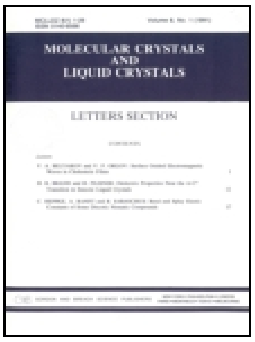


Molecular Crystals and Liquid Crystals

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

Mesomorphism dependence on molecular rigidity and flexibility

J. M. Patel & M. L. Chauhan

To cite this article: J. M. Patel & M. L. Chauhan (2016) Mesomorphism dependence on molecular rigidity and flexibility, Molecular Crystals and Liquid Crystals, 625:1, 38-46, DOI: 10.1080/15421406.2015.1068989

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1068989

MOL. CRYST. LIQ. CRYST.
2016, VOL. 625, 38–46
http://dx.doi.org/10.1080/15421406.2015.1068989

Taylor & Francis
Taylor & Francis Group

Mesomorphism dependence on molecular rigidity and flexibility

J. M. Patel[a] and M. L. Chauhan[b]

[a]Zydus Cadilla Healthcare Private Limited (R&D), Dabhsa Unit, Vadodara, Gujarat, India; [b]Sheth P. T. Arts & Science College, Godhra, Gujarat, India

ABSTRACT

A novel homologous series of mesogens was synthesized and studied with a view to understanding and establishing the relations between molecular structure and liquid crystal properties. Eleven members of the series were synthesized. Mesogenic behavior commences from the C_6 member and continues up to the C_{14} member. The rest of the members, C_1 to C_5 and C_{16}, are non-mesogenic. Mesogenic homologues (C_6 to C_{14}) are enantiotropically nematogenic. Textures of nematic phase are threaded or Schlieren. Transition temperatures were determined by an optical polarizing microscope equipped with a heating stage. Analytical and structural data confirm the molecular structures of homologues. Thermal stability for nematic phase is 198.0°C. Mesomorphic phase length ranges from 11.0°C to 50.0°C. Cr-I/N and N-I transition curves of a phase diagram behave in normal manner from C_1 to C_{12} members, and higher members C_{14} and C_{16} deviated from normal behavior. Mesogenic properties of present novel ester series are compared with the structurally similar series. Odd-even effect is missing for the N-I transition curve. Thus, the present series is partly nematogenic without exhibition of smectic property whose transition temperatures vary between 153°C and 210°C.

