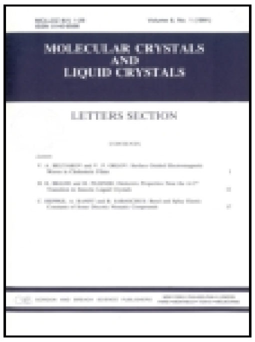

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Novel Cinnamate Esters—Synthesis and Mesomorphic Properties in Relation to Molecular Structure

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A novel homologous series 4-[4′-n-alkoxy cinnamoyloxy] benzyl cinnamates consisting of 11 homologs was synthesized and studied with a view to understanding and establishing the relation between molecular structure and mesomorphic behavior of a substance. Mesomorphic behavior of the series commences from the third homolog and then continues until the last hexadecyloxy homolog. The first and second members of a series are non-mesomorphic. Nematogenic mesophase formation is observed from the propoxy homolog to the hexadecyloxy homolog, but the smectogenic mesophase formation is observed from the hexyloxy homolog to the tetradecyloxy homolog. All mesomorphic transitions are enantiotropic in nature. Transition temperatures were determined by an optical polarizing microscopy equipped with a heating stage. The textures of the nematic mesophase are threaded or Schlieren in type and that of the smectic mesophases are focal conic fan shaped of the smectic A or smectic C type. A phase diagram of the series shows a normal behavior of the transition curves with a minor abnormality of the last three homologs for the nematic-isotropic transition curve. The average thermal stability for smectic and nematic mesophases is 176.0°C and 219.3°C, respectively. Analytical and spectral data agree with the molecular structures of homologs. Mesomorphic phase length varies between 22°C and 76°C. Smectic phase length varies from 6°C to 33°C and nematic phase length varies from 22°C to 54°C. Thus, the novel present series is predominantly nematogenic and partly smectogenic. Mesomorphic properties of the novel series are compared with structurally similar other known homologous series.

Keywords Enantiotropic; liquid crystals; mesomorphic; mesophase; nematic

Introduction

Benzoic and cinnamic acid derivatives exhibiting mesomorphic or non-mesomorphic properties are known for their microbial activity or as biologically active molecules. Their biological activity and/or mesomorphic behaviors are related to the molecular structure of the substance concerned as a consequence of rigid and flexible parts of the molecule. Thus, molecular rigidity and/or flexibility [1–3] play an important role to cause variations of properties and varying usefulness of all different substances. Thus, varying combined effects of molecular rigidity and flexibility can yield varying magnitudes of anisotropic or isotropic forces of intermolecular attractions [4], out of which suitable magnitudes of

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anisotropic forces of intermolecular attractions inducing a specific property, of some substances (not all) as mesomorphic property, which flows like a liquid on the surface and possess optical properties like a solid crystal. This special state of matter has a number of applications, particularly displays. The present investigation involves the synthesis of novel molecules that consist of three phenyl rings bridged through $-CH{=}CH-COO-$ and $-CH{=}CH-COO-CH_2-$ groups, which act as the rigid core and the terminal chain (–OR), which acts as a flexible moiety. Thus, the effect of molecular structure on mesomorphic properties can be studied by the proposed investigations.

Experimental

Synthesis

4-Hydroxy cinnamic acid was prepared by the reaction between 4-hydroxy benzaldehyde and malonic acid in pyridine by a usual established method [5] (m.p. 213°C, yield 84%). 4-Hydroxy cinnamic acid was alkylated by suitable alkylating agents (R-X) by a modified method of Dave and Vora [6] to form 4-*n*-alkoxy cinnamic acids. 4-Hydroxy benzyl cinnamate was prepared by a usual established method [7] (m.p. 150°C, yield 80%) and then condensed with the appropriate 4-*n*-alkoxy cinnamic acids through the corresponding acid chlorides [8] to form final cinnamoyloxy cinnamate ester derivatives. The final products [9] were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained. 4-Hydroxy benzaldehyde, malonic acid, pyridine, aniline, toluene, alkyl halides, MeOH, EtOH, thionyl chloride, 4-hydroxy cinnamic acid, benzyl alcohol, H_2SO_4, HCl, and KOH were used as received, except solvents that were dried and purified prior to use. The synthetic route to the series is outlined in Scheme 1.

