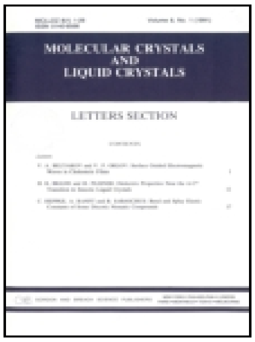

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Synthesis and Liquid Crystal Behavior of a Novel Ester Homologous Series

B. H. PATEL[1] AND A.V. DOSHI[2,*]

[1]Huntsman, Baroda Textile Effects Pvt. Ltd, Umraya village, Taluka Padra, Vadodara, Gujarat, India
[2]Dr K.N.Modi University, Plot No.INS-1, RIICo Industrial Area Ph-II, Newai, Dist. Tonk, Rajasthan, India

A novel ester homologous series of 4-[4'-n-alkoxy cinnamoyloxy] benzyl benzoates has been synthesized. The series consists of 12 homologues. Liquid crystal properties commence from the sixth member to the last member of the series with the exhibition of an enantiotropic nematic phase without the exhibition of any smectogenic mesophase. The remaining homologues do not exhibit liquid crystal behavior. The texture of the nematic phase is of the threaded or Schlieren type. The solid-nematic or isotropic transition curve adopts a zigzag path and the nematic-isotropic transition curve steeply rises and then falls in the phase diagram and behaves in normal manner. An odd–even effect is absent in the nematic-isotropic transition curve with an alteration of transition temperatures. The average thermal stability for the nematic mesophase is 153.1°C, and the nematogenic temperature ranges vary from 12°C to 50°C. Analytical data confirm the molecular structures of the homologues. The Liquid Crystal properties and transition temperatures were observed through an optical polarizing microscope, equipped with a heating stage. The mesomorphic characteristics of the novel ester series are compared with other, known and structurally similar series. The novel series is predominantly nematogenic with the absence of any smectogenic character, with relatively short mesophase temperature ranges and of the middle ordered melting type.

Keywords Liquid crystals; mesomorphism; monotropy; nematic; smectic

Introduction

Esters with vinyl carboxy (−CH=CH−COO−) and/or carboxy (−COO−) functional groups as a central bridge have been reported previously [1] to aid understanding and to establish the effect of molecular structure on liquid crystal properties. Such properties include the temperature of commencement of the smectic or/and the nematic mesophase formation, the degree of mesomorphism, the group efficiency order on the basis of thermal stabilities and the early commencement of mesophase formation, and includes a comparative study with structurally similar series as a consequence of favorable magnitudes of molecular rigidity and flexibility [2–4]. In order to further enhance understanding of structure property relationships, the present investigation is planned with a view to understanding the dependence of liquid crystal properties in terms of molecular rigidity and flexibility which has a direct relation with the thermodynamic property such as internal energy (ΔE) of an

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[*] Address correspondence to Brijesh H. Patel, A-21 Saket Bunglows Opp Yash Complex Gotri Baroda, 390021, Gujarat, India. E-mail: research@dknmu.org

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open system, operated at constant pressure or at atmospheric pressure for thermotropic liquid crystals. The proposed investigation involves the synthesis of a novel homologous ester series, that consists of three phenyl rings to be bridged through two central groups –CH = CH—COO– and –COO–CH_2– which act as a rigid core, and the left n-alkoxy (–OR) terminal end group acts as a flexible part of a molecule, without any substitution as a lateral and a terminal group at the other end of the molecule.

Experimental

Synthesis

4-Hydroxy cinnamic acid was alkylated by suitable alkylating agents (R-X) to generate the 4-n-alkoxy cinnamic acids. Alkoxy cinnamic acids were then linked with 4-hydroxybenzyl benzoate (B) (m.p. 110 °C) through acid chlorides (A) of alkoxy cinnamic acids using thionyl chloride [5,6] in dry cold pyridine. 4-Hydroxy benzyl benzoate (B) was used as received and recrystallized and dried before use. The final products A-B were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained. 4-Hydroxycinnamic acid, 4-hydroxy benzyl benzoate (B), methanol, KOH, ethanol, pyridine, alkyl halides (R–X), thionyl chloride, etc. required for the synthesis were used as received except for solvents which were dried and purified prior to use. The synthetic route to the series is outlined in scheme 1.