KEYWORDS
Liquid crystal; mesogen; nematic; smectic; thermotropic

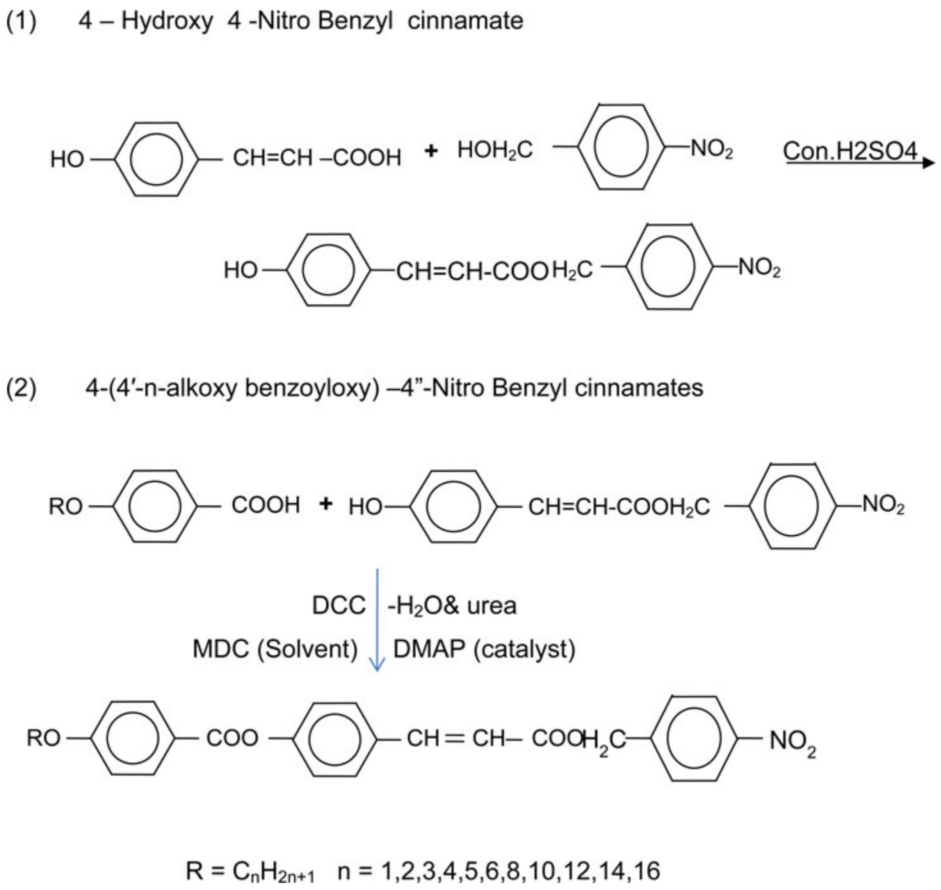
Introduction

The study of the liquid crystalline (LC) state [1] has attracted many researchers belonging to science and technology irrespective of their specialized branch with different aims and objectives [2–5] but all in the benefit of mankind [6–11]. Every researcher always needs novel substances to continue their research in their specialized objects. Therefore, we being chemists decided to synthesize novel thermotropically mesomorphic (LC) substances. Many LC substances have been reported [12–19] to date. The proposed novel investigation is planned with a view to synthesize novel substances through homologous series comprising three phenyl rings and one of the central groups $-CH{=}CH{-}COO{-}CH_2{-}$, which is novel and exploited only by Doshi–Patel [20] and Marathe–Doshi [21]. Thus, the present study will add some novel LC substances, which can be useful to researchers working in the field of liquid crystals. Thus, the present study is aimed to synthesize novel LC substances to understand and establish the effects of molecular structure [22–24] on LC properties, and the evaluated data will be interpreted in terms of molecular rigidity and flexibility [25–28].

CONTACT J. M. Patel jigopatel8588@gmail.com Zydus Cadilla Healthcare Private Limited (R&D), Dabhsa Unit, Vadodara, Gujarat, India.

Synthesis

- 4-N-alkoxy benzoic acids were prepared by the modified method of Dave and Vora [29] using a suitable alkylating agent (R-X).
- 4-Hydroxy 4’-nitro benzyl cinnamates was prepared by reacting 4-hydroxy cinnamic acid with the corresponding 4-nitro benzyl alcohol (dissolved in benzene) using modifying method of Doshi–Patel and Marathe–Doshi through the European patent [30].
- Acid was directly condensed with 4-hydroxy 4’-nitro benzyl cinnamates dissolved in Methylene Di Chloride (MDC) in portions with N,N′-dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) as catalyst by the stirring of reaction mixture [31]. Products were decomposed, filtered, washed, dried, and purified until the constant transition temperatures were obtained. 4-Hydroxy benzoic acid, alkyl halides (R-X), methanol, KOH, thionyl chloride, 4-hydroxy cinnamic acid, 4-nitro benzyl alcohol, concentrated H_2SO_4, DCC, DMAP, MDC, etc. required for synthesis were used as received except solvents, which were dried and distilled prior to use. The synthetic route to the series is shown in Scheme 1. The elemental analysis of methyloxy, ethyloxy, and propyloxy derivatives are shown in Table 1.



Scheme 1. Synthetic route to the series.

Table 1. Elemental analysis of methyloxy, ethyloxy, and propyloxy derivatives.

