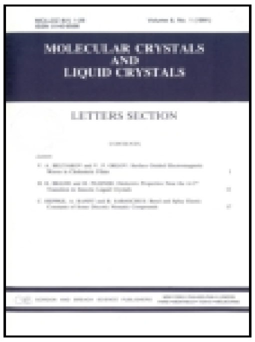
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Dependence of Mesomorphism on Molecular Rigidity with Reference to Lateral Substitution and Central Bridge

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ABSTRACT

A novel mesogenic ester homologous series is synthesized and studied with a view to understanding and establishing the effect of laterally substituted -OCH_3 on mesomorphic behavior. The series consists of twelve members. C_1 to C_4 members are nonmesogenic, C_6 to C_{12} are smectogenic in addition to nematogenic, and C_{14} to C_{16} are only smectogenic. The textures of smectic and nematic phases are A or C type and threaded or Schlieren, respectively. The transition curves in a phase diagram exhibit an odd–even effect and behave in normal manner except for the C_{14} and C_{16} derivatives in Sm-I transitions. Thermometric data were determined by an optical polarizing microscope equipped with a heating stage. Average thermal stability for smectic and nematic are 107.7°C and 121.0°C, respectively. Smectogenic and nematogenic mesophase length ranges from 11.0 to 44.0°C and 12.0°C to 39.0°C, respectively. The mesomorphic properties of present series are compared with structurally similar other known series. Thus, present series is predominantly smectogenic and partly nematogenic of middle ordered melting type.

KEYWORDS
Liquid crystal; mesogenic; mesomorphism; nematic; smectic

Introduction

The study of liquid crystalline (LC) or mesomorphic state is important from its ability to act in the interest of mankind since its discovery in 1888 [1]. Researchers of different groups are working with LC compounds with different aims and objectives. The present investigation is planned with a view to synthesize novel LC substances through a novel homologous series to understand and establish the effects of molecular structure on liquid crystal properties [2–5]. Several homologous series have been reported to date [6–10]. The scientific and technological research groups have developed and reported number of LC devices and their applications [11–17]. The proposed molecular structure of novel homologous series consists of two phenyl rings bonded through -COO- central bridge, two terminal end groups -OR and -CH$=$CH-$COOCH_2$-CH_2-CH_3 (n) and laterally substituted highly polar -OCH_3 group. The novel homologues are thermotropically and structurally characterized by evaluated data and then the mesomorphic behaviors will be discussed and interpreted in terms of molecular rigidity and flexibility [18–21]. The LC properties of present novel substances will be compared with

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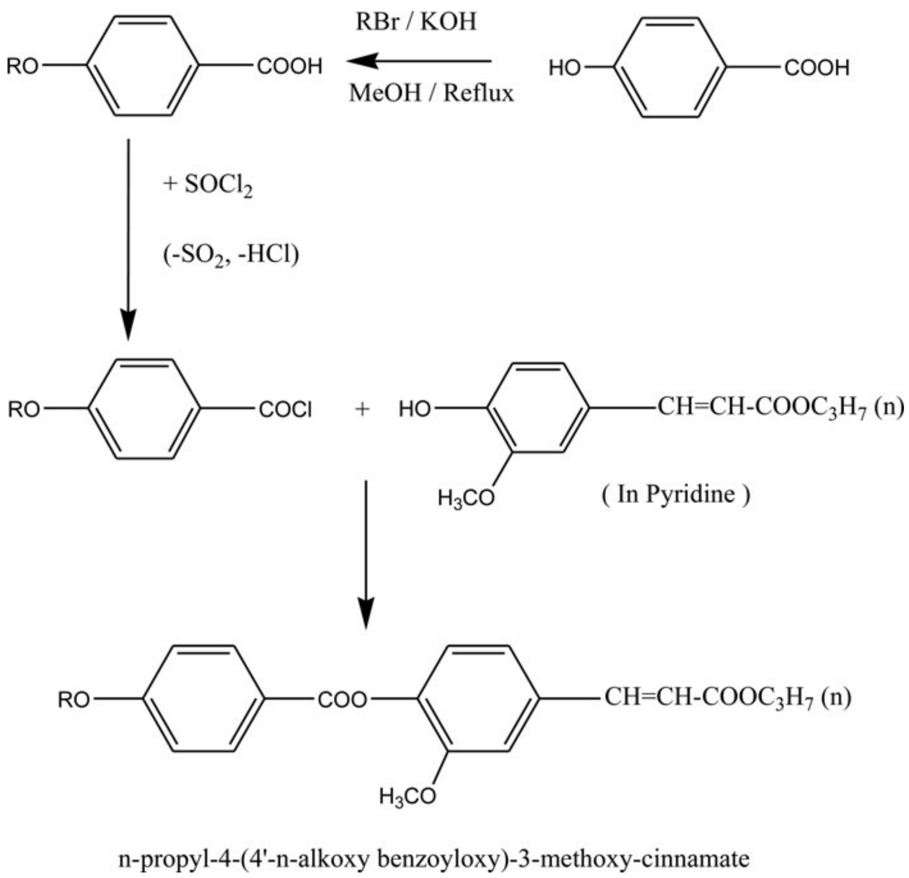


