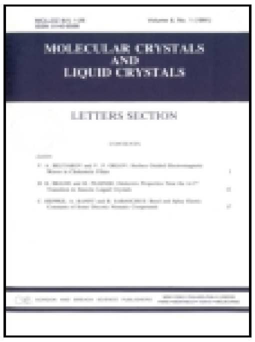


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Mesomorphism Dependence of Molecular Flexibility with Reference to Bromo Tail Group

M. D. Khunt, V. C. Kotadiya & U. C. Bhoya

To cite this article: M. D. Khunt, V. C. Kotadiya & U. C. Bhoya (2016) Mesomorphism Dependence of Molecular Flexibility with Reference to Bromo Tail Group, Molecular Crystals and Liquid Crystals, 626:1, 31-44, DOI: 10.1080/15421406.2015.1106226

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1106226

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 626, 31–44
http://dx.doi.org/10.1080/15421406.2015.1106226

Taylor & Francis
Taylor & Francis Group

Mesomorphism Dependence of Molecular Flexibility with Reference to Bromo Tail Group

M. D. Khunt, V. C. Kotadiya, and U. C. Bhoya

Department of Chemistry, Saurashtra University, Rajkot, Gujarat, India

ABSTRACT
Halogenated chalconyl derivatives of novel homologues of esters are synthesized and studied with a view to evaluate their liquid crystal (LC) properties and their dependence on molecular structure with reference to molecular rigidity and flexibility. Novel homologous series of chalconyl esters comprises 12 homologues. All the members of a series are enantiotropically smectogenic. Nematogenic mesophase is missing throughout the series. Textures of smectic phase are of type A or C, as judged either by observing directly the sample homologue through polarizing microscopy or some selected members of the series by miscibility method. Transition temperatures were observed through an optical polarizing microscope equipped with a heating stage. The Cr-Sm transition curve adopts zigzag path and behaves in a normal manner. Sm-I transition curve exhibits an odd-even effect and behaves in a usual established manner. The average thermal stability for smectic is 154.79°C, and the mesogenic phase length range is from 5.1 to 24.4°C. The LC properties of the novel series are compared with structurally similar other known series. Thus, present novel series is fully smectogenic with middle ordered melting type and short range of liquid crystallinity.

KEYWORDS
Liquid crystals; mesomorphism; nematic; smectic; thermotropic

Introduction

The importance of liquid crystalline (LC) state [1] of a substance is evergreen since 1888. The present investigation is planed with a view to synthesize novel LC substances through ester homologous series of chalconyl derivatives with a view to understanding and establishing the effect of molecular structure on thermotropic LC properties [2–6]. The object to synthesize chalconyl derivatives is important because chalconyl derivatives are biologically active molecules. Therefore, the novel substances may be useful as thermotropic LC and/or lyotropic LC, or as an ordinary substance in pharmaceutical or medicinal research [7–14]. Thus, the study will provide novel substances for further studying LC and LC-related fields and other fields of research. Several homologous series of LC substances have been reported [15–20]. The present novel homologous series contains three phenyl rings bonded through -COO- and -CO-CH=CH- central bridges and two end groups -OR and -Br as terminals in p'-p'' positions. Their phase transition temperatures will be determined, and selected members will be characterized by elemental analysis, infrared (IR), ^{1}H NMR, and mass spectra, and if possible by differential scanning calorimetry (DSC), including texture of mesophase

CONTACT U. C. Bhoya ✉ drucbhoya@gmail.com 🖃 Department of Chemistry, Saurashtra University, Rajkot 360005, Gujarat, India

Table 1. Elemental analysis for (1) methoxy, (2) ethyloxy, and (3) propyloxy derivatives.

		Elements found (%)			Elements calculated (%)		
Sr. No.	MF	C	H	O	C	H	N
1.	$C_{23}H_{17}BrO_4$	62.45	4.16	15.21	63.17	3.92	14.64
2.	$C_{24}H_{19}BrO_4$	66.21	6.12	12.87	67.29	5.84	11.95
3.	$C_{25}H_{21}BrO_4$	63.13	5.04	14.12	64.53	4.55	13.75

by miscibility method. The evaluated thermotropic data of novel substances will be interpreted and discussed in terms of molecular rigidity and flexibility [21–27]. The LC behaviors and properties of the present series will be compared with the structurally similar series and their minor dissimilarity will be correlated with difference in mutual LC behaviors in terms of molecular size, aromaticity, polarity and polarizability, thermal stability, commencement of mesophase, degree of liquid crysallinity, etc.