Characterization

Some representative members of the novel series were characterized by elemental analysis on a Perkin-Elmer PE 2400 CHN analyzer. Infra red spectroscopy employed a Perkin-Elmer spectrum GX spectrometer, and ^{1}HNMR spectroscopy employed a Bruker spectrometer using $CDCl_3$ as the solvent. The liquid crystal behavior, type of texture and transition temperatures of each homologues were recorded and observed through polarizing microscopy in conjunction with a heating stage and temperature controller. The type of nematic mesophase textures was determined by a miscibility method. Thermodynamic quantities enthalpy change (ΔH) and entropy change (ΔS) are qualitatively discussed.

Analytical Data

Spectral Data. ^{1}HNMR in ppm for the hexadecyloxy derivative: 1.183 ($-C_{15}H_{31}$ of $-C_{16}H_{33}$ group), 3.272 ($-OCH_2$ of $-OC_{16}H_{33}$ group), 3.984 ($-O{-}CH_2{-}C_6H_4$ group), 5.297 and 5.250 ($-CH{=}CH-$ group), 6.221, 6.261, 6.384, and 6.424 (p-substituted phenyl ring), 7.370 (mono-substituted phenyl ring), 7.674, 7.745, 7.784, and 7.863 (p-substituted phenyl ring).

IR in cm^{-1} for the hexyloxy derivative: 692 and 734 mono-substituted phenyl ring, 827 p-substituted phenyl ring, 1209 ether linkage of ($-C_6H_{13}O{-}C_6H_4$), 1718, 1280, and 1139 ($-COO-$ ester group), 993 (trans $-CH{=}CH-$ group).

IR in cm^{-1} for the decyloxy derivative: 694 and 732 mono-substituted phenyl ring, 829 p-substituted phenyl ring, 979 (trans $-CH{=}CH-$ group), 1676, 1282, and 1172 ($-COO-$ group), 1215 ether linkage of ($-C_{10}H_{21}O{-}C_6H_4$ group).

Mass Spectra. Mass spectra for the propoxy derivative:

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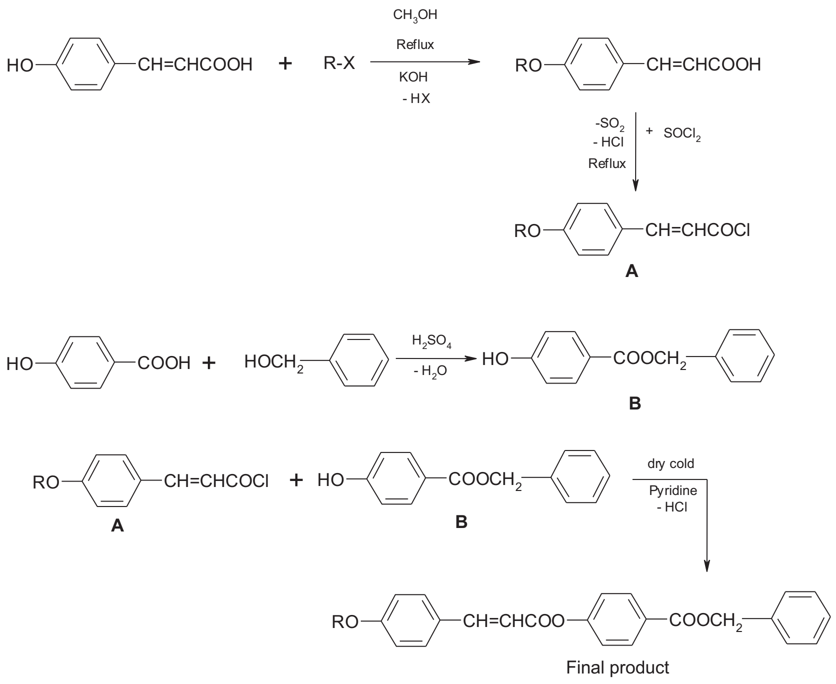
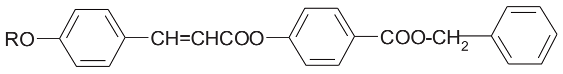


Where R = C_nH_{2n+1}; n = 1,2,3,4,5,6,7,8,10,12,14,16

Scheme 1. Synthetic route to the series.