Scheme 1. Synthetic route to the series. **R** = $-C_nH_{2n+1}$ where, $n = 1,2,3,4,5,6,7,8,10,12,14,16$.

structurally similar series. The probable utility of novel substances will be suggested; to extend and continue the research by researchers working in application part.

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agents (R-X) to convert it into dimeric 4-n-alkoxy benzoic acids by the modified method of Dave and Vora [22]. 4-Hydroxy-3-methoxy cinnamic acid (m.p. 64°C) was esterified by n-propenol by using conc. H_2SO_4 by usual established method [23]. The ester was very dense brown colored semisolid (yield 65.5%), which purified from n-hexane. Dimeric 4-n-alkoxy benzoic acids were individually condensed with 4-hydroxy-3-methoxy n-propyl cinnamate in dry cold pyridine through corresponding acid chlorides [24]. Final products were individually decomposed, filtered, washed, dried and purified until constant transition temperatures were obtained.

The synthetic route to the series is shown below in Scheme 1.

The chemicals required, 4-hydroxy benzoic acid, MeOH, KOH, alkyl halides (R-X), thionyl chloride, 4-hydroxy-3-methoxy cinnamic acid (Ferulic acid), n-propenol, Conc. H_2SO_4, pyridine, 1:1 HCl, $NaHCO_3$, NaOH, anhydrous $CaCl_2$, silicagel, petroleum ether, methyl acetate and n-hexane were used as received, except solvents which were dried and purified prior to use.

Characterization

Representative homologues of the series were selected for characterization of structure by elemental analysis, IR spectra, mass spectra and H^1 NMR spectroscopy. Microanalysis was performed on Perkin Element PE 2400 CHN analyzer. IR spectra were recorded on a Perkin Elmer spectra GX. H^1 NMR spectroscopy performed was recorded on a Bruker spectrometer using $CDCl_3$ as solvent.

Mesomorphic properties were investigated using hot stage polarizing microscopy.

Analytical data

IR spectra in cm^{-1} for octyloxy homologoue derivative

The IR spectrum of the compound showed

682.35 cm^{-1} polymethylene of -C_8H_{17} group.
721.45 and 822.57 cm^{-1} as p-sub. benzene ring,
1154.33 cm^{-1} as -CO- of alkoxy group,
1256.51, 1606.64 cm^{-1} and 1731.80 cm^{-1} Conforms -COO- & -CO- of ester group,
1456.41 cm^{-1} Confirms aromatic -C = C-,
1067.05 cm^{-1} Confirms trans -CH = CH- group,
2926.46 cm^{-1} Confirms alkyl group.
IR data support the molecular structures.

IR spectra in cm^{-1} for decyloxy homologoue derivative

The IR spectrum of the compound showed,

648.53 cm^{-1} & 691.22 cm^{-1} Confirms polymethylene of -$C_{10}H_{21}$ group,
843.85 cm^{-1} to 762.03 cm^{-1} Confirms p-sub. benzene ring,
2852.88 & 2923.04 cm^{-1} Confirms alkyl group,
1732.05 cm^{-1}, 1606.30 cm^{-1}, 1256.40 cm^{-1}, Confirms -COO- & -CO- group,
1508.58, 1418.53, 1435.24 & 1470.73 cm^{-1} Confirms aromatic -C = C-,
1636.13 cm^{-1} confirms aliphatic -C = C-,
1067.88 cm^{-1}, 1119.59 cm^{-1} and 1167.18 cm^{-1} as -CO- of alkoxy group,
986.33 cm^{-1} Confirms trans -CH = CH- group,
IR data support the molecular structures.

