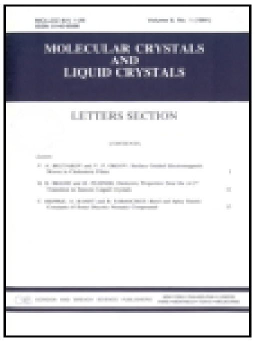


Molecular Crystals and Liquid Crystals

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

Study of Novel Symmetrical Liquid Crystalline Ester Dimers

V. C. Kotadiya & U. C. Bhoya

To cite this article: V. C. Kotadiya & U. C. Bhoya (2015) Study of Novel Symmetrical Liquid Crystalline Ester Dimers, Molecular Crystals and Liquid Crystals, 616:1, 19-27, DOI: 10.1080/15421406.2014.990186

To link to this article: http://dx.doi.org/10.1080/15421406.2014.990186

Mol. Cryst. Liq. Cryst., Vol. 616: pp. 19–27, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.990186

Study of Novel Symmetrical Liquid Crystalline Ester Dimers

V. C. KOTADIYA AND U. C. BHOYA*

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

*A novel homologous series of 12 symmetrical dimers, viz. 1,1'-Bis[4-(4'-*n*-alkoxy benzoyloxy)-3-methyl phenyl] cyclohexanes is reported. Nematogenic mesophase commences from the heptyloxy homologue dimer and continues up to the hexadecyloxy dimer in an enantiotropic manner without the exhibition of any smectogenic behavior. The rest of the dimers from methoxy to hexyloxy are nonmesogenic. The textures of the nematic phase are threaded or Schlieren. The transition temperatures and textures of the nematic phase were determined by an optical polarizing microscope equipped with a heating stage. Curves (solid-isotropic/nematic and N-I) of a phase diagram showing mesomorphism behave in normal manner except for a minor deviation at the dodecyloxy derivative. The analytical and spectral data confirm the molecular structure of dimers. The nematogenic mesophase lengths vary between 3.3°C and 26.6°C. The average thermal stability for nematic is 108.26°C; series is partly nematogenic with middle ordered melting type and low degree of mesomorphism. Liquid crystal properties of novel dimer series are compared with the structurally similar other known series.*

Keywords Dimers; enantiotropy; liquid crystal; nematic; smectic

Introduction

Liquid crystalline (LC) substances are useful in a wide range of applications. Therefore physicists, chemist, biologists, pharmacists, microbiologists, and engineers have exploited the special properties of liquid crystals. LC substances are flowing crystals discovered in 1888 [1–4] and since that time lots of novel conventional and unconventional LC substances have been synthesized through homologous series and/or binary systems and characterized by spectroscopic, microscopic, and other related analysis to derive the relations between molecular structure and LC behavior [5–7]. Oligomers with LC properties are useful materials. The simplest oligomer is a dimer [8,9]. Therefore, the work reported here is aimed to synthesize novel symmetrical dimers with two same mesogenic units bonded to a common spacer. The thermotropic symmetrical LC dimers will be studied through an optical polarizing microscope equipped with a heating stage. The results will be interpreted in terms of molecular rigidity and flexibility depending on molecular structure [10–13].