Experimental

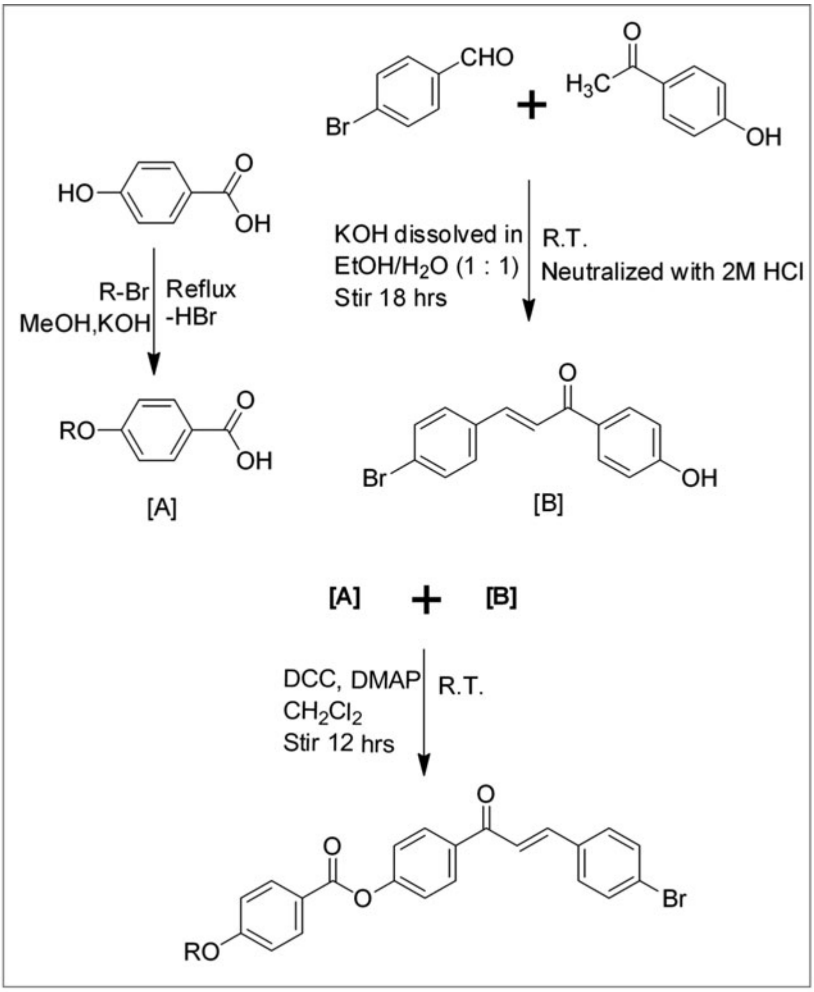
Synthesis

n-Alkoxy benzoic acids were prepared from 4-hydroxy benzoic acid and suitable alkylating agents by modified method of Dave and Vora [28]. α-4-hydroxy benzoyl β-4′-bromo phenyl ethylene was prepared by usual established method [29]. 4-n-Alkoxy benzoic acids and α-4-hydroxy benzoyl-β-4′-bromo phenyl ethylene were condensed in 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and CH_2Cl_2 [30]. Synthetic route to usual series is mentioned below as Scheme 1. Final products were individually decomposed, filtered, washed, dried, and purified until the constant transition temperatures were obtained.

Chemicals 4-hydroxy benzoic acid, 4-hydroxy acetophenon, 4-bromo benzaldehyde, alkylbomide (R-Br), methanol, KOH, 1,3-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, dichloromethane, ethanol, etc. were used as received except solvents, which were dried, purified, and distilled prior to use.

Characterization

Some selected members of the series were characterized by elemental analysis (Table 1), ^{1}H NMR spectra (Figs. 1 and 2), ^{13}C NMR spectra (Figs. 3 and 4), IR spectra (Figs. 5 and 6), and mass spectra (Figs. 7 and 8). Transition temperatures and textures of the smectic phase were determined by an optical polarizing microscopy equipped with a heating stage. Microanalysis was performed on Perkin Elmer PE 2400 CHN Analyzer, Waltham, MA. The structures of the materials were elucidated by IR spectroscopy (SHIMATZU FTIR-8400 infrared spectrophotometer, Nishinokyou Kuwabara-cho, Nakagyo-Ku, Kyoto, Japan), proton nuclear magnetic resonance (^{1}H NMR) spectrometry (BRUKER Avance-III [400 MHz] spectrometer, Billerica, MA) using $CDCl_3$ as a solvent, and mass spectrometry (Shimadzu GC-MS Model No. QP-2010, Nishinokyou Kuwabara-cho, Nakagyo-Ku, Kyoto, Japan). The analyses of the structures of the products and intermediates by spectroscopic methods were found to be consistent with the predicted structures.



α-4-(4'-n-Alkoxy benzoyloxy) benzoyl β-4"-bromo phenyl ethylenes

Where, R= C_nH_{2n+1} and n = 1 to 8 and 10,12,14,16

Scheme 1. Synthetic route to the novel series.

Analytical data

Spectral data

^1H NMR in ppm for Pentyloxy Derivative. 0.85–0.89 (t, 3H, -CH_3 of –OC_5H_{11} group), 1.17–1.42 (medium (m), 2H, polymethylene group of –OC_5H_{11}), 1.53–1.56 (p, 2H, Ar-O-$(CH_2)_2$-CH_2), 1.72–1.79 (p, 2H, Ar-O-CH_2-CH_2), 3.95–3.98 (t, 2H, Ar-O-CH_2), 6.89–6.91 (d, 2H, Ar-H), 7.27–7.29 (d, 2H, Ar-H), 7.42–7.49 (d, 4H, Ar-H), 7.66–7.70 (d, 1H, chalcone), 7.98–8.00 (d, 2H, Ar-H), 8.01–8.03 (d, 2H, Ar-H). 8.06–8.08 (d, 1H, chalcone). The NMR data are reliable with the molecular structure.

^1H NMR in ppm for Hexayloxy Derivative. 0.83–0.86 (t, 3H,-CH_3 of –OC_6H_{13} group), 1.18–1.30 (m, 4H, polymethylene group of –OC_6H_{13}), 1.37–1.43 (p, 2H, Ar-O-$(CH_2)_2$-CH_2), 1.72–1.79 (p, 2H, Ar-O-CH_2-CH_2), 3.96–4.04 (t, 2H, Ar-O-CH_2), 6.90–6.92 (d, 2H, Ar-H), 7.28–7.31 (d, 2H, Ar-H), 7.43–7.50 (d, 2H, Ar-H), 7.67–7.71 (d, 1H, chalcone), 7.99–8.01 (d, 2H,

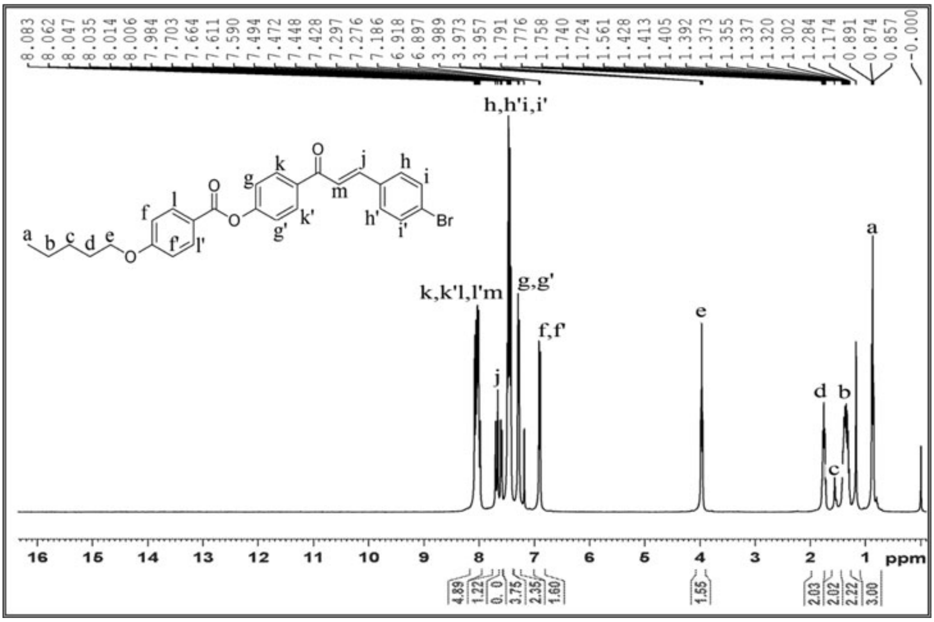


Figure 1. ^{1}H MNR spectrum of pentyloy derivative.

