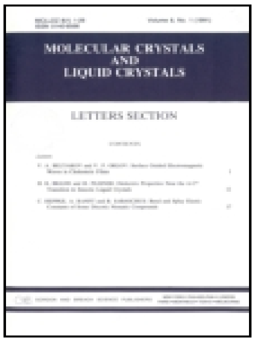

Molecular Crystals and Liquid Crystals

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Mesomorphism dependence on molecular flexibility

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Mesomorphism dependence on molecular flexibility

J. J. Travadi[a], M. S. Vadodaria[b], K. D. Ladva[b], and A. V. Doshi[c]

[a]Chemistry Department, Kamani Sc. College and Prataprai Arts College, Amreli, Gujarat, India; [b]Chemistry Department, Shree M. & N. Virani Sc. College, Rajkot, Gujarat, India; [c]Ex. Principal, Matushri Virbaima Mahila Science and Home Science College, Rajkot, Gujarat, India

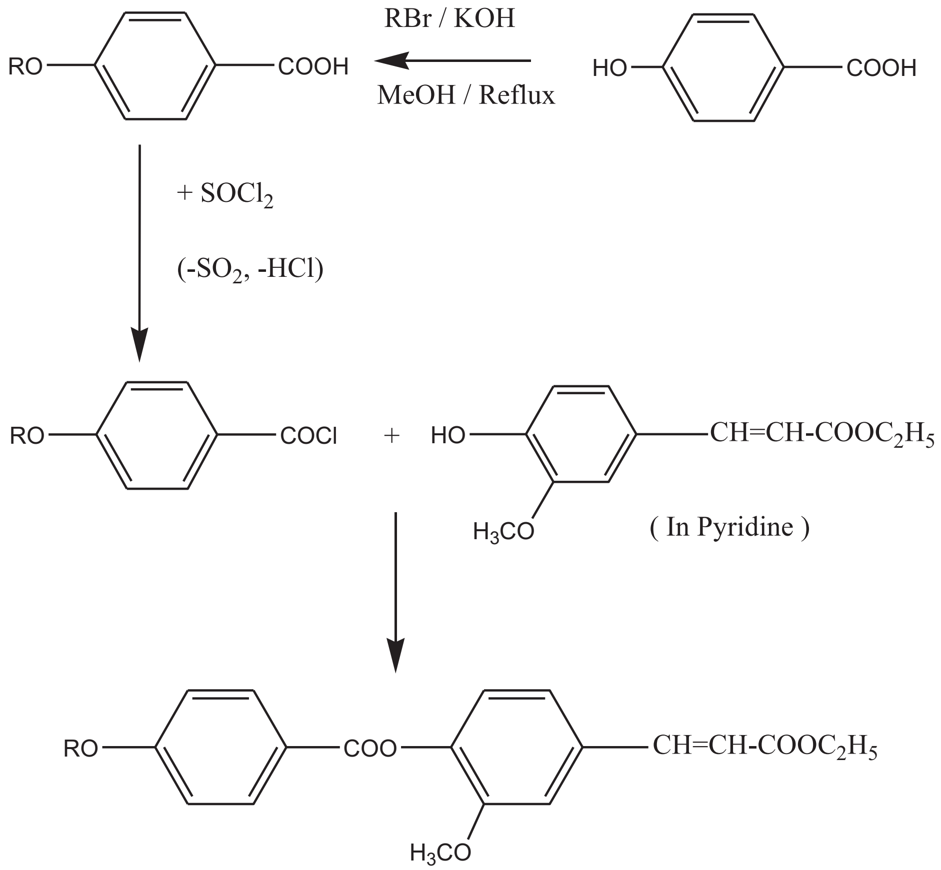
ABSTRACT
A novel ester homologous series of liquid crystals with a highly polar laterally substituted –OCH_3 group is synthesized and studied with a view to understanding and establishing the effects of molecular structure involving lateral substitution on liquid crystal behavior. The novel series $RO{\cdot}C_6H_4{\cdot}COO{\cdot}C_6H_3{\cdot}OCH_3$(ortho)$CH{=}CH{\cdot}COO{\cdot}C_2H_5$ consists of 12 homologs of which C_7, C_8, C_{10} are nematogenic and C_{12}, C_{14}, C_{16} homologs are smectogenic. The rest of the homologs are nonliquid crystals. The textures of nematic phase are threaded and the smectic phase is of the type A or C. Transition temperatures and the textures of mesophases were determined by an optical polarizing microscope equipped with a heating stage. Analytical and spectral data support the molecular structures. The N-I and Sm-I transition curves behave in normal manner without exhibition of an odd-even effect. Average thermal stability for smectic and nematic are 127.3°C and 129°C, respectively. The total mesophase length ranges from 17°C to 57°C and series is of a middle ordered melting type with transition temperatures varying between 82°C and 148°C. The liquid crystal properties of present novel series are compared with, structurally similar known homologous series.