---

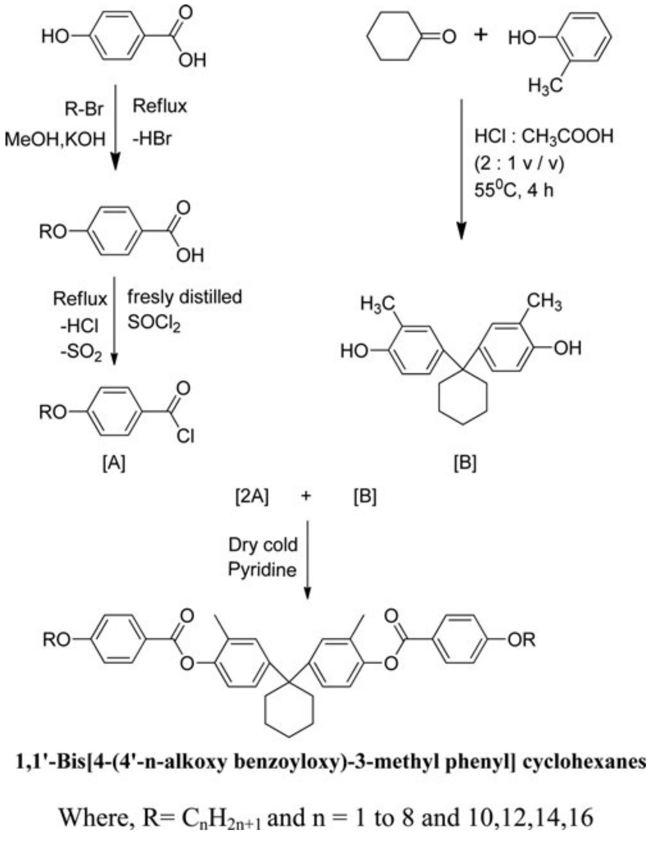
*Address correspondence to U.C. Bhoya, Department of Chemistry, Saurashtra University, Rajkot 360005, Gujarat, India. E-mail:drucbhoya@gmail.com

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

Experimental

Synthesis

As shown in Scheme 1, we synthesized 4-*n*-alkoxybenzoic acids by using 4-hydroxybenzoic acid and suitable alkyl bromides (R-Br) in methanol in the presence of KOH [14]. Different substituted 4-*n*-alkoxybenzoyl chlorides were prepared through the reaction between 4-*n*-alkoxybenzoic acids and an excess of thionyl chloride under reflux until the starting material was totally consumed [14]. 1,1-bis (3-methyl-4-hydroxyphenyl) cyclohexane material was synthesized by a reported method (m.p. 185–187°C) (yield 75–80%) [15]. The 4-*n*-alkoxybenzoyl chlorides and 1,1'-bis (3-methyl-4-hydroxyphenyl) cyclohexane in dry cooled pyridine were stirred overnight at room temperature [16]. Then reaction mixture was poured into cold 1:1 HCl in ice then filtered, washed, dried, and purified until constant transition temperatures were obtained. Purifications of all intermediate products and objective compounds were repeated many times and judged to be pure by TLC which showed only one spot.



Scheme 1. Synthetic route to the novel series.

4-Hydroxybenzoic acid, methanol, KOH, thionyle chloride, cyclohexanone, 2-methylphenol, pyridine, ethanol, acetic acid, hydrochloric acid, etc. were used as received, except for solvents, which were dried, purified, and distilled prior to use.

Table 1. Elemental analysis for (1) methyloxy, (2) propyloxy, and (3) tetradecyloxy derivatives

		Elements%found			Elements%calculated		
Sr. No.	Molecular formula	C	H	O	C	H	O
1	$C_{36}H_{36}O_6$	76.50	6.41	17.09	76.57	6.43	17.00
2	$C_{40}H_{44}O_6$	77.49	7.09	15.41	77.39	7.14	15.46
3	$C_{62}H_{88}O_6$	80.02	9.61	10.37	80.13	9.54	10.33

Characterization

The constitutions of all the synthesized compounds were characterized by various analytical techniques. Elemental analysis was performed using a Perkin Elmer PE 2400 CHN Analyzer-Waltham, Massachusetts, USA system (Table 1). The structures of the materials were elucidated by infrared (IR) spectroscopy (SHIMATZU FTIR-8400 Spectrophotometer Nishinokyou Kuwabara-cho, Nakagyo-Ku Kyoto, Japan. infrared spectrophotometer), proton nuclear magnetic resonance (^{1}H NMR) spectrometry (BRUKER Avance-III (400 MHz) Spectrometer-Billerica, Massachusetts, USA 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 expected structures.

