & Imerie, C. T., (2001). *Liq. Cryst.*, *28*, 463–472.
[18] Imerie, C. T., & Luckhrust, G. R. (1998). Liquid dimers and oligomers, In: *Handbook of liquid crystal, law molecular liquid crystals*, Vol. 2B, D. Demus, J.W. Goodby, G.W. Gray, H. Spiess and V. Vill (eds), Wiley-VCH: Weinheim, Germany, pp. 801–833.
[19] Hird, M., Toyne. K. J., Gray. G. E., Day, S. E., & McDonell, D. G. (1993). *Liq. Cryst.*, *15*, 123.
[20] Collings, P. J., & Hird, M. (1998). *Introduction of liquid crystals chemistry and physics*, Taylor and Francis Ltd: U.K.
[21] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Matter*, *4*, 285.
[22] Hird, M., Toyne. K. J., Gray, G. W., & Day, S. E. (1993). *Liq. Cryst.*, *14*, 741.
[23] (i) Suthar, D. M., & Doshi, A. V. *Mol. Cryst. Liq. Cryst.*, *575*, 76–83. (ii) Chauhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst.*, *570*, 92–100 (iii) Chaudhri, R. P., Chauhan, M. L., & Doshi, A. V. (2013). *575*, 88–95. (iv) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. *Mol. Cryst. Liq. Cryst.*, *552*, 104–110.
[24] Demus, D. (1988). *Mol. Cryst.*, *165*, 45–84.
[25] Demus Plenary, D. (1988). *Liq. Cryst.*, *5*, 75–110.

[26] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *527*, 51–58.
[27] Patel, B. H., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst.*, *608*, 38–46.
[28] Marathe, R. B., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst.*, *623*, 1–8.
[29] Doshi, A. V., Bhoya, U. C., & Travedi, J. J. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 10–15.
[30] Lohar, J. M., & Doshi, A. V. (1993). Proceeding of Indian Acad. of Science- Bangalore, *105*(3), 209–214.
[31] Dave, J. S., & Vora, R. A. (1970). In: Johnson, J. F., & Porter, R. S.,(eds.), *Liquid crystals and ordered fluids*, Plenum Press: New York, 477.
[32] Patel, R. B., Patel, V. R., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 3–9.
[33] Nagaveni, N. G. & Prasad, V. (2013). *Phase Tran.*, *86*(12), 1227–1240. DOI: 10.1080/01411594.2012.744837.
[34] Rola, R. R., Bhola, G. N., & Bhoya, U. C. (2015). International Letters of Chemistry, Physics and Astronomy ISSN: 2299-3843, *47*, 67–76.
[35] Dave, J. S. & Vora, R. A. (1971). *Mol. Cryst. Liq. Cryst.*, *14*, 319.