KEYWORDS
Azoester; liquid crystals; nematic; mesomorphism; smectic

Introduction

Liquid crystalline (LC) state of substance [1] is universally accepted as an useful physical state of a substance to human beings [2–6]. The present investigation was planned with a view to understanding and establishing the effects of molecular structure on LC properties by synthesis of novel LC materials through homologous series by changing molecular structural geometry with reference to laterally substituted group of esters. [7–10] Many homologous series have been reported to date [11–20]. The present series consists of two phenyl rings, bonded through –COO– central bridge, changing –OR and fixed –$CH{=}CH\text{-}COO\text{-}CH_2\text{-}CH_3$ flexible end groups as well as –OCH_3 laterally substituted functional group. The mesomorphicity, textures of mesophase and characterization of novel homologs will be performed and the results will be evaluated and interpreted in terms of molecular rigidity and flexibility [21–25]. Group efficiency order will be derived for smectic and nematic. Then, the data of the novel investigation will be compared with the structurally similar known series.

CONTACT J. J. Travadi j.travadi72@gmail.com Chemistry Department, Kamani Sc. College and Prataprai Arts College, Amreli, Gujarat, India.



Ethyl-4-(4'-n-alkoxy benzoyloxy)-3-methoxy-cinnamate

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

Scheme 1. Synthetic route to the series.

Experimental

Synthesis

4-hydroxy benzoic acid was alkylated by suitable alkylating agent (R-X) to convert it into dimeric 4-*n*-alkoxy benzoic acids by the modified method of Dave and Vora [26]. 4-Hydroxy 3-methoxy cinnamic acid (m.p. 64°C yield 67 %;) was esterified by ethanol by using conc. H_2SO_4 by usual established method [27]. The ester was cream-colored soft crystalline substance (M. Pt 63°C–65°C), which purified from distilled *n*-hexane. The yield was 67.5%;. Dimeric 4-*n*-alkoxy benzoic acids were individually condensed with 4-hydroxy, 3-methoxy, ethyl cinnamate in dry cold pyridine through corresponding acid chlorides [28]. Final products were individually decomposed, filtered, washed, dried, and purified till constant transition temperatures obtained.

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

The chemicals required, 4-Hydroxy benzoic acid, MeOH, KOH, Alkyl halide (R-X), Thionyl chloride, 4-hydroxy,3-methoxy, cinnamic acid (Ferulic acid), Ethanol, Conc. H_2SO_4, Pyridine, 1:1 HCl, $NaHCO_3$, NaOH, anhydrous $CaCl_2$, Silicagel, Petrolium ether, Methyl acetate, and *n*-hexane were used as received, except solvents which were dried and purified prior to use.

Characterization

Representative homologs of the series were selected for characterization of structure by elemental analysis, IR spectra and ^{1}H NMR spectroscopy.

Microanalysis was performed on Perkin Element PE 2400 CHN analyzer. IR spectra were recorded on Perkin Elmer spectra GX. Enthalpy-entropy concept discussed qualitatively without performance on DSC. ^{1}H NMR spectroscopy performed were recorded on Bruker using $CDCl_3$ as solvent.

Mesomorphic properties were investigated using hot stage polarizing microscope.