Ar-H), 8.02–8.05 (d, 2H, Ar-H). 8.07–8.09 (d, 1H, chalcone). The NMR data are reliable with the molecular structure.

^{13}C NMR ($CDCl_3$) in ppm for Pentyloxy Derivative. 14.06 (CH_3), 22.46–28.79 (CH_2), 68.38 (OCH_2), 122.00 (-CH=CH-C=O) 143.73 (-CH=CH-C=O) 114.41–163.82 (Ar-C), 164.44 (>C=O), 189.04 (>C=O of chalcone).

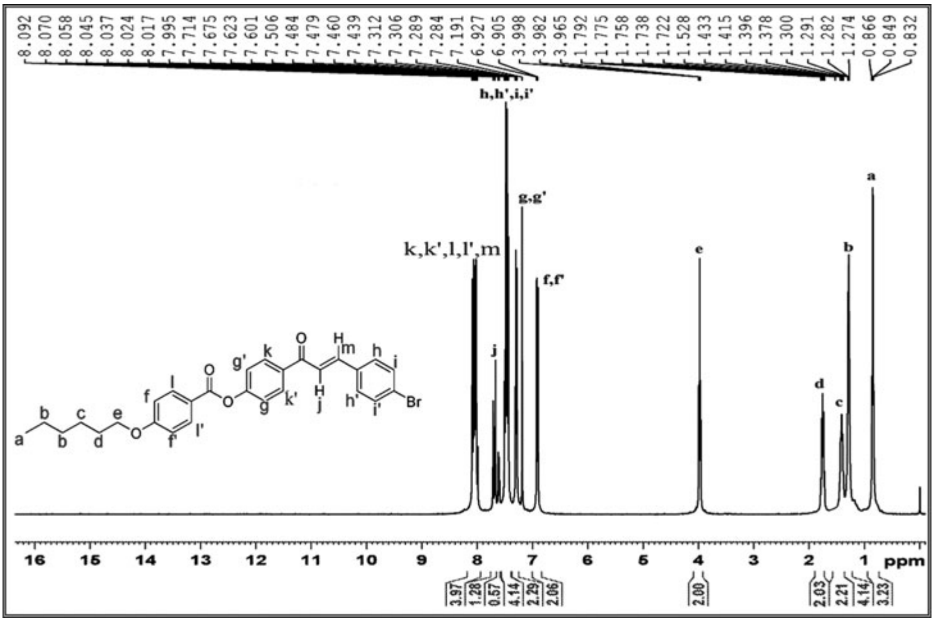


Figure 2. ^{1}H MNR spectrum of hexyloxy derivative.

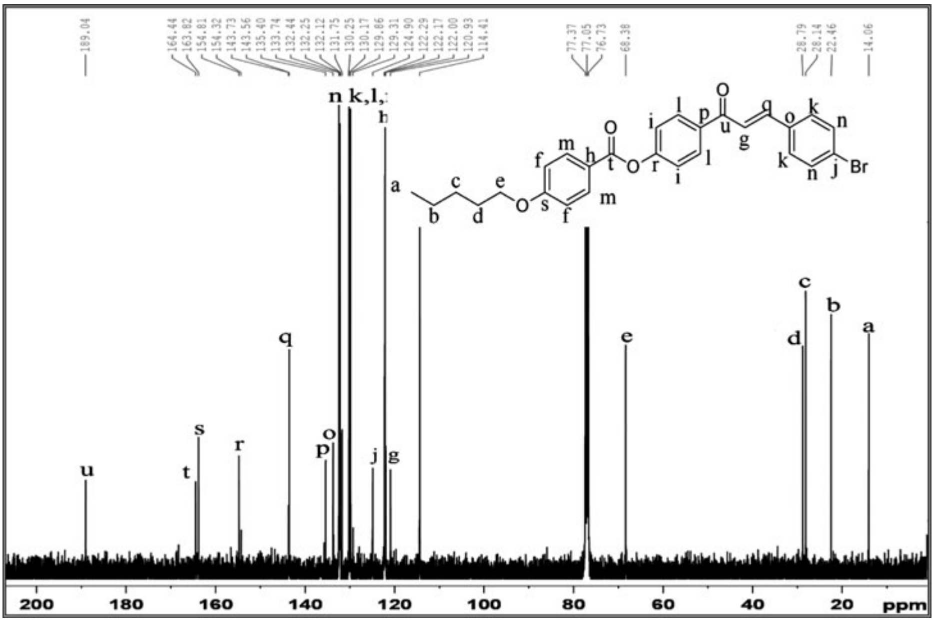


Figure 3. ^{13}C spectrum of pentyloxy derivative.

^{13}C NMR(CDCl$_3$) in ppm for Hexyloxy Derivative. 14.01 (CH$_3$), 22.93–31.64 (CH$_2$), 69.64 (OCH$_2$), 121.45 (-CH=<u>CH</u>-C=O) 144.36 (-<u>CH</u>=CH-C=O) 114.73–163.94 (Ar-C), 167.17 (>C=O), 190.98 (>C=O of chalcone).