		Elements found (%) (Calculated%)		
Sr. No.	Molecular formula	C	H	N
1.	$C_{24}H_{19}NO_7$	66.66 (66.51)	4.22 (4.38)	3.20 (3.23)
2.	$C_{25}H_{21}NO_7$	67.25 (67.32)	4.60 (4.69)	3.11 (3.13)
3.	$C_{26}H_{23}NO_7$	68.00 (67.97)	5.00 (5.01)	3.00 (3.05)

Characterization

Spectral data

^{1}H NMR in ppm for the decyloxy derivatives: 1.3, 1.5, 1.6 (alkyl chain H), 4.02, 4.06, 4.08 ($-OCH_2$ of $-OC_6H_{13}$), 5.47 ($-CH{=}CH-$ proton), 7.2, 7.4 (p-di-substituted benzene ring and mono-substituted benzene ring).

^{1}H NMR in ppm for the tetradecyloxy derivatives: 1.3, 1.5, 1.6, 2.1 (alkyl chain H) 3.9, 4.0, 4.06 ($-OCH_2$ of $-OC_{10}H_{21}$), 5.47 ($-CH{=}CH-$ proton), 7.2, 7.3, 7.34 (p-di-substituted benzene ring and mono-substituted benzene ring).

Infrared spectrum (IR) in cm^{-1} for octyloxy derivatives: 893 and 842 cm^{-1} para-di-substituted phenyl ring 1008, 1207, 1271 cm^{-1} ether linkage, 1442, 1608 cm^{-1} aromatic ring, 1525, 1305 nitro group present, 1737 cm^{-1} ester present, 2866, 2941 long chain alkane present.

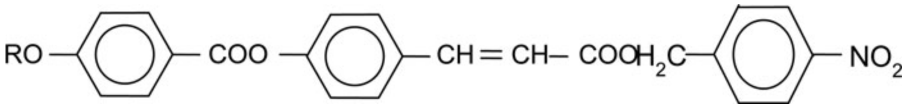
IR in cm^{-1} for octyloxy derivatives: 852 and 893 cm^{-1} para-di-substituted phenyl ring 1114, 1172, 1213 cm^{-1} ether linkage, 14811529 cm^{-1} aromatic ring, 1529, 1307 nitro group present, 1724, 1745 cm^{-1} ester present, 2860, 2941 long chain alkane present.

Texture: by miscibility method
Threaded nematic C_6
Schlieren nematic: C_{10} and C_{12}

Results and discussion

4-Hydroxy-4'-nitro benzyl cinnamate (m.p. yield%) is a non-mesomorphic substance. However, on condensing it with dimerized n-alkoxy benzoic acid yielded C_6 to C_{14} homologues as enantiotropic nematic without exhibiting smectogenic property. The rest of the homologues (C_1 to C_5 and C_{16}) are non-mesogenic. Transition temperatures (Table 2) as determined from an optical polarizing microscopy with heating stage were plotted against the number of carbon atoms present in n-alkyl chain bonded with phenyl ring through the oxygen atom of left flexible tail group. Similar or related points were linked to draw Cr-I/N, and N-T transition curves adopt a zigzag path of rising and falling values with an overall descending tendency of up to C_{12} homologue; then it deviates at C_{14} and C_{16} homologues from the usual expected behavior (Fig. 1). The N-I transition curve initially rises and then descends as series is ascended up to C_{12} homologue, and then deviates from normal expected behaviors, i.e. it is rising instead of falling for C_{14} homologue. The N-I transition curve is extrapolated (33, 34, 35, 36) to the non-mesomorphic C_{16} homologue to predict its probable N-I transition temperature keeping in view the trend of N-I transition curve. The mesogenic behavior of LC homologues vary from homologue to homologue in the present series with changing number of methylene unit or units in flexible n-alkyl chain. Keeping $-NO_2$ tail group intact throughout the same series. The disappearance of dimerization of n-alkoxy benzoic

Table 2. Transition temperatures.