Analytical data

IR spectra in cm^{-1} for propyloxy and hexyloxy homologoue derivatives

Propyloxy

The IR spectrum of the compound showed
693.95 cm^{-1} polymethylene of $-C_3H_7$ group.
847.42 and 771.69 cm^{-1} conforms para and ortho sub. benzene ring,
1165.74 and 1044.09 cm^{-1} as -CO- of alkoxy group,
1248.09, 1600.78, and 1708.40 cm^{-1} conforms -COO- of ester group,
966.59 cm^{-1} conforms trans -CH=CH- group,
2874.32 and 2964.13 cm^{-1} conforms alkyl group.
IR supports the structure.

Hexyloxy

The IR spectrum of the compound showed
691.50 and 644.09 cm^{-1} polymethylene of $-C_6H_{13}$ group.
844.67 and 769.44 cm^{-1} as p-sub. and ortho-substituted benzene ring,
1155.41 and 1024.09 cm^{-1} as -CO- of alkoxy group,
1730.82, 1679.84, 1601.77, and 1244.13 cm^{-1} as -COO- & -CO- of ester group,
984.12 cm^{-1} conforms trans -CH=CH- group,
2928.99 and 2868.20 cm^{-1} conforms alkyl group.
IR supports the structure.
^{1}H NMR spectra in ppm for pentyloxy and dodecyloxy derivatives

Pentyloxy

H^1 NMR data in δ ppm (*n*-pentyloxy derivative, 400 MHz, $CDCl_3$, standard TMS) 0.8863 ($-CH_3$ of $-C_5H_{11}$), 1.7454, 1.2628, and 1.1792 ($-CH_2-$ of $-C_5H_{11}$), 1.3475 ($-OCH_2-CH_2$ of $-C_5H_{11}$), 3.7744 ($-O-CH_3$), 3.9511 ($-O-CH_2-$ of $-C_5H_{11}$), 6.8715, and 7.1917 ($-O-C_6H_3-CH=CH-CO-$), 7.9651, and 7.9938 (p-sub. Benzene ring).

The data supports the molecular structure.

Table 1. Elemental analysis for propyloxy, hexyloxy, decyloxy, and dodecyloxy derivatives.

Compound no.	Molecular formula	%; of C Experimental	%; of H Theoretical	Experimental	Theoretical
C_3	$C_{22}H_{24}O_6$	69.23	68.74	6.80	6.29
C_6	$C_{25}H_{30}O_6$	70.87	70.40	7.38	7.09
C_{10}	$C_{29}H_{38}O_6$	72.39	72.17	8.19	7.94
C_{12}	$C_{31}H_{42}O_6$	73.18	72.91	8.47	8.29

Dodecyloxy

H^1 NMR data in δ ppm (n-dodecyloxy derivative, 400MHz $CDCl_3$, standard TMS): 0.8182 (-CH_3 of -$C_{12}H_{25}$), 1.2425 to 1.7711 (-CH_2- of -$C_{12}H_{25}$), 1.3928 (-OCH_2-CH_2 of -$C_{12}H_{25}$), 3.8128 (-O-CH_3), 3.9595 (-O-CH_2- of -$C_{12}H_{25}$), 6.8535 & 6.8668 & 7.1923 (-O-C_6H_3-CH=CH-CO-), 7.9644, and 7.9930 (p-sub. Benzene ring).

The data support the molecular structure.