H^1 NMR spectra in ppm for hexyloxy and dodecyloxy derivatives

Hexyloxy. H^1 NMR data in δ ppm (n-hexyloxy derivative, 400 MHz, $CDCl_3$, standard TMS):- 0.9159 (-CH_3 of -C_6H_{13}), 1.2670 & 1.3870 (-CH_2 of -C_6H_{13}), 1.7251 to 1.6427 (-OCH_2-CH_2 of -C_6H_{13}), 3.7480 (-O-CH_3), 4.0877 & 3.9422 (-O-CH_2- of -C_6H_{13}), 6.3153 to 7.1810 (-O-C_6H_3-CH = CH-CO-), 7.6066 to 8.0675 (p-sub. Benzene ring).

The data supports the molecular structure.

Dodecyloxy. H^1 NMR data in δ ppm (n-dodecyloxy derivative, 400 MHz, $CDCl_3$, standard TMS):-

Table 1. Elemental analysis for ethyloxy, butyloxy, octyloxy and decyloxy derivatives.

Compound no.	Molecular formula	% of C Experimental (Theoretical)	% of H Experimental (Theoretical)
C_2	$C_{22}H_{24}O_6$	68.74 (69.18)	6.29 (6.49)
C_4	$C_{24}H_{28}O_6$	69.88 (71.15)	6.84 (7.28)
C_8	$C_{28}H_{36}O_6$	71.77 (72.35)	7.74 (8.21)
C_{10}	$C_{30}H_{40}O_6$	72.55 (73.31)	8.12 (8.65)

0.9159 (-CH_3 of -$C_{12}H_{25}$), 1.0266 & 1.3156 (-CH_2 of -$C_{12}H_{25}$), 1.7537 to 1.8377 (-OCH_2-CH_2 of -$C_{12}H_{25}$), 3.8623 (-O-CH_3), 4.0543 & 4.1983 (-O-CH_2- of -$C_{12}H_{25}$), 6.4232 to 7.2859 (-O-C_6H_3-CH = CH-CO-), 7.6763 to 8.1773 (p-sub. Benzene ring).

The data supports the molecular structure.

Mass Spectra

Homologue:	Theoretical	Experimental
C_2	384.42	385.3
C_8	468.58	468.8

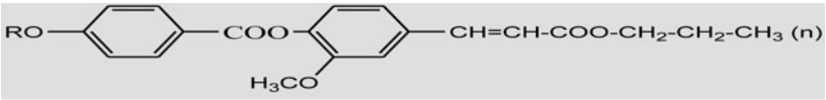
Texture Determination by Miscibility Method

- Hexyloxy homologue → Threaded nematic
- Octyloxy homologue → Schlieren nematic
- Tetradecyloxy homologue → Smectic—A

Results and discussion

The methoxy (C_1) to pentyloxy (C_5) homologues are nonmesomorphic, the hexyloxy (C_6) to dodecyloxy (C_{12}) homologues are smectogenic in addition to nematogenic, and the C_{14} to C_{16} homologues are only smectogenic. Transition temperatures (Table 2) and melting temperatures as determined from an optical microscopy equipped with a heating stage are plotted against the number of carbon atoms present in n-alkyl chain of left n-alkoxy end group.

Table 2. "Transition temperatures in °C".



Compound No.	R = -C_nH_{2n+1}	Smectic	Nematic	Isotropic
1	C_1	–	–	159.0
2	C_2	–	–	137.0
3	C_3	–	–	100.0
4	C_4	–	–	132.0
5	C_5	–	–	100.0
6	C_6	68.0	101.0	140.0
7	C_7	72.0	111.0	127.0
8	C_8	69.0	113.0	125.0
9	C_{10}	82.0	93.0	110.0
10	C_{12}	69.0	88.0	103.0
11	C_{14}	72.0	–	123.0
12	C_{16}	75.0	–	125.0