IR in cm^{-1}(KBr) for Dodecyloxy Derivative. 3072 (m, =C-H Str. of phenyl nucleus), 2928 and 2854 (strong (s), C-H aliphatic sym. and asym. str.), 1728 (s, Aromatic C=O Str.), 1654 (-C=O str. of chalcone), 1597 (C=C Str. of vinyl group of chalcone and aromatic), 1508 (m,

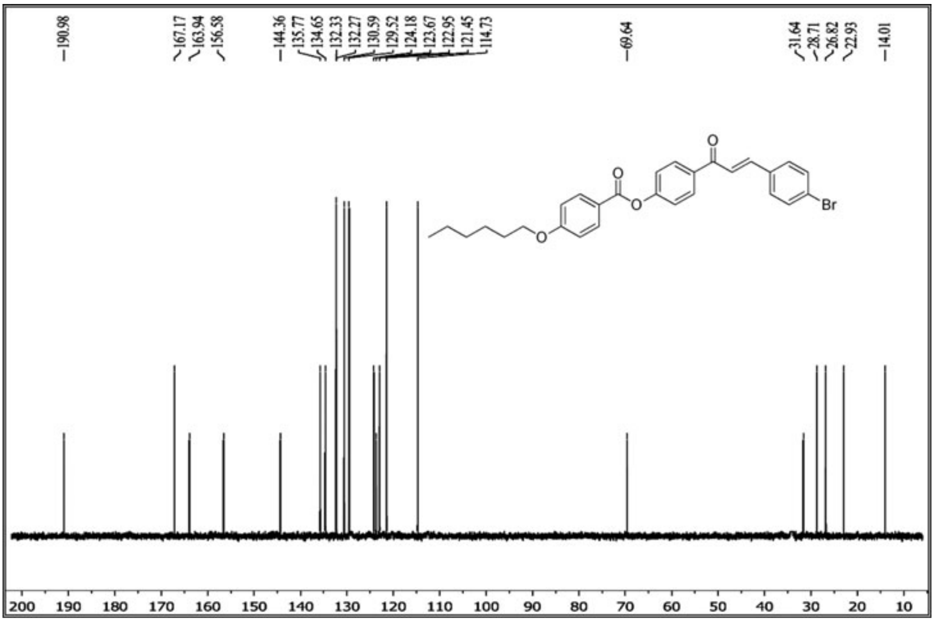


Figure 4. ^{13}C spectrum of hexyloxy derivative.

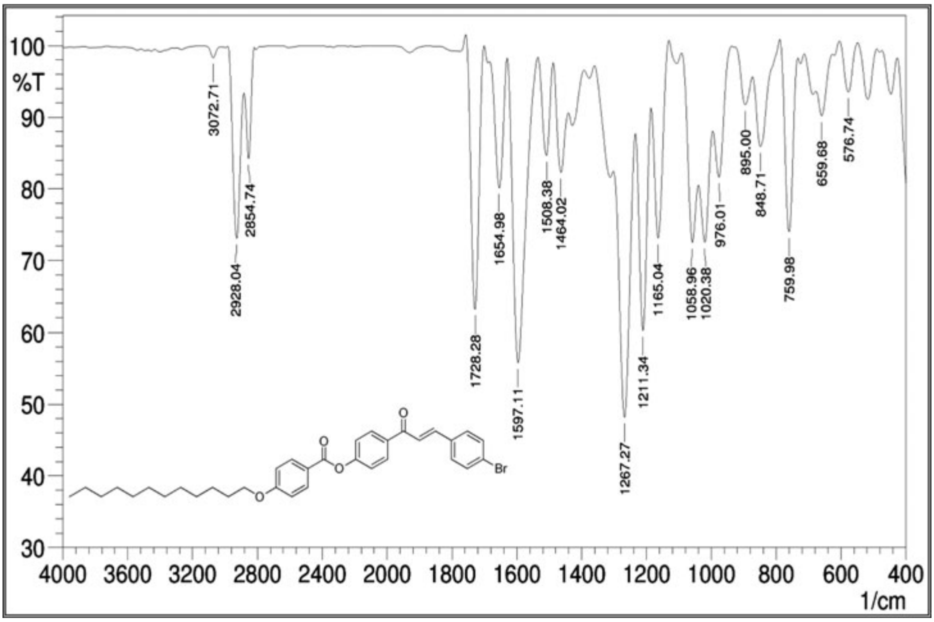


Figure 5. IR spectrum of dodecyloxy derivative.

C-C aromatic str.), 1464 (m, C-H bend alkanes), 1267–1058 (C-O-C Str. of alkoxy), 1185 (C-CO-C Str.) 848 (C-H oop. phenyl ring), 759 (C-H oop. bending of phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Tetradecyloxy Derivative. 3080 (m, =C-H Str. of phenyl nucleus), 2918 and 2847 (s, C-H aliphatic sym. and asym. str.), 1724 (s, Aromatic C=O Str.), 1658 (-C=O str. Of chalcone), 1597 (C=C Str. of vinyl group of chalcone and aromatic), 1508 (m, C-C aromatic str.), 1465 (m, C-H bend alkanes), 1247–1064 (C-O-C Str. of alkoxy), 1159 (C-CO-C Str.) 848

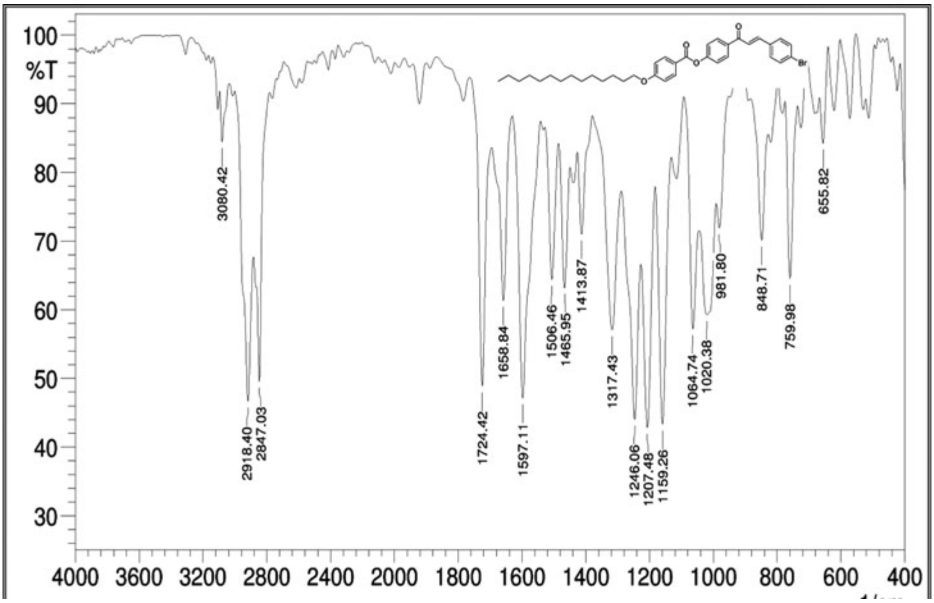


Figure 6. IR spectrum of tetradecyloxy derivative.

Figure 7. Mass spectrum of butyloxy derivative.