Mass spectra

Homolog	Theoretical	Experimental
C_6	426.50	427.30
C_{10}	482.61	483.40

Textures of mesophase by miscibility method

Octyloxy homolog→Threaded Nematic
Tetradecyloxy homolog → Smectic–C

Results and discussion

4-Hydroxy-3-methoxy ethyl cinnamate (M. Pt 64°C) is a nonmesomorphic in character, but on linking it with the dimeric 4-n-alkoxy benzoic acids yielded LC homologs, whose mesomorphism commences from C_7 homolog and continued up to C_{16} homolog. The transition temperatures of homologs are lower than corresponding n-alkoxy acids and alternates throughout the series. C_7–C_{10} homologs are nematogenic and C_{12}–C_{16} homologs are smectogenic. Rest of the C_1–C_6 homologs are nonliquid crystals. Transition temperatures as determined from an optical polarizing microscopy equipped with a heating stage are recorded in Table 2. Smooth transition curves are drawn by linking like or related points for Cr-M, N-I or Sm-I transitions; as depicted in a phase diagram as shown in Figure 1. A Cr-M/I transition curve follows a zigzag path of rising and falling with overall descending tendency as series is ascended and behaved in normal manner. N-I transition curve descends from C_7 to C_{10} without exhibition of odd-even effect. Sm-I transition curve ascended from C_{12} to C_{16} homolog without exhibition of odd-even effect. Thus, N-I and Sm-I transition curves drawn for number of carbon atoms present in n-alkyl chain of a left n-alkoxy terminal end group versus transition temperatures behaved in normal manner. Sm-I transition curve and N-I transition curve are extrapolated [29–31] to C_{10} and C_{12}, respectively; to determine latent transition temperature for smectic of C_{10} homolog and to examine absence of nematic property for C_{12} homolog beyond smectic property. Mesomorphic property and thermal behaviors from homolog

Table 2. Transition temperatures in °C.

Compound no. $R = \text{-}C_nH_{2n+1}$	*n*-Alkyl group Sm	*N*	Isotropic	
1	C_1	—	—	110.0
2	C_2	—	—	120.0
3	C_3	—	—	114.0
4	C_4	—	—	148.0
5	C_5	—	—	114.0
6	C_6	—	—	82.0
7	C_7	—	84	141.0
8	C_8	—	94	131.0
9	C_{10}	—	88	115.0
10	C_{12}	100.0	—	117.0
11	C_{14}	91.0	—	130.0
12	C_{16}	94.0	—	135.0

to homolog in a same novel series which undergo variations keeping flexible -CH=CH-COO-CH_2-CH_3 group and the molecular rigidity constant. Thus, homologous series under discussion is partly smectogenic and partly nematogenic of middle ordered melting type whose smectogenic and nematogenic average thermal stabilities are 127.3°C and 129.0°C, respectively.

The disappearance of dimerization of alkoxy acids and the lowering of transition temperatures of homolog ester derivatives (C_1–C_{16}) as compared to corresponding dimerized *n*-alkoxy acids are attributed to the breaking of hydrogen bonding between two molecules of aromatic acids, by esterification process. The exhibition or nonexhibition of mesophases is attributed to the favorable or unfavor disalignment of molecules at an angle either perpendicular to the plane of floating surface or at an angle less than 90° depending upon the thermal

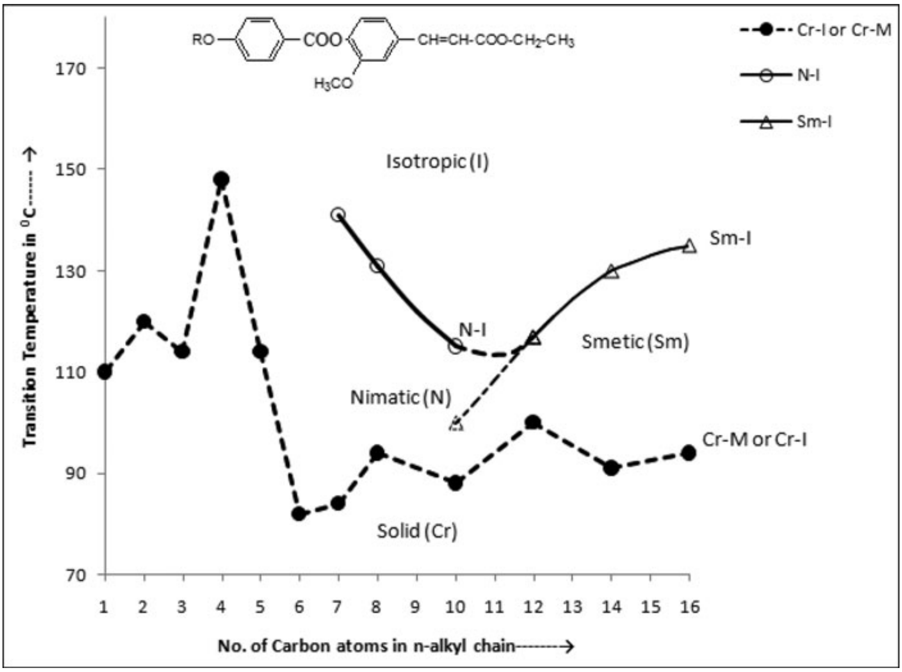


Figure 1. Phase behaviors of series.