		Transition temperatures in °C		
Sr. No.	n-alkyl group	Smectic	Nematic	Isotropic
1.	Methyl	–	–	190
2.	Ethyl	–	–	210
3.	Propyl	–	–	200
4.	Butyl	–	–	185
5.	Pentyl	–	–	192
6.	Hexyl	–	169	180
7.	Octyl	–	197	217
8.	Decyl	–	170	200
9.	Dodecyl	–	163	190
10.	Tetradecyl	–	153	203
11.	Hexadecyl	–	–	198

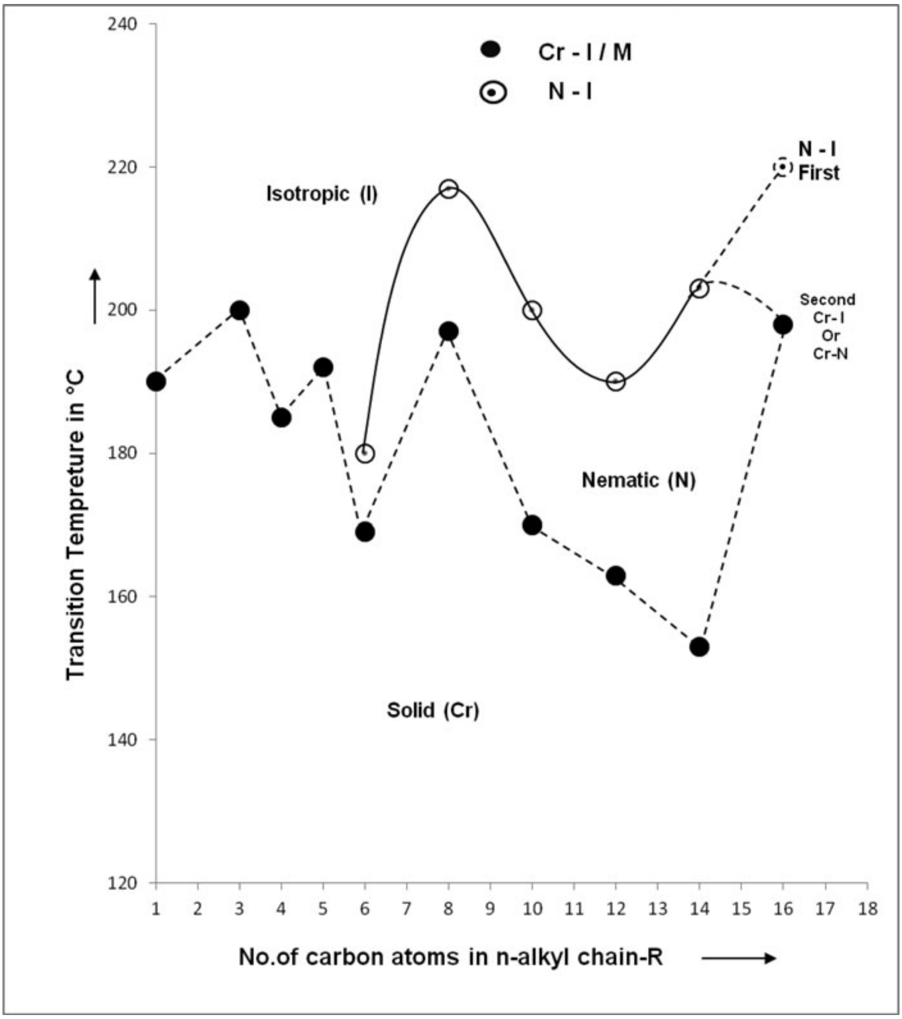
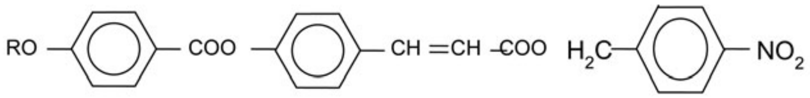


Figure 1. Phase behavior of series.