Series: 4-[4'-n-Alkoxy Cinnamoyloxy] benzyl benzoates



Molecular formula $C_{26}H_{24}O_5$ Calculated Molecular weight 416. Practical mass observed by Mass Spectrometry 416.

Texture of Nematic Phase by Miscibility Method.

Octyloxy derivative ———— Threaded nematic
Dodecyloxy derivative ————Schlieren nematic

Results and Discussion

4-n-Alkoxy cinnamic acids and 4-hydroxy benzyl benzoate are nonliquid crystal components; however, the liquid crystal property is induced by linking them by —COO—CH_2– central bridges through acid chloride formation of the corresponding n-alkoxy acids. The novel homologous series consists of 12 homologues. The methyl to pentyl homologues are not liquid crystals, the hexyl to the hexadecyl homologues of the series show liquid crystal behavior enantiotropically with nematogenic mesophase formation only, without the formation of any smectogenic mesophase. The transition temperatures of the homologues (Table 2) as determined from an optical hot stage polarizing microscopy are plotted versus the number of carbon atoms present in the n-alkyl chain of the left n-alkoxy group. A phase diagram (Fig. 1) is obtained by joining like or related points,

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Table 1. Elemental analysis for methoxy, ethoxy and propoxy derivatives

Sr. No.	Molecular formula	Elements % found (% calculated) C	Elements % found (% calculated) H
1	$C_{24}H_{20}O_5$	74.35 (74.22)	5.26 (5.15)
2	$C_{25}H_{22}O_5$	74.51 (74.62)	5.31 (5.47)
3	$C_{26}H_{24}O_5$	74.98 (75.00)	5.79 (5.76)

showing the phase behavior of the novel series. The solid-isotropic or nematic transition curve follows a zigzag path of rising and falling values and behaves in normal manner. A nematic to isotropic transition curve steeply rises from hexyloxy homologue to octyloxy homologue and then descended as series is ascended. An odd–even effect is