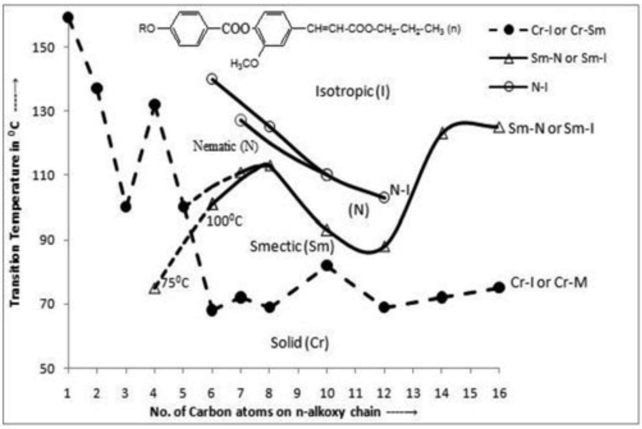


Figure 1. "Phase Behaviors of Series".

Smooth curves are drawn through like or related points; in a phase diagram (Fig. 1) showing phase behaviors of series. Cr-I/Sm follows a zigzag path of rising and falling manner with over all descending tendency as series is ascended. N-I transition curve is descended up to C_{12} homologue in usual established manner as series is ascended. Sm-N/I transition curve rises from C_6 homologue, passes through maxima at C_8 and then descended for C_{10} and C_{12} homologues, but, then it again rises and reaches to second maxima through C_{14} to C_{16} homologue derivative. Thus, it behaves in normal manner from C_6 to C_{12} members of the series and abnormally behaves for C_{14} and C_{16} member of a series. Sm-N/I transition curve is extrapolated [25–28] for odd and even-membered transition curves to C_5 and C_4 homologues to determine latent transition temperature for nematic and smectic, respectively, and to highlight or intensify odd–even effect of Sm-N/I transition curve. N-I and Sm-N/I transition curves exhibited odd–even effect. The N-I and Sm-N/I transition curves for odd and even members merges into each other at the C_{10} and C_8 members of a series respectively and then propagate as a single transition curve from and beyond C_{10} and C_8 homologue, respectively, for higher homologues. The N-I transition curve for odd members occupy lower position then even-membered transition curve, but odd-membered Sm-N transition curve occupy higher position then even-membered transition curve. The mesomorphic properties from homologue to homologue in a same novel series undergo variations. The present series of ester homologues is predominantly smectogenic and partly nematogenic with middle ordered degree of mesomorphism and 107.7 as well as 121.0 thermal stability for smectic and nematic mesophases, respectively xref.

The disappearance of dimerization of n-alkoxy benzoic acid is attributed to the breaking of hydrogen bonding between the acid molecules by esterification process. The nonmesomorphicity of C_1 to C_5 homologues is attributed to their high crystallizing tendency arising from unsuitable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions due to the law dipole–dipole interactions and the law magnitudes of dispersion forces by the interactions between instantaneous dipoles produced by the spontaneous oscillations of electron clouds of the molecules concerned, inducing high crystallizing tendency. The exhibition of smectogenic mesophase indicates the presence of preoccupied lamellar packing of molecules in their rigid crystal lattices, which forms layered structure. The intermolecular forces and closeness arising from various factors like molecular polarity and polarizability, size, aromaticity, molecular rigidity and flexibility, lateral and/or terminal end groups etc.