acids is due to the braking of hydrogen bonding between two molecules of aromatic carboxylic acids by esterification process. The non-mesogenic property of homologues C_1 to C_5 and C_{16} members of the present series is attributed to their high crystallizing tendency. This tendency arises from inability of respective non-mesogenic homologues to resist externally exposed thermal vibrations as a consequence of unsuitable magnitudes of molecular rigidity and flexibility induced by low dipole–dipole interactions and the low magnitude of dispersion forces by interaction between instantaneous dipoles produced by the spontaneous oscillations of electron clouds of molecules, which hinder the suitable magnitudes of anisotropic forces of intermolecular cohesion and disallow molecular arrangement required for definite range of temperature (i.e. zero temperature range). Highly polar and polarizable $–NO_2$ terminal situated as an end group is high in nematic order similar to –CN group, and low in smectic order. $–NO_2$ group has strong dipole, which lies along the long molecular axis. Such dipole gives repulsion between molecules, which lie parallel to one another, i.e. side by side, and perpendicular to the layer planes of smectic liquid crystal. Thus, end-to-end attractions predominated more than lateral attractions. Therefore, more ordered sliding layered arrangement of molecules is less favored to facilitation formation of smectic phase against less bordered, statistically parallel orientational order of molecules in floating condition on the surface to cause nematogenic mesophase formation. Thus, $–NO_2$ end group present in the molecule of the presently investigated novel series enhances nematic thermal stability and diminishes the stabilization of smectic mesophase formation. Absence of odd-even effect in the N-I transition curve is attributed to the absence of mesophase forming tendency from C_1 to C_5 homologues and absence of odd-even effect for higher homologues with longer n-alkyl chain, which can be attributed to uncertainty in the status of relatively longer n-alkyl chain, which may coil or bend or flex, or couple to lie with major axis of core structure of molecules. Therefore, intermolecular cohesive forces of C_{16} homologue are weakened to such an extent that even statically parallel orientation order of molecules (C_{16}) is not facilitated to cause nematic mesophase formation, but molecules of C_{16} homologue randomly orient in all possible directions with high order of disorder or entropy ($\Delta S = \Delta H/T$).



Homologous series: 4(4’-N-alkoxy benzoyloxy)-4”-nitro benzyl cinnamates

Hence, reasons for the non-mesomorphicity character of C_1 to C_5 and C_{16} are different. Extrapolation (first) of the N-I transition curve is hypothetical and not realistic, but the other extrapolation (second) extended to Cr-I point is real and merges into isotropic point of C_{16}, which indicates that mesomorphic phase length of C_{16} is really zero and not above the isotropic point as shown in the first extrapolation based on the trend of N-I curve. The observed deviation from expected behavior transition curves for C_{14} and C_{16} can be attributed to unexpected status of longer n-alkyl chain and highly polar and polarizable and flexible nitro tail group which may have enthalpy value (H) unusually higher than normal of suitable magnitudes, which can exhibit mesophase formation in monotropic condition (special for C_{16} homologue). Variation in mesogenic properties of the present series from homologue to homologue is due to the sequentially or progressively added $-CH_2-$ unit, which added molecular polarization and length or size of each homologue molecule in the same series, keeping the rest of the molecular part unchanged. Thus, the series under discussion is partly nematogenic and partly non-mesogenic with absence of smectogenic character. The

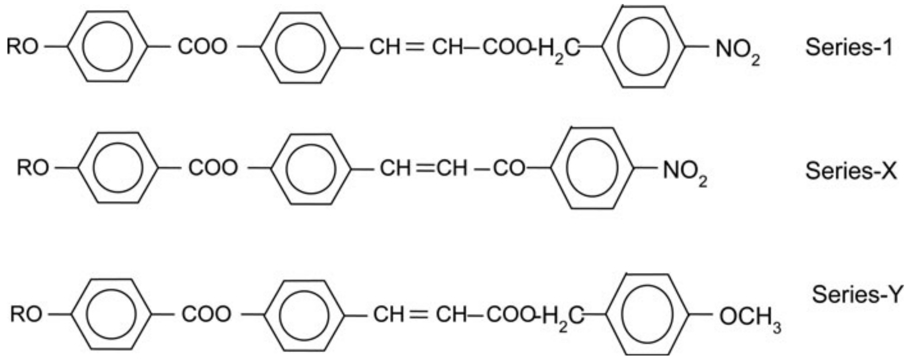


Figure 2 . Structurally similar series.

mesogenic behavior of the present series 1 is compared with structurally similar homologous series X [31] and Y [30] as shown in Fig. 2.