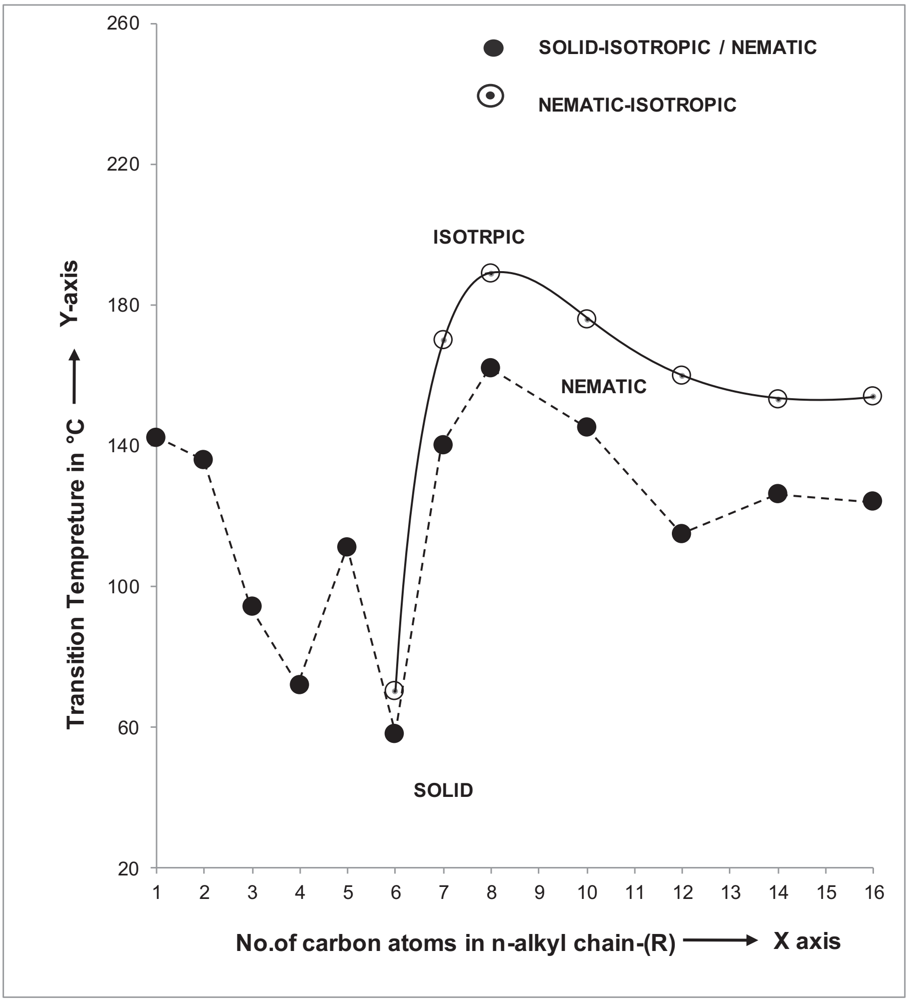

Figure 1. Phase behavior of series.

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

		Transition temperature in °C		
Compound no.	n-alkyl group ($-C_nH_{2n+1}$) (*n*)	*Sm*	*N*	Isotropic
1	1	—	—	142.0
2	2	—	—	136.0
3	3	—	—	94.0
4	4	—	—	72.0
5	5	—	—	111.0
6	6	—	58.0	70.0
7	7	—	140.0	170.0
8	8	—	162.0	189.0
9	10	—	145.0	176.0
10	12	—	115.0	160.0
11	14	—	126.0	153.0
12	16	—	124.0	154.0

Sm: Smectic *N:* Nematic

absent for the nematic-isotropic transition curve. The nematogenic mesophase temperature ranges vary between 12°C and 50°C. The average thermal stability for the nematic phase is 153.1°C. Hence, the phase diagram and curves behave in normal manner. Thus, the novel homologous series is only nematogenic with the absence of smectogenic character and is of a middle ordered melting type of considerable temperature range of liquid crystallinity.

The exhibition of liquid crystal properties by some of the novel molecules formed from two nonliquid crystal components (A and B) is attributed to the suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of the net molecular rigidity [2–4] and flexibility within the molecules. The methyl to pentyl homologues are not liquid crystals because these five molecules are unable to resist and withstand thermal vibrations exposed upon them from an external source of thermodynamic surroundings. As a result of their inability to resist thermal vibrations, all the molecules of the first five homologues of the novel series possess high crystallizing tendency and transform directly into the isotropic liquid without passing through an intermediate liquid crystal state. As the n-alkyl chain is gradually lengthened the molecular flexibility increases and the mesophase character strengthens keeping molecular rigidity unchanged. Hence, the capacity of a molecule to withstand thermal vibrations exposed upon them rises and, the molecules under exposed thermal vibrations disalign at an angle less than 90° on the plane of a surface within a definite temperature range showing exhibition of liquid crystal properties. The molecules of the present series from the hexyl to hexadecyl homologues arrange themselves in statically parallel orientational order of a two dimensional array in a floating condition [9], as a consequence of suitable magnitudes of end to end intermolecular attractions causing a threaded or a Schlieren texture of the nematogenic mesophase within a definite temperature range. On further heating the molecules of the nematogenic sample randomly, orient in all possible directions with high order of disorder or entropy ($\Delta s = \Delta H/T$) and convert to the isotropic state from the anisotropic state in enantiotropic manner. The absence of smectic character in the homologues of a present series is attributed to the absence of