which stabilizes an existence of a molecule in varying physical state, to which the forces holding the planes of the layers together in the rigid crystal are weakened relatively to the lateral attractions among the molecules within a given layer at Cr-M transition temperature and the planes of the layers may become free to slide and rotate over one another giving rise to formation and appearance of smectic phase under the influence of exposed thermal vibrations in floating condition for definite range of temperature, which is termed as mesophaselength range or the degree of smectogenic mesophaselength depending upon magnitudes of molecular thermal resistivity (ΔH). Now on further heating to the smectic to a higher temperature, the intermolecular forces between the sides of the molecules are weakened to such an extent that resultant intermolecular end to end attractions are sufficient and of suitable magnitudes, which maintains, the statically parallel orientational order of molecules for C_6 to C_{12} homologues in floating condition causing hindrance to slide out the layers and induces nematogenic phase formation at Sm-N transition temperature. Thus, C_6 to C_{12} homologues exhibited smectic in addition to nematic phase for definite range of temperature. However, C_{14} and C_{16} homologue molecules are unable to resist exposed thermal vibrations to such an extent that, resultant end to end and lateral intermolecular forces allow the molecules to maintain only sliding layered molecular arrangement for some temperature difference, but do not allow a statistically parallel orientational order of molecules in floating condition. Thus, molecules are randomly oriented in all possible directions, beyond exhibition of smectic phase with high order of disorder or high entropy ($\Delta S = \Delta H/T$) at Sm-I transition temperature. The isotropic mass of C_6 to C_{12} homologues and C_{14} to C_{16} homologues, on carefully cooling, causes reappearance of nematic and smectic or only smectic phase (C_{14} and $C_{16)}$ reversibly at the same transition temperatures at which they were appeared on heating. Odd–even effects observed for Sm-N/I and N-I transition curves are attributed to the sequentially added methylene unit or units at the left terminal end group. The disappearance of odd–even effect from and beyond merging of curves for odd and even members is due to the coiling or bending or fluxing or coupling of *n*-alkyl chain with the principle axis of core structure. Laterally substituted methoxy group increases intermolecular distance and molecular polarizability operatable at a time for the same reason, and acting oppositely with respect to magnitudes of intermolecular attractions to each other. The extent of molecular noncoplanarity delays commencement of mesophase from C_6 homologue. The absence of mesophase formation from C_1 to C_5 is attributed to the unsuitable magnitudes of anisotropic forces of intermolecular cohesion as a consequence of unfavorable molecular rigidity and flexibility possessed by the molecule. The abnormal or unexpected behavior of C_{14} and C_{16} members in a transition temperature curve is attributed to unusual status of longer n-alkyl chain of the left n-alkoxy terminal end group [29] in the presence of highly polar $-OCH_3$ lateral group on second phenyl ring. Thus, variations in mesomorphic properties from homologue to homologue in the same present series is governed by number of carbon atoms present in n-alkyl chain keeping tail group and a lateral $-OCH_3$ group unchanged. The mesomorphic properties of present series are compared with the structurally similar other known series as under in Figure 2.

The homologous series-1 of present investigation and series-X [30] and Y [31] chosen for comparison are structurally resembled each other with respect to two phenyl rings and flexible terminal end group $-CH=CH-COO-CH_2-CH_2-CH_3$ as well as -OR for the same homologue from series to series under comparative study. However, they differ with central bridge or laterally substituted functional group. Thus, the minor dissimilarity in molecular structure of substance or substances in their mesomorphic properties and the degree of mesomorphism as a result of changing molecular rigidity and flexibility associated with individual molecules for the same homologue from series to series and from homologue to homologue in the same

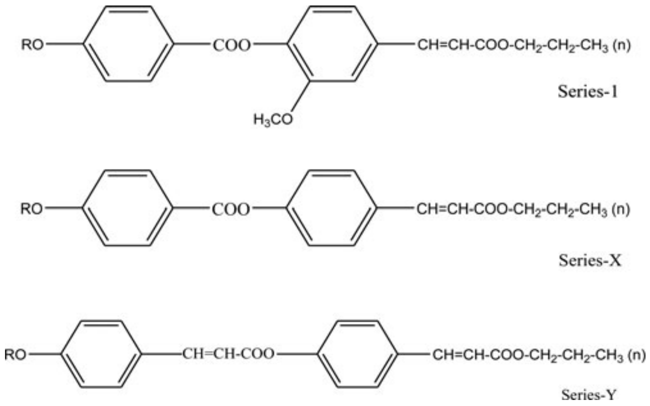


Figure 2. Structurally Similar Series.

series. Some mesomorphic properties of series 1, X and Y are mentioned below in Table 3 as under, which varies with the changing molecular structure.

Above Table 3 represents the thermal stabilities for smectic and nematic, commencement of smectic and/or nematic, mesophaselength etc for the series 1, X and Y respectively, described as under.

- Homologous series 1 and X are smectogenic in addition to nematogenic, whereas series-Y is only smectogenic.
- Smectogenic mesophase commences from C_6 and C_8 homologues for series 1 and X, but it does not commence till the last member (C_{16}) of a series-Y.
- Nematic mesophase commences from C_6 member of the series 1, X and Y, but it continue till different homologue i.e. C_{12}, C_{16} and C_{14} member of series 1, X and Y, respectively.
- Total mesophaselength range bears decreasing tendency for the degree of mesomorphism, from series-1 to X to Y.
- Thermal stabilities for smectic and nematic are equal for the series 1 and X, but, the smectogenic commencement differs. Moreover nematic thermal stability, greatly differs of series-Y as compared to series-1 and X with complete destabilization of smectic phase.