Analytical Data

Elemental analysis (Table 1)

Spectral Data

^{1}H NMR in ppm for Butyloxy Derivative

8.072–8.050 (d,4H, Ar–H), 7.313–7.305 (d, 2H, Ar–H), 7.221–7.200 (d, 2H, Ar–H), 7.126–7.104 (d, 2H, Ar–H), 7.094–7.073 (d, 4H, Ar–H), 4.104–4.072 (t, 4H, 2 × Ar–OCH_2–), 2.116 (s, 6H, 2 × Ar-CH_3), 1.901–1.857 (t, 4H, cyclohexane–H), 1.751–1.714 (t, 4H, 2×Ar-OCH_2-CH_2), 1.421–1.495 (m, 10H, cyclohexane–6H&aliphatic–4H), 0.961–0.924 (t, 6H, 2 × Ar-O-$(CH_2)_3$-CH_3). The ^{1}H NMR data are consistent with the molecular structure.

^{1}H NMR in ppm for Pentyloxy Derivative

8.094–8.048 (d,4H, Ar–H), 7.311–7.302 (d, 2H, Ar–H), 7.222–7.218 (d, 2H, Ar–H), 7.201–7.148 (d, 2H, Ar–H), 7.122–7.072 (d, 4H, Ar–H), 4.096–4.064 (t, 4H, 2 × Ar–OCH_2–), 2.115 (s, 6H, 2 × Ar-CH_3), 1.920–1.844 (t, 4H, cyclohexane–H), 1.761–1.724 (t, 4H, 2 × Ar-OCH_2-CH_2), 1.490–1.406 (m, 10H, cyclohexane–6H&aliphatic–4H), 1.335–1.300 (m, 4H, aliphatic–4H), 0.900–0.865 (t, 6H, 2 × Ar-O-$(CH_2)_4$-CH_3). The ^{1}H NMR data are consistent with the molecular structure.

IR in cm^{-1} for Ethyloxy Derivative

3061.13 (w, C—H Str. of aromatic ring), 2928.04, 2860.53 (s, C—H Str. of alkane, Sp^3 carbon), 1730.21(s, C = O Str. ester), 1604.83, 1504.53 (C = C Str. in aromatic ring), 1452.45 (m, C—H bend alkane), 1257.63 (s, aromatic C—O Str. & C = C Str.)1163.11, 1114.89, 1057.03 (s, aliphatic C—O Str. & second overtone C—-H Str.), 860.28, 763.84 (meta-, ortho-, and para-substituted phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Octyloxy Derivative

3068.85 (w, C—H Str. of aromatic ring), 2941.54, 2858.60 (s, C—H Str. of alkane, Sp^3 carbon), 2505.52, 2422.67, 2333.94 (combination of C—H Str.), 1728.28 (s, C = O Str. ester), 1604.83,1504.53 (C = C Str. in aromatic ring), 1450.50 (m, C—H bend alkane), 1267.27 (s, aromatic C—O Str. and C = C Str.) 1192.11, 1161.19.89, 1072.46(s, aliphatic C—O Str. and second overtone C-H Str.), 858.35, 767.69 (meta-, ortho-, and para-substituted phenyl ring) The IR data are consistent with the molecular structure.Where, s = strong, m = medium, w = weak.