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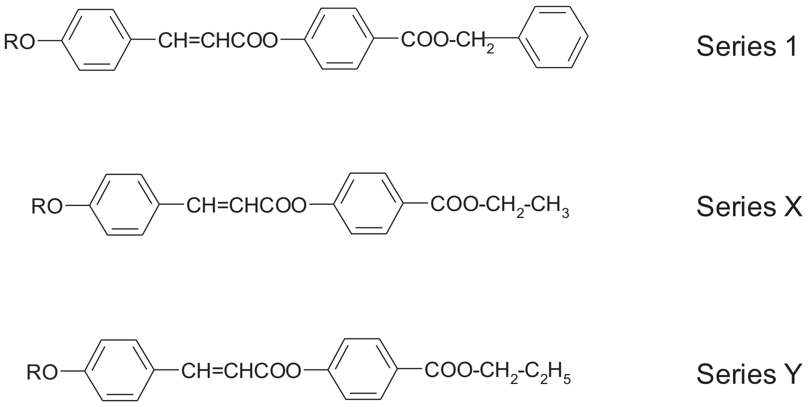

Figure 2. Structurally similar homologous series.

lamellar packing of molecules in their crystal lattices [10] due to inadequate intermolecular attractions, for the reason of absence of flexible terminal end group or laterally substituted group on right side of the molecules. Thus, lamellar packing of molecules in the crystal lattices and the smectogenic mesophase formations is hindered because of unsuitable magnitudes of intermolecular forces of adhesion. The absence of an odd–even effect in the nematic-isotropic transition curve is attributed to the absence of liquid crystallinity in the odd members of the alkyl chain. A longer n-alkyl chain may coil, flex, bend, or couple to lie with the major axis of the core without showing an odd–even effect from and beyond the hexyloxy homologue which are of an even numbered chain length. The nematogenic phase temperature length is a minimum of 12 °C at the hexyloxy homologue and a maximum of 50 °C at the octyloxy homologue, which is attributed to the steep and drastic rise of nematic-isotropic transition curve for a sudden rising tendency of molecular flexibility in combination with its molecular rigidity. Thereafter, molecular rigidity and flexibility gradually diminish on progressive addition of methylene units. The references [1–4] indicating a descending tendency of a transition curve as the series is ascended. The average thermal stability 157.1 °C of the series indicates a heat-resisting tendency as related to the enthalpy change (ΔH) of the homologues, which is responsible for liquid crystal mesophase formation. Thus, the novel series is only nematogenic without the exhibition of any smectic property even in the monotropic condition, and is of a middle ordered melting type. The liquid crystal properties and behavior of presently investigated novel series-1 are compared with structurally similar other known homologous series-X [11] and series-Y [12] as shown below in Fig. 2.

As can be seen from Fig.-2 homologous series-1, series-X, and series-Y are structurally identical with respect to two phenyl rings bridged through a –CH $=$ CH—COO– central group and a left n-alkoxy (–OR) terminal end group, with the only difference being what is attached to the –COO–CH$_2$– group. Therefore, variation in mesomorphic or liquid crystal behavior of series-1, series-X, and series-Y can be attributed to the differing part of the molecules of series-1, series-X, and series-Y by –C$_6$H$_5$, –CH$_3$, and –C$_2$H$_5$ respectively. Table 3 shows the average thermal stabilities and commencement of the smectic and the nematic phase as well as the homologues showing type of mesophase or mesophases as mentioned below.

Table 3 summarizes the following significant points.

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Table 3. Average thermal stability in °C

Series→	Series-1	Series-X	Series-Y
smectic-nematic or smectic-isotropic commencement of smectic phase	—	120.75	118.0
		(C_7—C_{12}) C_2	(C_6—C_{12}) C_2
nematic-isotropic commencement of nematic phase	153.1	119.7	115.7
	(C_6–C_{16}) C_6	(C_5–C_6) C_1	(C_3–C_6) C_1

- The presently investigated novel series is only nematogenic while series-X and series-Y chosen for comparison are nematogenic in addition to smectogenic in character.
- The nematic-isotropic thermal stability of the novel series-1 is the highest (153.1 °C) and decreases in passing from series-1 to series-X to series-Y.
- Series-X and series-Y exhibit smectogenic behavior with very similar average thermal stability.
- The smectic mesophase commences from the second member of a series in case of series-X and series-Y, while it does not occur at all in series-1.
- The nematic mesophase commences from the first member of series-X and series-Y, while it commences from the sixth member of the present novel series-1.