resistivity of molecules by suitable or unsuitable magnitudes of anisotropic forces of intermolecular anisotropic end-to-end or/and lateral attractions and closeness; as a consequence of resultant favorable or unfavorable molecular rigidity and flexibility. The nonexhibition of mesophase formation of C_1–C_6 is attributed to the inability to resist exposed thermal vibrations by nonmesomorphs whose crystal lattices are abruptly breaking. Consequently, they sharply transform into isotropic liquid without exhibition of an intermediate state of existence, called as LC state. Such nonmesomorphic tendency arises due to their (C_1–C_6) high crystallizing tendency which arises from low dipole–dipole interactions and low magnitudes of dispersion forces by the interactions between instantaneous dipoles produced by the spontaneous oscillations of electron clouds of the molecules. The exhibition of nematic mesophase by C_7, C_8, and C_{10} is attributed to disalignment of molecules resisting exposed thermal vibrations by the suitable magnitudes of anisotropic end-to-end cohesive forces to arrange the molecules in statistically parallel orientational order under floating condition; due to favorable molecular rigidity and flexibility. However, on increasing *n*-alkyl chain length of left *n*-alkoxy group, the longer *n*-alkyl chain bearing C_{12}, C_{14}, and C_{16} homologs in which laterally substituted -OCH_3 group due to molecular polarizability factor activate formation of lamellar packing in crystal lattices and forms layered structure in rigid crystal; which forms sliding layered arrangement under the influence of externally exposed thermal vibrations between two temperatures showing smectogenic mesophase formation. The appearance of all mesomorphic or nonmesomorphic homologs (C_1–C_{16}) from and beyond isotropic temperature become identical at which molecules under investigation are randomly oriented in all possible directions with high order of disorder or high entropy ($\Delta S = \Delta H/T$); but on cooling the same with proper rate of cooling the isotropic melt; the mesogenic homologs reversibly exhibited reappearance of respective smectic or nematic phase which was appeared on heating the sample. None of the mesogenic homolog showed monotropic transition or mesophase (monotropically) irreversible manner on cooling sample.

The absence of odd-even effect is attributed to the late commencement of mesophase from C_7 homolog and the subsequent mesogenic homologs are of even number, i.e., C_8, C_{10}, C_{12}, C_{14}, and C_{16}. The LC properties of varying left flexible *n*-alkoxy terminal end group and fixed right handed flexible tail end group, including fixed flexible lateral -OCH_3 group with unchanging rigidity of presently investigated series, in which mesogenic thermometric behaviors vary from homolog to homolog as a consequence of changing molecular flexibility by sequential addition of methylene unit or units. The extrapolated LTT for smectic of C_{10} homolog is predicted at 100°C, but it is not realizable due to its high crystallization tendency. The extrapolation of N-I transition curve to C_{12} homolog matches with Sm-I transition curve of C_{12}; indicating the impossibility of nematic phase formation, because N-I and Sm-I transition temperatures coincide at the same point in the phase diagram (Figure 1).

Some LC properties of presently investigated homologous series-1 are compared with a structurally similar other known series-*X* [32] and *Y* [33] as mentioned below in Figure 2.

Homologous series-1 of present investigation-1 and series-*X* selected for comparative study, resemble to each other in all respect, i.e., two phenyl rings, central bridge -COO- right handed tail $-CH{=}CH\text{-}COOCH_2\text{-}CH_3$, left *n*-alkoxy end group for the same homolog, but differs with respect to laterally substituted -OCH_3 group. Homologous series-*Y* differs from series-1 with respect to laterally substituted -OCH_3 group and a part of tail end group -CH_3 or -C_6H_5 of series-1 and -*Y*, respectively. Thus, series-1, *X*, and *Y* differs with respect to molecular polarity, polarizability and flexibility or rigidity due to, lateral -OCH_3 group (series-1), the part of tail end groups -CH_3 (series-*X*) and -C_6H_5 (series-*Y*) for the same homolog from