Novel homologous series 1, X, and Y are identical with respect to three phenyl rings and central bridge linking first and middle phenyl ring. Moreover, left n-alkoxy flexible terminal end group C_nH_{2n+1}, i.e. RO- is the same for the same homologue from series to series. But remaining part of each series differs from each other, i.e. series 1 and X differ with respect to central bridges linking middle and third phenyl rings, and molecular rigidity differs but molecular flexibility remains unaltered. Homologous series Y and 1 are identical with respect to central bridge linking middle and third phenyl rings as $CH{=}CH{-}COO{=}CH_2{-}$ but differ with respect to flexible tail groups $-OCH_3$ and $-NO_2$ respectively for the same homologue from series to series, i.e. molecular flexibility is altered keeping molecular rigidity unaltered for the same homologue from series to series. Thus, variations in mesogenic properties and the degree of mesomorphism observed are depended upon the altering magnitudes of either molecular rigidity or molecular flexibility in the presently investigated series 1 and the homologous series X and Y chosen for comparative study. Table 3 presents some mesogenic properties such as average thermal stabilities, commencement of mesophase or mesophases, mesophase lengths, etc. to indicate effect of molecular structure on liquid crystal properties in terms of or as a consequence of altering molecular rigidity or flexibility.

It is clear from Table 3 that

- presently investigated novel series 1 and Y are only nematogenic, whereas series X is nematogenic in addition to smectogenic;
- smectic property commences from C_6 homologue of series X, whereas it does not commence till the lest member of series 1 and Y;
- nematic mesophase commences from the C_6 homologue of series 1, whereas it commences from C_3 and C_1 homologues of series X and Y respectively;
- total mesophase length range of series 1 is relatively lower than series X and Y;

Table 3. Average thermal stability in °C.

Series	1	X	Y
Smectic–isotropic or	–	125.6	–
or			
Smectic–nematic		(C_6-C_{14})	
Commencement of smectic phase		C_6	
Nematic–isotropic Commencement of nematic phase	198.0 (C_6-C_{14}) C_6	154.6 (C_3-C_{16}) C_3	211.54 (C_1-C_{16}) C_1
Mesophase length range in °C from (Sm+N) $C_n\alpha$ to $C_n\beta$	11–50 C_6 C_{14}	18–73 C_3 C_8 and C_{16}	17–72 C_{14} C_3

- coincidentally, ranges of total mesophase length are equal for series X and Y chosen for comparison.

Mesogenic characteristic difference of a substance varies with changing structural part of molecules under comparison. The changing molecular structural part in series 1 and X is a central bridge linking middle and tail phenyl ring, which are $-CH{=}CH-COO-CH_2-$ and $-CH{=}CH-CO-$, keeping the rest of molecular parts of series 1 and X identically the same. Both central bridges contribute molecular rigidity of different magnitudes, although $-CH{=}CH-$ unit is commonly present in both central bridges. The remaining uncommon parts, other than $-CH{=}CH-$ common unit, are $-COO-CH_2-$ for series -1 and $-CO-$ for series X. The $-COCH_2$ unit of series 1 is longer than the $-CO-$ group of series X, which links with the $-C_6H_4-NO_2$ common unit of both series (1 and X) under comparison. However, linking of uncommon longer unit $-COO-CH_2-$ is bonded with common sp^2-hybridized $-C_6H_4-NO_2$ unit through sp^3 carbon of $-CH_2$, whereas the sp^2 carbon of shorter $-CO$ group of uncommon part of a central bridge of series X is bonded to a common sp^2-hybridized $-C_6H_4-NO_2$ unit. Thus, longer and shorter differing units of the present novel series 1 and X bonded with common tail unit $-C_6H_4-NO_2$ through sp^3 or sp^2 carbon respectively. Such differences induce differences into molecular polarity and polarizability as a consequence of molecular rigidity, keeping molecular flexibility unchanged for the same homologue from series 1 to series X, which causes difference of suitable magnitudes of anisotropic forces of intermolecular end-to-end attractions, commencement of mesophase, thermal stability, mesophase length range, and other mesogenic properties. Homologous series 1 and Y are identical in all respects for the same homologues except tail groups $-NO_2$ and $-OCH_3$ bonded to third phenyl ring of sp^2 carbon. Thus, $C-NO_2$ and $C-OCH_3$ bond polarity and polarizability differ due to the difference in the electronegativity of nitrogen atom of $-NO_2$ and oxygen atom of $-OCH_3$ (more C–O as compared with C–N). This induces suitable or unsuitable magnitudes of intermolecular end-to-end and/or lateral attractions to facilitate nematic and smectic mesophase formation related to the disalignment of molecules perpendicular to the plane of a floating surface or less than 90° on the plane of the surface inducing resistivity against exposed thermal vibrations, which facilitate stabilization of either nematic mesophase or smectic with nematic mesophase possessing more or less degree of mesomorphism. Hence, occurrence of mesogenic mesophase formation and the degree of mesomorphism depend upon the molecular structure of the substance concerned.