Mass Spectra of Octyloxy Derivative

m/z (rel. int%): 760 (M)$^+$, 599,482,233,121

Mass spectra of Decyloxy Derivative

m/z (rel. int%): 817(M)$^+$,534, 414, 294,121

Results and Discussion

The novel homologous series of symmetrical dimers of 1,1′-bis[4-(4′-*n*-alkoxy benzoyloxy)-3-methyl phenyl] cyclohexanes consist of two identical mesogenic units involving —COO— central groups bonded to a cyclohexyl ring at the 1 and 4 positions. The mesogenic units are derived from *n*-alkoxybenzoic acids, whose dimerisation disappears by the esterification process. The methoxy to hexyloxy dimers are nonliquid crystals (NLC), while the heptyloxy, octyloxy, decyloxy, dodecyloxy, tetradecyloxy, and hexadecyloxy homologues are LC as enantiotropic nematogenic character. Smectogenic property is totally absent for all the LC members of the series. Transition and melting temperatures of homologues were determined by an optical polarizing microscope equipped with a heating stage. Transition temperatures of the homologues (Table 2) as well as the textures of homologues were plotted versus the number of carbon atoms present in *n*-alkyl chain of the left *n*-alkoxy terminal end group. Transition curves, viz., solid-nematic and nematic-isotropic were obtained by linking like or related transition points forming a phase diagram showing phase behaviors of the novel series of dimers (Fig. 1). The solid-nematic transition curve follows a zigzag path of rising and falling values with an overall descending tendency and behaves in a normal manner. The nematic-isotropic transition curve initially rises and then descends to the dodecyloxy homologue and then ascends to the tetradecyloxy dimer and again descends to the hexadecyloxy derivative. Thus, the N-I transition curve adopts a serpentine shape. The textures of the nematic mesophases are threaded or Schlieren as determined by a miscibility method. The N-I transition curve exhibits an odd-even effect. The curves for

Table 2. Transition temperatures in °C of series-1

		Transition temperature in °C		
Compound no.	n-alkyl group C_nH_{2n+1} group (n)	Sm	N	Isotropic
1	1	—	—	117.9
2	2	—	—	115.8
3	3	—	—	120.4
4	4	—	—	110.2
5	5	—	—	130.8
6	6	—	—	90.1
7	7	—	96.1	101.7
8	8	—	93.0	98.0
9	10	—	95.6	122.2
10	12	—	100.2	111.1
11	14	—	90.8	115.1
12	16	—	98.2	101.5

Abbreviations: Sm, smectic; N, nematic.

odd and even homologues merge at the decyloxy dimer and then propagate as a single curve for the higher homologues. The nematogenic mesophase behavior of the series varies from homologue to homologue with the variation of number of carbon atom in n-alkyl chain. The average thermal stability for the nematic phase is 108.26°C and the mesophase length varies from a minimum of 3.3°C at the hexadecyloxy homologue to a maximum of 26.6°C at the decyloxy homologue. Thus, the present dimer series is partly nematogenic and partly nonmesomorphic with a poor degree of mesomorphism and a middle ordered melting type. The N-I transition curve is extrapolated to the pentyloxy homologue to determine its latent

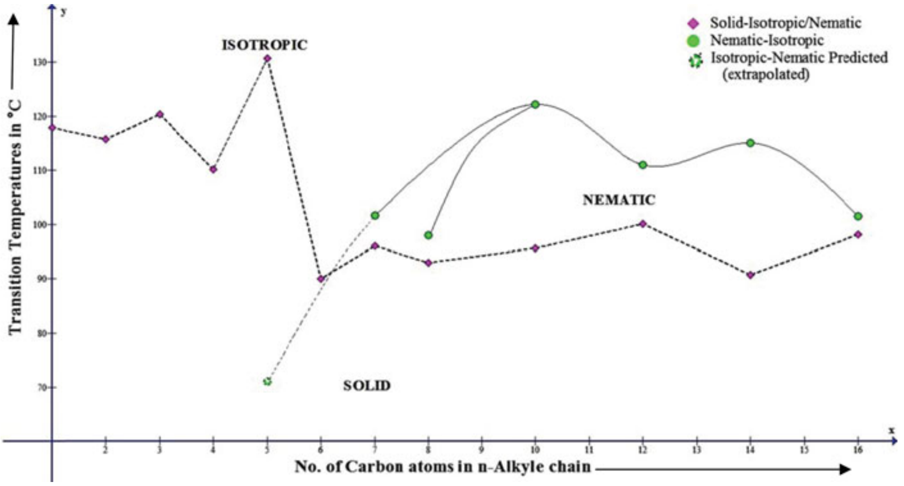


Figure 1. Phase behavior of series.