The presently investigated novel series-1, and the comparison series-X and series-Y are all structurally comparable with the structure (Z) of 4-(4′-n-alkoxy cinnamoyloxy) methyl benzoates [1(c)(iii)] as shown in Fig. 3.

Homologous series-Z [1(c)(iii)] is analogous to presently investigated series-1, and series-X, series-Y chosen for comparison. They all resemble to each other for the unchanging molecular part, but differ with respect to the moiety that is linked to the –COO–CH_2– unit, which is a nonpolar benzene ring in case of the novel series-1 and a polar methyl (–CH_3) and ethyl (–C_2H_5) group in case of series-X and series-Y respectively. Thus, variations in mesomorphic (liquid crystal) behavior and the degree of mesomorphism can be correlated or linked with the differing molecular part, nonpolar benzene ring, and polar n-alkyl (methyl and ethyl) groups linked to terminal –COO–CH_2– group. The changing molecular part causes variations in molecular rigidity and/or flexibility, that is, the terminal phenyl ring in series-1 increases molecular length but decreases molecular polarity and flexibility, (or increases molecular rigidity) whereas, the methyl and ethyl groups increase molecular polarity in comparison with series-1. Therefore, variations occur in the molecules of series-1, series-X, and series-Y in terms of length to breadth ratio, the ratio of the molecular polarity to polarizability, molecular rigidity, and flexibility as well as

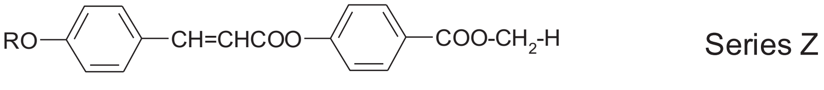

Figure 3. General structure for series-Z.

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molecular shape, size and polarity [1]. Thus, the suitable magnitudes of anisotropic forces of intermolecular attractions varies from series to series due to the changing molecular part of series-1, series-X, and series-Y compared with the –H of the analogous series-Z.

The molecules of series-1, series-X, and series-Y disalign at an angle less than ninety degrees and show liquid crystalline behavior. However, the molecules of series-1 are unable to form lamellar packing of molecules in their crystal lattices, while the molecules of series-X and series-Y form lamellar packing of molecules in their crystal lattices due to the presence of polar $–CH_3$ and $–C_2H_5$ group at the end. Thus, increased molecular polarity and flexibility favors the formation of smectic mesophase, because of suitable magnitudes of anisotropic forces of adhesion, responsible to maintain sliding layered molecular ordered arrangement in floating condition; in case of series-X and series-Y. But, same does not happen in case of series-1. Thus, smectogenic behavior is absent for the presently investigated novel series-1. However, disalignment of molecules at an angle less than 90° with adequate anisotropic forces of intermolecular end to end attractions which withstand exposed thermal vibrations to float the molecules in a two dimensional array with statistically parallel orientational order on a surface to show only nematogenic mesophase formation, but formation of the smectogenic mesophase is hindered for the presently investigated series-1, yet not hindered for series-X and series-Y. The higher value of nematic thermal stability of series-1 is attributed to the absence of the smectic phase and relatively higher molecular rigidity caused by the third phenyl ring. The absence of lamellar packing of molecules of series-1 is due to the presence of a nonpolar phenyl ring at the molecular end, which reduces molecular flexibility and increases molecular rigidity. Thus, nematic mesophase stabilizes more at the cost of losing smectic mesophase formation. Hence, the highest nematic thermal stability (153.1 °C) among the series-1, series-X, and series-Y is observed. The variations in mesomorphic behavior from homologue to homologue in the same series is attributed to the sequentially and progressively added methylene unit in n-alkyl chain [1]. Similarly, variations in mesomorphic behavior and the degree of mesomorphisim for the same homologue from series to series is attributed to the changing molecular part, keeping the rest of the molecular part unchanged [1–4]. Early or late commencement of the smectic mesophase depends upon the extent of noncopolarity caused by a molecule [8,9], that is, the molecules of series-X and series-Y are equally coplanar. Hence, the smectic mesophase commences from the second member of each series-X and series-Y, but it does not appear at all in series-1.