(C-H oop. phenyl ring), 759 (C-H oop. bending of phenyl ring). The IR data are consistent with the molecular structure.

Mass Spectra of Butyloxy Derivative. m/z (rel. int%): 480 $(M)^+$, 177 (base peak, ester linkage break), 121 (p-hydroxy benzoic acid).

Mass Spectra of Octyloxy Derivative. m/z (rel. int%): 536 $(M)^+$, 538 (M+2) (bromo pattern), 423 ($M-C_8H_{17}$), 233 (base peak, ester linkage break), 121 (p-hydroxy benzoic acid).

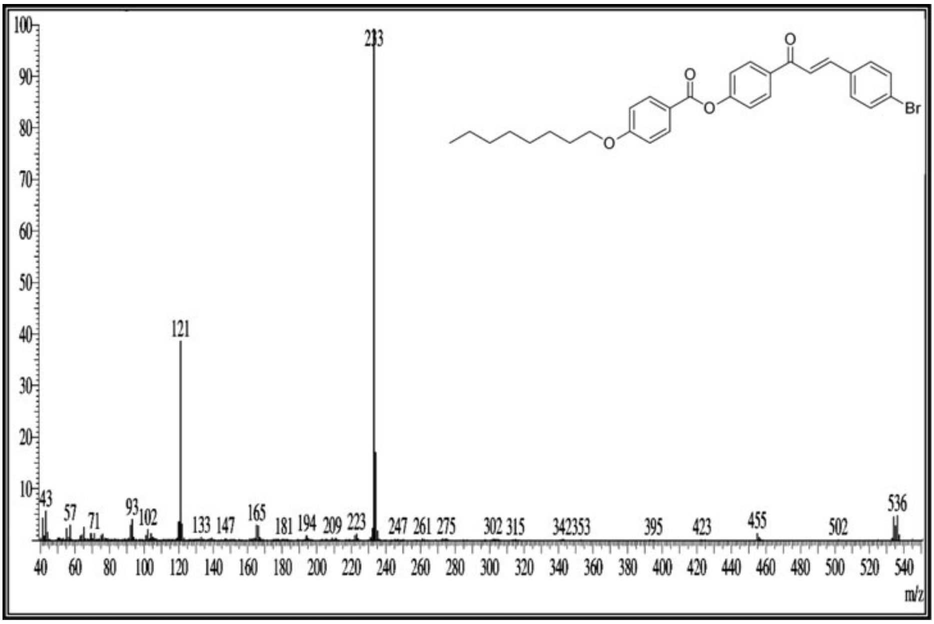


Figure 8. Mass spectrum of octyloxy derivative.

Table 2. Transition temperatures of series 1.

		Transition temperatures (°C)		
Compound No.	R = n-alkyl group	Sm	N	Isotropic
1	Methyl	177.3	—	185.8
2	Ethyl	147.9	—	158.4
3	Propyl	168.5	—	173.6
4	Butyl	142.2	—	150.3
5	Pentyl	139.3	—	148.4
6	Hexyl	146.5	—	156.2
7	Heptyl	140.4	—	154.1
8	Octyl	141.1	—	151.2
9	Decyl	137.1	—	148.0
10	Dodecyl	136.7	—	145.1
11	Tetradecyl	122.1	—	143.8
12	Hexadecyloxy	118.2	—	142.6

Sm: smectic; N: nematic.

Texture determination by the miscibility method:

- Octyloxy homologue: smectic-C.
- Tetradecyloxy homologue : smectic-A.

Results and discussion

Novel homologous series of chalconyl ester derivatives of 12 enantiotropically smectogenic homologues is prepared by linking non-mesomorphic component α-4-hydroxy benzoyl β-4′-bromo phenyl ethylene (m.p. 165–170°C, yield 72–74%) and dimeric 4-n-alkoxy benzoic acids. Nematogenic character of the series is absent. Textures of smectogenic mesophase are judged directly from the heating top of an optical polarizing microscopy except some selected members of the series by the miscibility method. Transition and melting temperatures (Table 2) as determined by an optical polarizing microscopy equipped with a heating stage are plotted against the number of carbon atoms present in n-alkyl chain of the left n-alkoxy flexible terminal end group. Transition curves Cr-Sm and Sm-I are obtained by linking similar or related points as depicted in phase diagram shown in Fig. 9. Cr-Sm transition curve in a phase diagram rises and falls in zigzag path as series is ascended with overall descending tendency. Sm-I transition curve initially falls for odd and even members of a series up to pentyloxy (C_5) homologue and then rises and pass through maxima at hexyloxy (C_6) homologue and then continuously descends, as series is ascended up to C_{16} homologue. Sm-I transition curve exhibited odd-even effect. Thus, both transition curves (Sm-I and Cr-Sm) behaved in a normal established manner. The transition curves for odd and even members up to C_5 homologue adversely occupied their positions, i.e., a curve for even members in Sm-I transitions occupies lower position as compared with the position of Sm-I curve drawn for odd members (C_1 to C_5). The curves for odd and even members merge into each other at C_5 homologue and extend as a single transition curve. The LC properties of a novel series varies from homologue to homologue in the same series, whose isotropic transition temperature varies between 142.6°C and 185.8°C, and the Cr-Sm transition temperature varies between 118.2°C and 177.3°C from the last (C_{16}) to the first (C_1) homologue. Thus, present novel series is fully smectogenic with higher middle ordered melting type and short range liquid crystallinity without exhibition of nematic phase.