Conclusions

A novel homologous series comprising three phenyl rings and two ester central bridges, which act as a rigid core, and two end groups contributing flexible core of molecules, induces nematic type of mesomorphism with, in general, absence of smectic property. The series is middle-ordered melting-type with high thermal stability.

Group efficiency orders derived on the basis of (i) thermal stability, (ii) commencement of mesophase, and (iii) total mesophase length for smectic and nematic with reference to molecular rigidity/flexibility are as follows:

(i) Smectic.

(a) Rigidity $-CH{=}CH-CO- > -CH{=}CH-COO-CH_2-$

(b) Flexibility $-NO_2{=}-OCH_3{=}\text{zero}$

Nematic

(a) Rigidity $-CH{=}CH{-}COO{-}CH_2- > -CH{=}CH{-}CO-$

(b) Flexibility $-OCH_3 > -NO_2$

(ii) Smectic.

Rigidity $-CH{=}CH{-}CO- > -CH{=}CH{-}COO{-}CH_2$-

Flexibility $-NO_2{=}{-}OCH_3$=zero

Nematic

Rigidity $-CH{=}CH{-}CO- > -CH{=}CH{-}COO{-}CH_2$-

Flexibility $-OCH_3 > -NO_2$

(iii) Total (Sm + N): (Central group + terminal group)

$-CH{=}CH{-}CO{-}{=}{-}CH{=}CH{-}COO{-}CH_2- >$ series 1

Series X Series Y

- Suitable magnitudes of combined effect through molecular rigidity and flexibility can induce mesomorphism.
- Mesomorphism is very sensitive and susceptible to molecular structure.
- Present novel ester compounds may be useful in the study of binary systems and agricultural field.
- Presence of vinyl group is predominantly nematogenic.

Acknowledgments

Authors acknowledge thanks to the S.P.T. Science College, Godhra, for research facilities and services as and when needed. Authors are obliged to Dr. A. V. Doshi of M.V.M. Science College, Rajkot, for Experimental. Authors are also thankful to Drs. N.N. Vyas and V.R. Patel for their valuable helping hand and microscopic facility. Thanks are due to the Choksi Laboratory, Vadodara, and CSIR, Bhavnagar for analytical service.