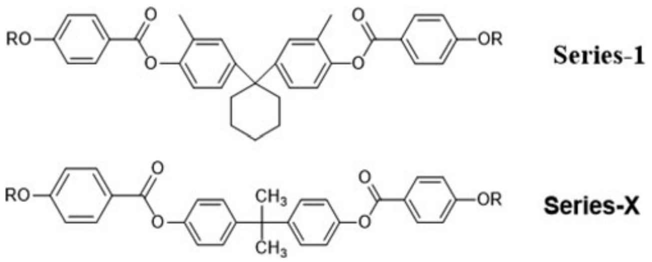


Figure 2. structurally similar dimer series.

transition temperature(LTT). The 1,1′-bis(3-methyl-4-hydroxyphenyl)cyclohexane (m.p. - 185 to 187°C) spacer to which two identical mesogenic units are linked is nonmesogenic. Though mesogenic temperatures of the dimer homologue are lower than the corresponding *n*-alkoxy benzoic acids, but the degree of mesomorphism of the novel dimers is reduced by esterification process. The presence of two methyl groups symmetrically situated under identical lateral positions increases intermolecular distance and molecular width. Therefore, increased intermolecular distance decreases the intermolecular attractions on one hand and at the same time increase the intermolecular distance by lateral substitution, and the methyl groups increase molecular polarizability and increase intermolecular attractions on the other hand. In the present investigation of the novel dimer series, the first effect predominates against second effect emerged by the polarizability effect. Therefore, suitable magnitudes of anisotropic forces of intermolecular end to end attractions are sufficient to resist exposed thermal vibrations for some temperature differences to maintain parallel orientational order of molecules in a floating condition on the surfaces, but the same magnitudes of anisotropic forces of intermolecular attractions is insufficient to cause lamellar packing of molecules in the crystal lattices of mesogenic dimers. Thus, only nematogenic mesophase of short range of liquid crystallinity occur very late from the heptyloxy homologue dimer without exhibition of any smectic property. The disappearance of dimerisation of *n*-alkoxy benzoic acids by esterification process is attributed to the breaking of hydrogen bonding between two molecules of *n*-alkoxy benzoic acids. The NLC behavior of the methoxy to hexyloxy homologues is attributed to their high crystallizing tendency arising from unsuitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of unfavorable molecular rigidity and flexibility, which induces an inability to resist exposed thermal vibrations. The merging of curves for the odd and even members of the series from and beyond the decyloxy homologue into a single curve for higher homologues is because of the coiling or bending or flexing or coupling of the longer *n*-alkyl chains of the mesogenic units to the principle axis of the core structure of molecules. The changing mesomorphic behavior from homologue to homologue in the series is due to the sequentially added methylene unit, which contributes to the molecular flexibility in varying proportions for the same series. The laterally substituted methyl groups reduce intermolecular end to end attractions. The isotropic temperatures of mesomorphic dimers vary between 98°C and 122.2°C. The LTT for nematic of pentyloxy homologue derivative is predicted 71°C by extrapolation [17,18] method. However, its realization is difficult due to its high crystallizing tendency and the temperature of isotropic-nematic transition being far below by 59°C from its isotropic temperature. The liquid crystal behaviors of the present series-1 are compared with another structurally similar series-X [19] as shown in Fig. 2.

Table 3. Average thermal stability in °C

Series	[1]	[X]
Smectic-nematic or isotropic	—	129.0
Commencement of smectic phase	—	$[C_6\text{-}C_{10}]$ C_6
Nematic –isotropic	108.26	147.7
Commencement of nematic phase	$[C_7\text{-}C_{16}]$ C_7	$[C_6\text{-}C_{16}]$ C_6

Homologous series-1 of present investigation and series-X chosen for comparison are identical with respect to mesogenic units, but they differ with respect to rest of the molecular part between the two mesogenic parts. Therefore the variations of mesomorphic properties and the degree of mesomorphism observes from series to series for the same homologue dimer and homologue to homologue for the same series can be attributed to the varying molecular part of the respective dimer series under comparison. Table 3 shows the liquid crystal properties of series-1 and X. The comparative points are mentioned below.