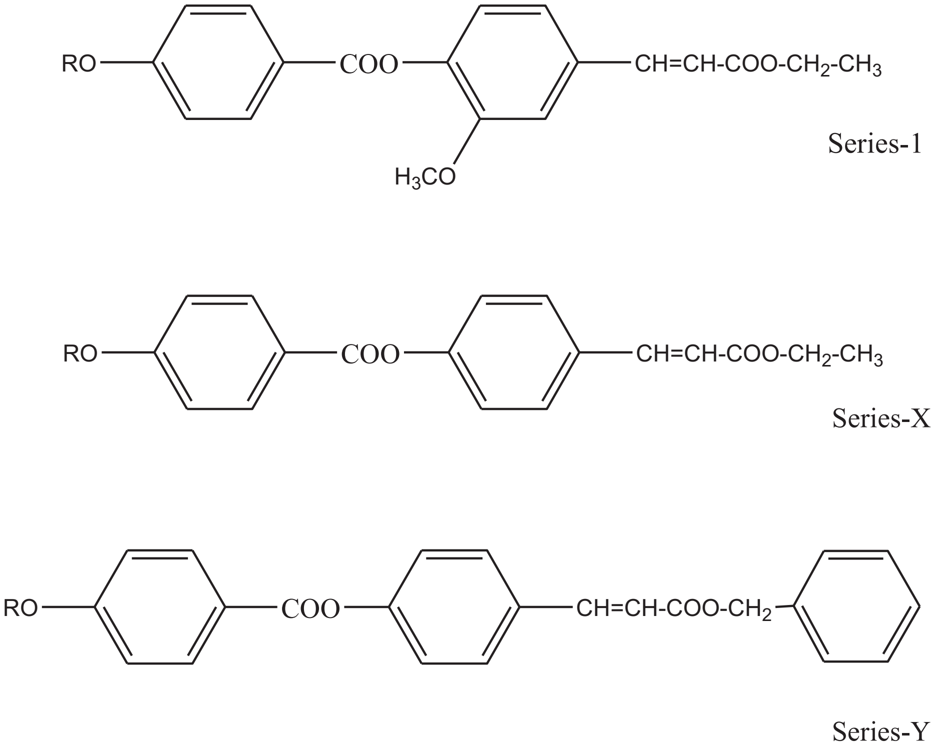


Figure 2. Structurally similar series.

series to series. Hence, the changing magnitudes of either molecular rigidity and/or flexibility will be reflected to variations in mesomorphic properties and the degree of mesomorphism from homolog to homolog in the same series or for the same homolog from series to series. Following Table 3 represents some mesomorphic properties, commencement of mesophase, thermal stability, total mesophaselength range, etc., for the series under comparative study.

Table 3. Relative thermal stability in °C.

Series	1	*X*	*Y*
Smectic-isotropic or Smectic-nematic	127.3 (C_{12}–C_{16})	74.8 (C_6–C_{16})	144.1 (C_6–C_{16})
Commencement of smectic phase	C_{12}		
C_6			
C_6			
Nematic-isotropic	129.0		
(C_7–C_{10})	98.6		
(C_4–C_{16})	171.4		
(C_5–C_{16})			
Commencement of nematic phase			
C_7			
C_4			
C_5			
Total mesophaselength (Sm +N) in °C			
C_i–C_p	17–57		
C_{12} C_7	25–57		
C_4 C_{10}	33–59		
C_6 C_{12}			