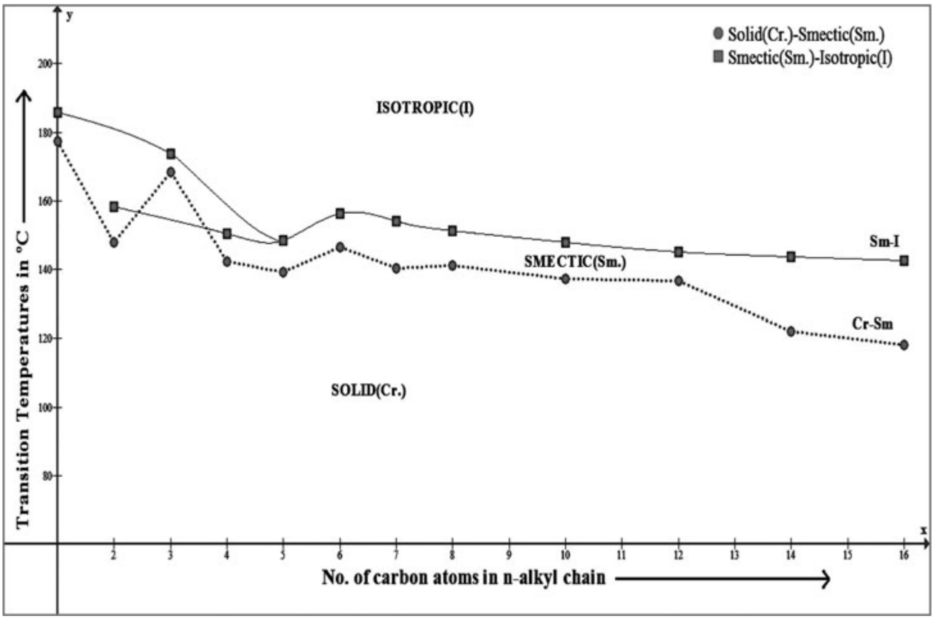


Figure 9. Phase behavior of series.

First two members of 4-n-alkoxy benzoic acid series are non-mesomorphic and the rest of the homologues are smectic and/or nematogenic. However, only smectogenic mesomorphism was induced in the present novel series by linking α-4-hydroxy benzoyl β-4′-bromo phenyl ethylene with 4-n-alkoxy benzoic acids because the molecular length or size increased. Consequently, molecular polarity and polarizability enhanced, which increased suitable magnitudes of anisotropic forces of lateral intermolecular attractions due to permanent dipole moment across long molecular axis, dipole–dipole interactions, and dispersion forces to set lamellar packing of molecules in their crystal lattices to favor the formation of focal conic molecular arrangement to induce smectogenic property under exposed thermal vibrations in floating condition. Disappearance of dimerization of 4-n-alkoxy benzoic acids is attributed to the breaking of hydrogen bonding between two molecules by esterification process. Alternation of transition temperatures observed from C_1 to C_7 homologues is due to even and odd numbered methylene units present in n-alkyl chain of left n-alkoxy end group. The exhibition of only smectic property by all the members (C_1 to C_{16}) of a series is attributed to the suitable magnitudes of anisotropic forces of intermolecular lateral attractions because of preoccupied lamellar packing of molecules in their rigid crystal lattices, which forms focal conic textures under the influence of exposed thermal vibrations. This weakens intermolecular cohesion, and the molecular layers in their crystal lattices become free to slide and rotate over one another, inducing commencement of smectic phase at Cr-Sm transition temperature, and continue till Sm-I transition temperature gives smectogenic mesophase length of 5.1 to 24.4°C. However, on continued heating the smectic phase, the forces holding the planes of layers between the sides of the molecules weaken to such an extent that the resultant intermolecular end-to-end attractions fail to maintain parallel orientational order of molecules. This hinders or diminishes the possibility of nematic mesophase formation, or nematic mesophase is missing beyond smectic mesophase, and molecules under examination are randomly oriented in all possible directions with high order of disorder or high entropy ($\Delta S = \Delta H/T$) at isotropic temperature. The isotropic state of a sample on cooling with proper rate of cooling reproduce

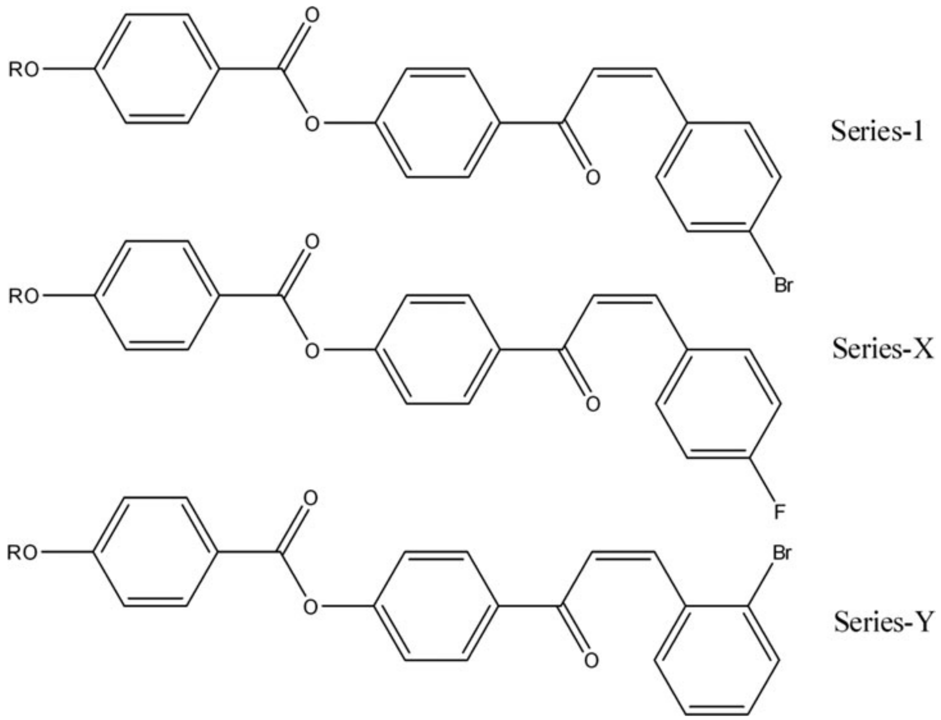


Figure 10. Structurally similar homologous series

smectic phase at a temperature at which it disappeared, i.e., smectic phase reversibly appears enantiotropically at the cost of nematic mesophase formation. The odd-even effect from and beyond C_5 homologue disappears because of longer n-alkyl chain of left n-alkoxy terminal end group, which may coil or bend or flex or couple to lie with major axis of core structure. Thus, unexpected status of n-alkyl chain from and beyond C_5 gives rise to single transition curve with missing odd-even effect. Variations in mesogenic properties from homologue to homologue in the present series are attributed to the sequentially added methylene unit or units at the n-alkyl chain. This alters permanent dipole moment across the long molecular axis, dipole–dipole interactions, electron–electron interactions, dispersion forces, molecular flexibility, etc. Thus the present fully smectogenic homologous series is upper middle ordered melting type and short degree of mesomorphism. Some mesogenic properties of the presently investigated series 1 are compared with the structurally similar known series X [31] and Y [32] as shown in Fig. 10.