Conclusions

The presently investigated novel homologous series-1 of 4-[4′-n-alkoxy cinnamoyloxy] benzyl benzoates is summed up as follows.

- Nematogenic only without exhibition of any smectogenic property.
- Reduction in molecular flexibility or enhancement of molecular rigidity decreases the possibility of smectic mesophase formation.
- Suitable magnitudes of molecular rigidity and flexibility play an important role in inducing liquid crystal properties of a substance.
- Group efficiency order derived on the basis of thermal stabilities for smectic and nematic are as under.
  Smectic: $–CH_3 > C_2H_5 > –C_6H_5$
  Nematic: $–C_6H_5 > –CH_3 > –C_2H_5$

- Group efficiency order derived on the basis of early commencement of mesophase is as under.
  Mesophase (smectic and/or nematic): $-CH_3 = -C_2H_5 > -C_6H_5$
- Variations in mesomorphic property from series to series for the same homologue and from homologue to homologue in the same series are due to the changing part of a molecule at right handed terminal end group and sequentially added methylene unit in the left n-alkoxy terminal end group respectively.
- Series-1 is a middle ordered melting type with relatively high thermal stability for the nematic mesophase.

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References

[1] (a) Gray, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystal*, Academic Press: London and New York. (b) Gray, G. W., & Windsor, P. A. (1974). *Liq. Cryst. and Plastic Cryst.* Vol. 1, Chapter 4, Ellis Horwood Ltd.: Chichester; Halsted Press: New York, London. (c) (i) Demus, D. (1988). 100 years of liquid crystal chemistry. *Mol. Cryst. Liq. Cryst.*, *165*, 45—. (ii) Gray, G. W., & Jones, B (1956). Mesomorphism aand chemical constitution part-7, the effect of halogen substitution on the mesomorphism of the n-alkxoy cinnmic acids. *J. Chem. Soc.*, 1417. (iii) Lohar, J. M., Mashru, Urvashi. (1981). *Indian J. Chem. Sec. A Inorg. Phys. Theoritical Anal.*, *20*, 125.

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

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

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

[5] Dave, J. S., & Vora, R. A. (1970). *Liquid Crystals and Ordered Fluids*, Plenum Press: New York, 477

[6] (a) Furnish, B. S., Hanford, A. J., Smith, P. G. W., & Tatchell, A. R. (1989). *Vogel's Textbook of Practical Organic Chemistry,* 4th ed., publishers Pvt. Ltd.: Longman, Singapore. (b) (i) Chauhan, M. L., & Doshi, A. V. (August 2007). *J. Indian Chem. Soc.*, *84*, 774. (ii) Patel, R. B., & Doshi, A. V. (2011). *Derpharma Chemica*, *3*(2), 147.

[7] (a) Patel, V. R., & Doshi, A. V. (2010). *Derpharma Chemica*, *2*(*6*), 429. (b) Patel, R. B., & Doshi, A. V. (2011). *Derpharma Chemica*, *3*(2), 147. (c) Chauhan, M. L., Pandya, R. N., & Doshi, A. V. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 228. (d) Doshi, A. V., & Makwana, N. G. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 220. (e) Patel, R. B., Patel, V. R., & Doshi A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 3. (f) Doshi, A. V., Odedara, D. A., & Patel, R. B. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 97.

[8] Bhoya, U. C., & Doshi, A. V. (2000). *J. Inst. Chem. (India)*, *72*(part-1), 15.

[9] Ganatra, K. J., & Doshi, A. V. (1999). *Proc. Ind. Acad. Sci. (Chem. Sci.)*, *4*(11), 562.

[10] (a) Chauhan, H. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *569*, 33. (b) Suthar, D. M., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *569*, 64.

[11] Lohar, J. M., & Mashru, Urvashi (1980). *J. Indian Chem. Soc.*, *57*, 904.

[12] Mashru, U. A. (1979). PhD thesis, Liquid Crystal Study of the Mesomorphic State. Maharaja Sayajirao University, Baroda-Vadodara.