References

[1] Reinitzer, F. (1888). *Monatsh*, *9*, 21.
[2] Naemura, S. (2001). *Displays*, *22*(1), P-1.
[3] Kim, W. S., Elston, S. J., & Raynes, F. P. (2008). *Display*, *29*, 458–463.
[4] Tadwee, I., Shahi, S., Ramteke, V., & Syed, I. (2012). *IJPRAS 1*(2), 06–11. ISSN 2277-36.
[5] Hertz, E., Lavorel, B., & Faucher, O. (2011). *Nature Photo.*, *5*, 78–79.
[6] Gray, G. W., & Windsor, P. A. (1974). *Liq. Cryst. and Plastic Cryst.,* The role of liquid crystals in life processes by Stewart, G.T., 1, 308–326.
[7] Calliste, C. A., Le Bail, J. C., Trouilas, P., Pougth, C., Chulia, A. J., & Duroux, L. J. (2001). *Anticancer Res.*, *21*, 3949–3956.
[8] Jahng, Y., Zhao, L., Moon, Y., Basnet, A., Kim, E., *et al.* (2004). *Bioorg. Med. Chem. Lett.*, *14*, 2559–2562.
[9] Modzelewska, A., Pettit, C., Achanta, G., Davidson, N. E., Huang, P., & Khan, S. R. (2006). *Bioorg. Med. Chem.*, *14*, 3491–3495.
[10] Rajesh, G., Mansi, K., Srikant, K., Baba Sahib, B., Nagesh, D., *et al.* (2008). *Chem. Pharm. Bull.*, *56*, 897–901.
[11] Lee, Y. S., Lim, S. S., Shin, K. H., Kim, Y. S., Ohuchi, K., & Jung, S. H. (2006). *Biol. Pharm. Bull.*, *29*, 1028–1031.

[12] Demus, D. (1988). *Mol. Cryst. Liq. Cryst.*, *165*, 45–84.
[13] Demus, D. (1988). *Liq. Cryst.*, *5*, 75–110.
[14] Imrie, C. T., & Luckhrust, G. R. (1998). Liquid cryst. dimers and oligomers. In: *Handbook of Liquid Crystals, Law Molecular Liquid Crystals*, Vol. 2B, D. Demus, J. W. Goodby, G. W. Graw, H. W. Spiess, & V. Vill (Eds.), Wiley VCH: Weinheim, Germany, pp. 801–833.
[15] Vora, R. A., Prajapati, A. K., Kevat, J. B., & Raw, K. K. (2001). *Liq. Cryst.*, *28*, 983–998.
[16] (a) Suthar, D. M., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *575*, 76–83. (b) Chauhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *570*, 92–100. (c) Chaudhari, R. P., Chauhan, M. L., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *575*, 88–95. (d) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 104–110.
[17] (a) Youngw, R. (1970). *Mol. Cryst. Liq. Cryst.*, *10*, 237. (b) Dietrich, H. J., & Stekier, E. L. (1972). *Mol. Cryst. Liq. Cryst.*, *16*, 263.
[18] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *582*, 79–87.
[19] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *577*, 51–58.
[20] Brijesh, H. Patel, & Doshi, A. V. (2014) *Mol. Cryst. Liq. Cryst., 605*, 23–31.
[21] Marathe, R. B., & Doshi, A. V. (2015). *Mol. Cryst. Liq. Cryst., 616*, 74–82.
[22] Gray, G. W. (1962). *Molecular Structure and Properties of Liquid Crystals*, Academic Press: London.
[23] Gray, G. W. (1974). In: *Liquid Crystals and Plastic Crystals*, Vol. 1, G. W. Gray & P. A. Winsor (Eds.), Chapter 4, pp. 103–153.
[24] Imrie, C. T. (1999). *Liq. Cryst. Dimmers Struct. Bond*, *95*, 149–192.
[25] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *15*, 123.
[26] Marcos, M., Omenat, A., Serrono, J. L., & Ezcurra, A. (1992). *Adv. Mater.*, *4*, 285.
[27] Collings, P. J., & Hird, M. (1998). *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis: London.
[28] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741.
[29] Dave, J. S., & Vora, R. A. (1970). In: *Liquid Crystals and Ordered Fluids*, J. F. Johnson & R. S. Porter (Eds.), Plenum Press: New York, NY, 477 p.
[30] (a) Patel, B. H., & Doshi, A. V. (2014). *Mol. Cryst. Liq. Cryst.*, *16*, 263. (b) Ryuzo Ueno, Hiroaki Tsuchiya, Shigeru Itoh, Ichiro Yamamoto (Inventors); Kabushiki Kaisha Ueno Seiyaku Oyo Kenkyuj (Applicant) (November 1987). Process of producing benzyl ester of aromatic hydroxy carboxylic acid. European patent EP0117502 B1.
[31] Suthar, D. M., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *571*(1), 1–8.