Homologous series-1 of present investigation is laterally substituted by highly polar—OCH_3 functional group. Therefore two opposing forces are operated at a time. Intermolecular forces (i) which undergo reduction due to molecular branching by -OCH_3 lateral substitution due to increase in the intermolecular distance or by molecular widening, whereas (ii) intermolecular forces enhanced due to increase in the molecular polarizability by laterally substituted -OCH_3 group. Thus, two opposing intermolecular forces are operated at a time for the same reason. Therefore, the net intermolecular force operated between two molecules of same homologue will depend upon the predominancy of the factor, either (i) or (ii) or the resultant magnitudes of net anisotropic forces of intermolecular attractions which

Table 3. Average thermal stability in °C.

Series:	1	X	Y
Smectic–nematic or Smectic–isotropic	107.7 (C_6-C_{16})	107.5 (C_8-C_{10})	–
Commencement of Smectic phase	C_6	C_8	–
Nematic–isotropic	121.0 (C_6-C_{12})	121.0 (C_6-C_{16})	183.8 (C_6-C_{14})
Commencement of nematic phase	C_6	C_6	C_6
Total mesophaselength range in °C (Sm + N)	28.0 to 72.0	12.0 to 44.0	10.0 to 34.0
C_i C_p	C_{10} C_6	C_{14} C_8	C_6 C_{16}

is suitable to cause mesomorphism from C_6 to C_{16} homologues as a consequence of favorable molecular rigidity and flexibility; depending upon permanent dipole moment across the long molecular axis, dipole–dipole interactions, electron–electron interactions, dispersion forces etc. However, in case of homologous series-X, the branching of a molecule is absent for all the homologues, which do not affect to the resultant intermolecular cohesive forces and closeness. But, coincidently the suitable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions together approaches nearest or equivalent to each other for the series-1 and X, though, their reasons for occurrence differ from each other; the part of which is related to molecular resistivity against exposed thermal vibrations to facilitate and stabilize smectic and then nematic phase. Their commencement of smectic phase differs (C_6 and C_8) but the commencement of nematic phase and Sm-N/I and N-I thermal stabilities are identical but their ending mesophase homologue differs; with differing intermolecular cohesive energy associated with individual molecules. The molecular constitution being different for the same homologue from series-1 to series-X, the individual thermometric behaviors are differing except their thermal stabilities for smectic and nematic as well as commencement of nematic mesophase. The absence of smectogenic character in series-Y may be attributed to the absence of lamellar packing due to the replacement of -COO- by -CH = CH-COO- central bridge joining first and middle phenyl ring which increases molecular rigidity due to the added -CH = CH- unit and hinders to facilitate smectic mesophase formation and favors the less-ordered nematic phase formation at the cost of smectic phase. The suitable magnitudes of end to end intermolecular forces are strengthened by the presence of multiple bond in vinyl carboxy group; and the reduction of the extent of noncoplanarity between two molecules of the same homologues. Thus, the change in mesomorphic properties from homologue to homologue and for the same homologue from series to series depends upon molecular structure and the extent of dissimilarity of molecular structure among the comparing molecules.

Conclusions

- Present novel ester series is predominantly smectogenic and partially nematogenic with sufficient mesophaselength range.
- Group efficiency order derived for smectic and nematic on the basis of (I) Thermal stabilities (ii) early commencement of mesophase (iii) total mesophaselength (Sm + N) as under.

  (i) **Smectic**:-
  Series-1 = Series-2 > Series-3
  1 (Presence of lateral -OCH_3 group) (Absence of lateral group) (Replacement of -COO- by -CH = CH-COO- central bridge)
  Nematic:-
  (-CH = CH-COO-) > -COO- = -COO- (with lateral substitution)

  (ii) **Smectic :-**
  -COO- > -COO- > -CH = CH-COO-
  (with lateral substitution) (without lateral substitution)
  Nematic:-
  -COO- = -CH = CH-COO- = -COO-
  (without lateral substitution) (without lateral substitution) (with lateral substitution)

  (iii) **(Sm + N) :-**

-COO- > -COO- > -CH = CH-COO-
(with lateral substitution) (without lateral substitution) (without lateral substitution)

- Suitable magnitudes of favorable molecular rigidity and flexibility can induce mesomorphism depending on molecular structure.
- A phenomena of mesomorphism is very sensitive and susceptible to molecular structure.
- Ester derivatives containing -CH = CH- unit may be useful in agricultural production.