Figure 10 represents structurally similar homologous series 1, X, and Y. Series 1, X, and Y are identical with respect to three phenyl rings and two common central bridges –COO– and –CO-CH=CH– constituting molecular rigidity, which is almost equivalent for series 1, X, and Y. However, the magnitudes of flexibility contributed to the total flexibility, which varies from homologue to homologue in the same series but remains identical for the same homologue from series to series. Thus, molecular rigidity and part of flexibilities for the same homologue from series 1 to Y are almost equivalent. The flexibility contribution by tail groups, viz. para-Br, para-F, and ortho-Br varies for the same homologue from series 1 to X to Y but remains unaltered from homologue to homologue in the same series. Thus, variation in liquid crystal properties and the degree of liquid crystallinity for the same homologue undergoes variations

Table 3. Average thermal stability (°C).

Series	1	X	Y
Smectic–isotropic or Smectic–nematic	154.79 $[C_1\text{-}C_{16}]$	158.55 $[C_1\text{-}C_{16}]$	100.60 $[C_{14}\text{-}C_{16}]$
Commencement of smectic phase	C_1	C_1	C_8
Nematic–isotropic commencement of nematic phase	—	—	—
Total mesophase length in °C (Sm + Nm)	5.1 to 24.4 C_3 C_{16}	5.1 to 74.5 C_{12} C_{14}	2.9 to 15.3 C_{14} C_{16}

due to variations in molecular flexibility induced by tail groups either by changing tail terminal group's para-Br and para-F or by changing the substitutional position of -Br from para to ortho (series Y). Hence, changing trend in mesogenic properties in the present comparative study predominantly undergoes alteration, which is based on changing magnitudes of molecular flexibility. Table 3 represents some LC properties of series 1, X, and Y under comparison.

Table 3 represents type of mesophase induced, commencement of mesophase, mesophase length range from minimum to maximum, etc. Table 3 is summarized as under:

- Homologous series 1, X, and Y are only smectogenic without exhibition of nematogenic property.
- Smectic thermal stability for series 1 and X is almost nearer and differs by about 4 units and is higher by 54.19 units from isomeric series Y.
- Smectogenic mesophase commences from the very first member of series 1 and X, and continued up to the last C_{16} member of the series in enantiotropic manner. The commencement of smectic phase takes place from octyloxy (C_8) homologue in monotropic manner and continued in monotropic manner for higher homologues C_{10} and C_{12}, and in enantiotropic manner for C_{14} and C_{16} homologues.
- Total mesophase length of series 1 is lower than series X but higher than an isomeric series Y.
- Nematic mesophase formation is missing for all the three series (1, X, and Y) under comparative study.
- The exhibition of only smectic property by all the series under comparative study is attributed to the preoccupied lamellar packing of molecules in rigid crystal lattices, which resist exposed thermal vibrations and occupy sliding layered arrangement in floating condition at Cr-M transition temperature and then continue till the other higher transition till Sm-N or Sm-I transition temperature. In the present comparison, the end-to-end intermolecular attractions are weakened to such an extent that exhibition of nematic phase is not entertained by thermometric environment to float on the surface with statistically parallel orientational order at Sm-I transition temperature, and the nematogenic mesophase formation is restricted to occur at the cost of smectogenic mesophase formation. Variation in the size of halogen atoms -Br and -F is due to atomic radii, which contribute to the magnitudes of molecular polarity, polarizability, and intermolecular closeness as well as the extent of molecular non-coplanarity for the same homologue from series to series. Moreover, in the case of para-Br (aeries 1) and ortho-Br (series Y) substitution, although both groups are the same, their positions of substitution are different. Their contribution toward molecular rigidity, polarity, polarizability, intermolecular closeness, extent of non-coplanarity of a molecule, etc. differs for the same homologue from series 1 to Y. The extent of molecular non-coplanarity

for series 1 and X being nearly equal or equivalent, the smectic property commences from the very first member of the series. However, for series Y, the -Br group, being substituted at ortho position, increases intermolecular distance and reduces suitable magnitudes of intermolecular lateral attractions. Therefore, smectic mesophase commences late from the octyloxy (C_8) member of series Y due to differing in the extent of molecular non-coplanarity, which facilitates smectic phase in monotropic condition for C_8 to C_{12} and in enantiotropic condition for C_{14} and C_{16} homologues. Smectic-isotropic thermal stabilities for homologous series X, 1, and Y are in the decreasing order as the atomic size of tail group increases from series X to 1 (-F to -Br), but in the case of isomeric series 1 and Y, the atomic size is the same but their place of substitution (para-Br and ortho-Br) is different. Para-substituted -Br group is more flexible than ortho-substituted -Br group, which is influenced by steric hindrance, but its lateral position increases polarizability as compared with series 1. Thus, the intermolecular distance factor predominates for isomeric series Y more effectiveness to reduce intermolecular cohesion. Thus, energy stored in molecule (ΔH) for the same homologue reduces from series 1 to Y. Hence, the facilitation of smectogenic mesophase takes place late from C_8 homologue with lower value of thermal stability for an isomeric series Y as compared with series 1 of the present investigation. The homologous series 1 with para-substituted -Br tail group is less non-coplanar than the ortho-substituted -Br lateral group, which induces early (C_1) smectic phase as compared with smectic phase that appeared late from octyloxy (C_8) homologue. Thus, molecular structure of a substance plays an important role to mesogenic behaviors and the degree of mesomorphism.

Conclusions

- Novel chalconyl ester homologue of para bromo-substituted tail group is entirely smectogenic in enantiotropic condition, whereas isomeric series or the bromo-substituted tail group is partly smectogenic and partly non-mesogenic.
- The mesophase length reduces regardless of increasing size of -Br group which should increase polarizability but it may reduce comparatively flexibility due to its bulkiness and hence it may be less effective to thermal stability.
- Halogen-substituted tail group induces preferably smectogenic character in a substance, and probably avoids inducing nematic property.
- The group efficiency order derived on the basis of (i) thermal stability, (ii) early commencement of mesophase, and (iii) mesophase length range are as follows
  - (i) *Smectic*:para-F > para-Br > ortho-Br
  - (i) *Nematic*:para-Br = para-F = ortho-Br.
  - (ii) *Smectic*: para-Br = para-F > ortho-Br.
  - (iii) *Smectic*:para-F > para-Br > ortho-Br.
- Suitable magnitudes of combined effect of molecular rigidity and flexibility can induce mesogenic property in a substance.
- Phenomenon of mesomorphism is very sensitive and susceptible to molecular structure.
- Thermotropic LC behaviors of the present novel chalconyl derivatives are less important for their utility due to poor range of liquid crystallinity and upper middle order of transition temperature, but chalconyl structure, being biologically active, can be useful

and exploited for pharmaceutical and medicinal purpose. However, novel substances are always useful for scientific and technological research.