It is clear from Table 3 that,

- Homologous series-1, *X*, and *Y* under comparative study are smectogenic in addition to nematogenic.
- Smectic and nematic thermal stability of series-1 is more than a series-*X* and less than series-*Y*.
- Smectic mesophase commences from C_{12}, C_6, and C_6 homologs respectively for series-1, *X* and *Y*.
- Nematogenic mesophase commences from C_7, C_4, and C_5 homologs for series-1, -*X*, and -*Y*, respectively.
- Total mesophaselength range adopts decreasing order from series-1 to -*X* to -*Y*.
- All the three series under comparative study have the potential to exhibit and stabilize smectic mesophase in addition to nematic mesophase in usual establish manner. However, their thermal stabilities, commencement of mesophase formation and the range of liquid crystalanity differ for the same homolog from series to series or from homolog to homolog in the same series due to varying magnitudes of molecular rigidity and/or flexibility as a consequence of variable factors like length to breadth ratio, aromaticity, permanent dipole moment across the long molecular axis, dispersion forces, dipole-dipole interactions, electronic interactions, length-to-breadth ratio, molecular polarity, and polarizability, inter molecular closeness as well as suitable magnitudes of anisotropic end-to-end and lateral attractions, the bipolarity of $-CH_2-CH_3$ or $-CH_2-C_6H_5$ bond or $C-OCH_3$ bond etc. Homologous series-1 is laterally substituted by highly polar $-OCH_3$ group which induces molecular polarizability relatively more than the series-*X* and -*Y*; whereas; series-*X* and -*Y* are linear and lath like with stratified structure bears, difference of magnitudes of intermolecular closeness causing difference of suitable magnitudes of anisotropic end-to-end and lateral attractions. Thus, the resistivity toward exposed thermal vibrations adopts different total mesophaselength range, which follows the decreasing order. Thus, highest order of series-1 is attributed to laterally substituted $-OCH_3$ group, which predominantly induces and operates polarizability factor. The sp^3 carbon of a part of tail terminal end group is bonded with sp^3 carbon of $-CH_3$ in series-1 and -*X*, but sp^3 carbon of the identical part of series-*Y* is bonded with sp^2 carbon of a phenyl ring $-C_6H_5$ that causes difference of molecular rigidity and flexibility and intermolecular cohesive energy. Moreover, the extent of molecular noncoplanarity which results into the early or late commencement of mesophases, viz., smectic and nematic. The values of thermal stabilization and facilitations of mesophases are dependent upon the values of heat of formation (ΔH) which varies from homolog to homolog in the same series and series to series for the same homolog. Thus, difference of transition temperatures of mesogenic homologs stabilize smectic and nematic phase based on molecular structure, which alters from series to series for the same homolog by changing fixed tail group or/and a lateral group, including changing number of methylene unit or units.

Conclusions

- A novel homologous series of esters with two phenyl rings and lateral substitution is partly smectogenic and partly nematogenic with middle ordered melting type and considerable mesophaselength range.
- The group efficiency order derived on the basis of (a) thermal stability (b) early commencement of mesophase, and (c) total mesophaselength range for smectic and nematic are as under.

(a) Smectic

$$-CH=CH-COOCH_2{\cdot}C_6H_5 > \underset{\text{with lateral group}}{-CH=CH-COOCH_2{\cdot}CH_3}$$

$$> CH=CH-COOCH_2{\cdot}CH_3$$

Nematic

$$-CH=CH-COOCH_2 \cdot C_6H_5 > \underset{\text{with lateral group}}{-CH=CH-COOCH_2 \cdot CH_3}$$

$$> -CH=CH-COOCH_2 \cdot CH_3$$

(b) Smectic

$$CH=CH-COOCH_2{\cdot}C_6H_5 = -CH=CH-COOCH_2{\cdot}CH_3$$

$$> \underset{\text{with lateral group}}{CH=CH-COOCH_2{\cdot}CH_3}$$

Nematic

$$-CH=CH-COOCH_2{\cdot}CH_3 > -CH=CH-COOCH_2{\cdot}C_6H_5$$

$$> \underset{\text{with lateral group}}{-CH=CH-COOCH_2{\cdot}CH_3}$$

(c) Total mesophaselength range (Sm + N)

$$\underset{\text{with lateral group}}{-CH=CH-COOCH_2{\cdot}CH_3} > -CH=CH-COOCH_2{\cdot}CH_3$$

$$> -CH=CH-COOCH_2{\cdot}C_6H_5$$

- Favorable molecular rigidity and flexibility are governing mesomorphism depending on molecular structure.
- A phenomenon of mesomorphism is very sensitive and susceptible to molecular structure.
- Present investigation may be useful for the study of binary systems to operate LC devices at desired temperature between 60°C and 100°C and agricultural production.
- Present investigation supports the early views about the effects of molecular structure on mesomorphism and raises credibility to the established concepts.

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