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References

[1] Reinitzer, F. (1888). *Monatsch. Chem.*, 9, 421.
[2] Gray, G. W. (1974). In: *Liquid. Crystals and Plastic Crystals*, Gray, G. W. & Windsor, P. A. (Eds.), Chapter 4. Vol. 1, pp. 103–153..
[3] Gray, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystals*, Academic Press: London.
[4] Gray, G. W., & Windsor, P. A. (Eds). *Liquid. Crystals and Plastic Crystals*, 1, 308.
[5] Imrie, C. T. (1999). *Liq. Crystal dimers. Struct. Bond*, 95, 149.
[6] Demus, D. (1988). *Mol. Cryst. Liq. Cryst.*, 165, 45.
[7] Demus, D. (1989). *Liq. Cryst.*, 5, 75.
[8] Imrie, C. T., & Luckhrst, G. R. (1998). In: *Hand Book of Liquid Crystals, Law Molecular Liquid Crystals*, Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W. & Vill. V. (Eds.), Vol. 2B, pp. 801–833, Wiley-VCH. Weinheim.
[9] (i) Suthar, D. M., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 575, 76. (ii) Chauhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 570, 92–100. (iii) Chaudhari, R. P., Chauhan, M. L., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 575, 88. (iv) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, 552, 104–110.
[10] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 527, 51-.
[11] Naemura, S. (2001). *Displays*. 22(1), 1.
[12] Kim, W. S., Elston, S. J., & Raynes, F. P. (2008). *Displays*, 29, 458.
[13] Tadwee, I., Shahi, S., Ramteke, V., & Syed, I. (2012). *IJPRAS.*, 1(2), 06—11, ISSN 2277–3657.
[14] Hertz, E., Lavorel, B., & Faucher, O. (2011). *Nature Photon.*, 5, 78.
[15] Calliste, C. A., et al. (2001). *Anticancer Res.*, 21, 3949.
[16] Jahng, Y., et al. (2004). *Bioorg. Med. Chem. Lett.*, 14, 2559.
[17] Rajesh, G., et al. (2008). *Chem. Pharm. Bull.*, 56, 897.
[18] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Adv. Mater.*, 4, 285.
[19] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, 14, 741.
[20] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Mc Donnell, D. G. (1993). *Liq. Cryst.*, 15, 123.
[21] Collings, P. J., & Hird, M. (1998). *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis Ltd.: U. K.
[22] Dave, J. S., & Vora, R. A., (1970). In: *Liquid Crystal and Ordered Fluids*, Johnson, J. F. & Porter R. S. (Eds.), p. 477, Plenum Press: New York.
[23] Vogel, A. I. (1989). *Text Book of Practical Organic Chemistry*, 5th ed, ELBS, Longman: London: p. 946.
[24] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 582, 79.
[25] Lohar, J. M., & Doshi, A. V. (1993). In: *Proceedings of the Indian Acad. of Science – Bangalore*, 105(3), p. 209.
[26] Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, 552, 104–110.
[27] Doshi, A. V., Bhoya, U. C., & Travadi, J. J. (2012). *Mol. Cryst. Liq. Cryst.*, 552, 10.

[28] Ganatra, K. J., & Doshi, A. V. (2000). *J. Indian Chem. Soc.*, 77, 322.
[29] (a) Young, W. R. (1970). *Mol. Cryst. Liq. Cryst.*, 10, 237. (b) Dietrich, H. J., & Steiger, E. L. (1972). *Mol. Cryst. Liq. Cryst.*, 16, 263.
[30] Chauhan M. L., & Doshi A. V. (2014). *Mol. Cryst. Liq. Cryst.*, Taylor & Francis, LCMH 289.
[31] Patel, R. B., & Doshi, A. V. (2011). *Der Pharma Chemica*, 3(1), 538.