- Present series-1 is only nematogenic with the absence of smectogenic property, whereas series-X is smectogenic in addition to nematogenic character.
- Nematogenic mesophase commences from the heptyloxy dimer of the present series-1 while, it commences from hexyloxy dimer of a series-X.
- Smectogenic mesophase does not commence until the last member of the present series-1 while it commences from the hexyloxy dimer of a series-X.
- Thermal stability for nematic in case of series-1 is 108.26°C while thermal stabilities for nematic and smectic are 147.7°C and 129.0°C.
- Mesophase length varies between 3.3°C and 26.6°C for series-1 and it varies between 18°C and 56°C for series-X.

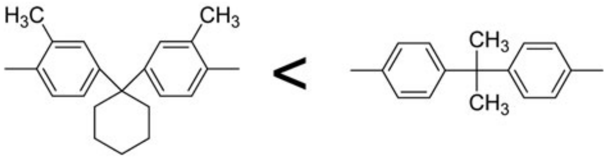
The presence of the cyclohexyl ring in the molecules of series-1 and two methyl groups substituted in the neighboring phenyl ring, comparatively increase the intermolecular distance more than for series-X. Thus, the intermolecular distance factor in the case of series-1 and X maintain suitable magnitudes of anisotropic forces of intermolecular end to end attractions to facilitate nematic mesophase formation for both series (1 and X). However, it is adequately sufficient for series X, but inadequately insufficient for series-1 to induce smectic mesophase formation due to unfavorable molecular polarizability factor. Thus, mesophase length and thermal stability of series-1 are relatively lower than for series-X. The absence of a smectic mesophase in series-1 is also attributed to the steric hindrance induced by the cyclohexyl ring and the presence of two methyl groups on the neighboring phenyl rings, and the relative extent of molecular noncoplanarity. Hence, variations of mesomorphic behaviors from homologue to homologue in same series and for the same homologue from series to series are due to the sequentially added methylene unit and changing molecular part at the middle of a molecule linking two phenyl rings or linking two same mesogenic units of each molecule of dimer series-1 and X.

Conclusions

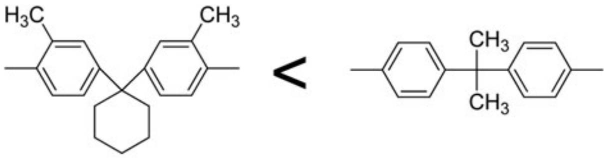
The presently investigated novel ester homologous series of symmetrical dimers is nematogenic without exhibition of smectogenic character, whose, mesophase length is shorter and is of middle ordered melting type.

Smectic and nematic group efficiency order derived on the basis of (i) thermal stabilities and (ii) the early commencement of mesophase are as under

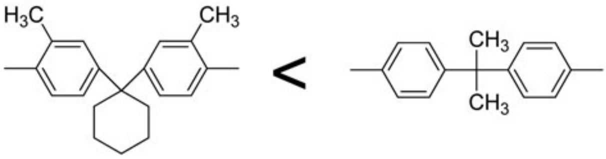
(i) ● **Smectic:**



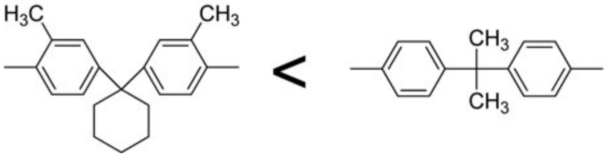
● **Nematic:**



(ii) ● **Smectic:**



● **Nematic:**



Solid-nematic transition temperature vary between 90°C and 100°C

Mesomorphism phenomenon is sensitive, susceptible, and depends upon a combine effect of molecular rigidity and flexibility.

Molecular rigidity and flexibility are totally depending upon only molecular structure of a substance.

Molecular flexibility varies with the status of *n*-alkyl chain bonded through oxygen atom to a phenyl ring.

Acknowledgments

The Authors acknowledge thanks to the Department of Chemistry (DST-FIST Funded & UGC-SAP Sponsored), Saurashtra University, Rajkot, for research work. Authors are also especially thankful to Dr. A.V. Doshi, Ex. Principal M.V.M. Science and Home Science College, Rajkot, for his valuable co-operation during 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). *Monatsch*, *9*, 421.