Acknowledgments

Authors acknowledge thanks to the Department of Chemistry (DST-FIST funded & UGC-SAP sponsored), Saurashtra University, Rajkot, for research work. Authors are also thankful to Dr. A. V. Doshi, Ex. Principal M.V.M. Science and Home Science College, Rajkot, for his valuable cooperation during the present investigation as and when needed. Also, thanks are due to the National Facility for Drug Discovery through New Chemical Entities (NCEs), for analysis of samples.

References

[1] Reinitzer, F. (1888). *Monatsh Chem*. *9*, 421.

[2] Gray, G. W. (1962). *Molecular Structure and Properties of Liquid Crystals*, Academic Press: London.

[3] Stewart, G. T. (1974). The role of liquid crystals in life processes. In: *Liquid Crystals & Plastic Crystals*, Ellis Horwood: Chichester, UK, Vol. 1, Gray, G. W. & Winsor, P. A. (Eds.), Chapter 6.2, pp. 308–326.

[4] Gray, G. W., & Jones, B. (1954). *J. Chem. Soc., 1*, 2556–2562.

[5] Gray, G. W., & Winsor, P. A. (1974). *Liquid Crystals & Plastic Crystals*, Ellis Horwood: Chichester, UK, Vol. 1, Chapter 4, pp. 103–153.

[6] Imrie, C. T. (1999). *Struct. Bond*., *95*, 149–192.

[7] Naemura, S. (2001). *Displays*, *22*(1), 1.

[8] Kim, W. S., Elston, S. J., & Raynes, F. P. (2008). *Display*, *29*, 458–463.

[9] Tadwee, I., Shahi, S., Ramteke, V., & Syed, I. (2012). *IJPRAS*, *1*(2), 6–11.

[10] Lee, Y. S., Lim, S. S., Shin, K. H., Kim, Y. S., Ohuchi, K., et al. (2006). *Biol. Pharma. Bull*., *29*, 1028–1031.

[11] Jahng, Y., Zhao, L., Moon, Y., Basnet, A., Kim, E., et al. (2004). *Bioorg. Med. Chem. Lett*., *14*, 2559–2562.

[12] Rajesh, G., Mansi, K., Srikant, K., Babasaheb, B., Nagesh, D., et al. (2008). *Chem. Pharm. Bull*., *56*, 897–901.

[13] Gaikwad, P. P., & Desai, M. T. (2013). *Int. J. Pharma. Res. Rev*., *2*(12), 40–52.

[14] Jain, U. K., Bhatia, R. K., Rao, A. R., Singh, R., Saxena, A. K., et al. (2014). *Trop. J. Pharma. Res*., *13*(1), 73–80.

[15] Demus, D. (1988). *Mol. Cryst. Liq. Cryst*., *165*, 45–84.

[16] Demus, D. (1989). *Liq. Cryst*., *5*, 75–110.

[17] Imrie, C. T., & Luckhrust, G. R. (1998). Liquid crystal dimmers and oligomers. In: *Handbook of Liquid Crystals*, Vol. 2B, *Low Molecular Weight Liquid Crystals*, Demus, D., Goodby, J., Gray, G. W., Spiess, H. W. & Vill, V. (Eds.), Wiley-VCH: Weinheim, Germany, pp. 801–833.

[18] (i)Suthar, D. M., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst*., *575*(1), 76–83. (ii) Chauhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst*., *570*(1), 12–19. (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.

[19] (a) Patel, B. H., & Doshi, A. V. (2014). *Mol. Cryst. Liq. Cryst*., *605*, 23–31. (b) Patel, B. H., & Doshi, A. V. (2014). *Mol. Cryst. Liq. Cryst*., *605*, 42–51. (c) Patel, B. H., & Doshi, A. V. (2014). *Mol. Cryst. Liq. Cryst*., *605*, 61–69. (d) Kotadiya, V. C., Khunt, M. D., & Bhoya, U. C. (2014). *Mol. Cryst. Liq. Cryst*., *593*, 165–176. (e) Khunt, M. D., Kotadiya, V. C., & Bhoya, U. C. (2014). *Mol. Cryst. Liq. Cryst*., *605*, 32–41.

[20] (a) Kotadiya, V. C., & Bhoya, U. C. (2015). *Mol. Cryst. Liq. Cryst*., *608*, 116–124. (b) Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst*., *577*, 51–58. (c) Chauhan, H. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst*., *569*, 33–39. (d) Chaudhari, R. P., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst*., *582*, 63–71.

[21] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Mc Donnell D.G. (1993). *Liq. Cryst*., *15*, 123.

[22] Collings, P. J., & Hird, M., (1998). *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis: London.

[23] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Adv. Mater.*, *4*, 285.

[24] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741.

[25] Lohar, J. M., & Doshi, A. V. (1993). *Ind. Acad. Sci. Chem. Sci.*, *105*(3), 209–214.

[26] Doshi. A. V. & Ganatra, K. J. (2000). *J. Ind. Chem. Soc.*, *77*, 322–325.

[27] Bhoya, U. C., Travadi, J. J., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*(1), 10–15.

[28] Dave, J. S., & Vora, R. A., (1970). In: *Liquid Crystal and Ordered Fluids*, Johonson, J. F. & Porter R. S. (Eds.), Plenum Press: New York, NY, pp. 477.

[29] Patel, R. B., Patel, V. R., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 3–9.

[30] Nagaveni, N. G., & Prasad, V. (2013). *Phase Tran.*, *86*(12), 1227–1240.

[31] Rola, R. R., Bhola, G. N., & Bhoya, U. C. (2015). *Int. Lett. Chem. Phys. Astron.*, *8*(1), 67–76.

[32] Maheta, S. A., Bhola, G. N., & Bhoya, U. C. (2015). *Int. Lett. Chem. Phys. Astron.*, *8*(1), 77–86.