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

[3] Demus, D. (1989). Plenary Lectures 100 years of Liquid crystal chemistry; Thermaotropic liquid crystals with conventional and unconventional molecular structure. *Liq. Cryst.*, 5.

[4] (a) Gray, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystal*. Academic Press: London, vii + 314 pp. illus. 63s. (b) Gray, G. W. (1958). *Steric Effects in Conjugated System*. G. W. Gray ed., Bulterworths: London, pp. 150–159.

[5] Talwee, I., Shahi, S., Ramteke, V., & Syed, I. (2012). *Int. J. Pharm. Rese. Appl. Sci.*, *1*, 06–11.

[6] Gray, G. W., & Windsor, P. A. (1974). *Liquid Crystallogy &Plastic Crystallogy*, Ellis Horwood Ltd., Chichester: Ralsted Press. A division of John Wiley and Sons, Inc. New York, London, UK, Vol. 1, pp. 327–356, Chapters 4 and 7.

[7] (a) Darshanraj, B. K. et al. (2013). *Derpharma Chemica*, *5*(3), 305–317. (b) Kazuki, I. et al. (2013). *Appl. Biomater. Liq. Cryst.*, *18*, 4703–4717.

[8] (a) Imrie, C. T. (1999). *Struct. Bond.*, *95*, 149–192. (b) Imrie, C. T., & Henderson, P. A. (2007). *Chem. Soc. Rev.*, *36*, 2096–2124.

[9] (a) Ferarrini, A., Luckhurst, G. R., Nordio, P. L., & Roskily, S. J. (1993). *Chem. Phys. Lett.*, *214*, 409–417. (b) Ferarrini, A., Luckhurst, G. R., Nordio, P. L., & Roskily, S. J. (1996). *Liq. Cryst.*, *21*, 373–382. (c) Attard, G. S., Date, R. U., Imrie, C. T., Luckhurst, G. R., & Roskily, S. J. (1994). *Liq. Cryst.*, *16*, 529–581. (d) Md Lutfor, R., Asik, J., Kumar, S., Silong, S., & Zaki, M. Ab Rahman (2009). *Phase Transition*, *82*(3), 228–239.

[10] (a) Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741. (b) Hird, M., Toyne, K. J., & Gray, G. W., Day, S. E., & Mc Donnell, D. G. (1993). *Liq. Cryst.*, *15*, 123.

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

[12] Collings, P. J., & Hird, M., (1997). *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis: NewYork.

[13] Gonzales, Y., Ros, M. B., Serrano, J. L., & Pereziubind, A. (1998). *Liq. Cryst.*, *18*, 751.

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

[15] (a) Rao, M. V., Rojivadia, A. J., Parsania, P. H., & Parekh, H. H. (1987). *J. Ind. Chem. Soc.*, *64*, 758–759. (b) Garchar, H. H., Shukla, H. N., & Parsania, P. H. (1991). *Ind. Acad. Sci.-Chem. Sci.*, *103*, 149–153.

[16] (a) Doshi, A. V., & Ganatra, K. J. (1999). *Proc. Ind. Acad. Sci. (Chem. Sci.).*, *4*(11), 562. (b) Suthar, D. M., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *569*, 64. (c) Doshi, A. V., & Makwana, N. G. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 220. (d) Imrie, C. T., & Taylor, L. (1989). *Liq. Cryst.*, *6*, 1.

[17] (a) Travadi, J. J., Bhoya, U. C., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 10–15. (b) Ganatra, K. J., & Doshi, A. V. (2000). *J. Ind. Chem. Soc.*, *77*, 61–64.

[18] (a) Lohar, J. M., & Doshi, A. V. (1993). *Ind. Acad. Sci. Chem. Sci.*, *105*(3), 209–214. (b) Bhoya, U. C., Vyas, N. N., & Doshi, A. V., (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 104–110.

[19] Kotadiya, V. C., Khunt, M. D. & Bhoya, U. C. (2015). *Mol. Cryst. Liq. Cryst.*, *607*, 135–143.