Characterization

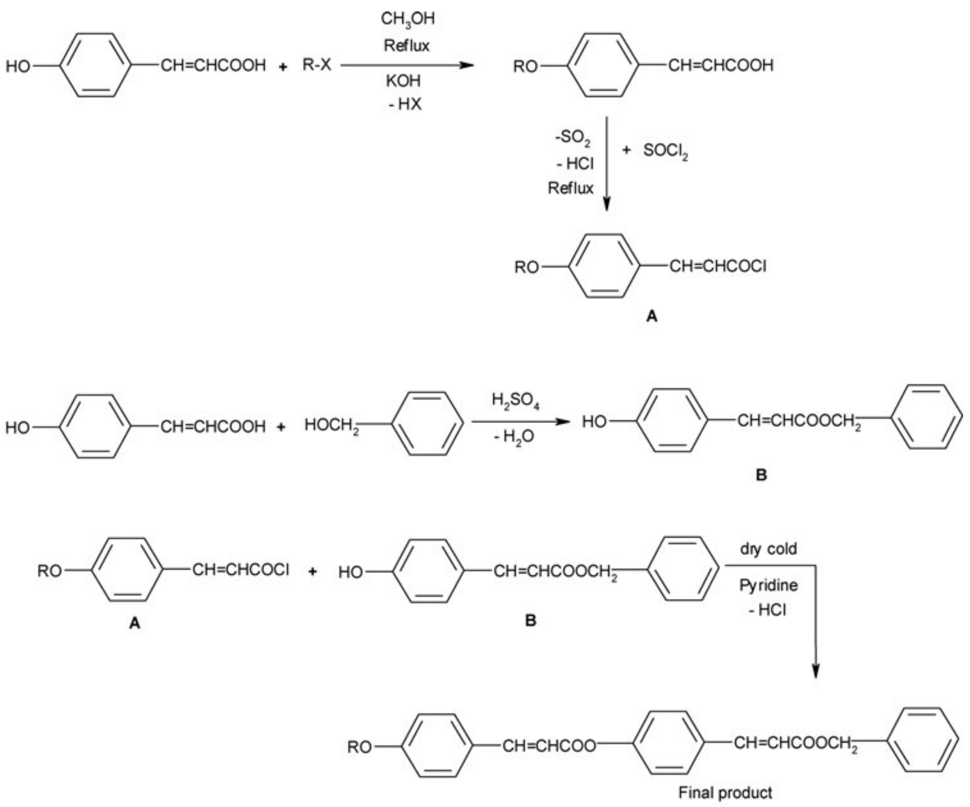
Some selected members of the present novel series were characterized by elemental analysis, infrared spectra, ^1H NMR spectra, and mass spectra. Microanalysis was performed using a Perkin-Elmer PE 2400 CHN analyser (Waltham, Massachusetts, U.S.A.), ^1H NMR spectra were recorded on a Bruker spectrometer (Billerica, Massachusetts, U.S.A.) using DMSO solvent. Infrared spectra were recorded on a Perkin Elmer spectrum GX spectrometer (Shelton, Connecticut, U.S.A.). Transition temperatures and the textures of smectic and nematic mesophases were determined by a miscibility method, and were characterized by an optical polarizing microscope equipped with a heating stage. Thermodynamic properties enthalpy change (ΔH) and entropy change ($\Delta S = \Delta H/T$) are qualitatively discussed.

Analytical Data (Table 1)

Spectral Data

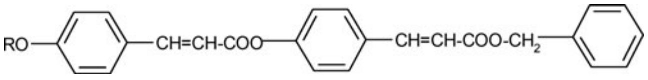
^1H NMR in ppm for the Decyloxy Derivative. 1.24 (long alkyl chain), 1.7 ($-CH_2-CH_2-O-$ of $C_{10}H_{21}$), 3.3 ($-OCH_2$ of $-OC_{10}H_{21}$ group), 3.9 ($-COO-CH_2-C_6H_5$), 6.3 and 6.9 (*p*-substituted phenyl ring), 7.5 (mono-substituted phenyl ring), 4.00 (*trans* $-CH{=}CH-$ group).

^1H NMR in ppm for the Tetradecyloxy Derivative. 1.3 (long alkyl chain), 1.7 ($-CH_2-CH_2-O-$ of $C_{14}H_{29}$), 3.3 ($-OCH_2$ of $-OC_{14}H_{29}$ group), 3.9 ($-COO-CH_2-C_6H_5$), 6.2–6.3



where R = C_nH_{2n+1}; n = 1--8, 10, 12, 14, 16.

Scheme 1. Synthetic route to the series.



and 6.8–6.9 (*p*-substituted phenyl ring), 7.5 (mono-substituted phenyl ring), 4.1 (*trans* —CH═CH— group).

IR in cm^{-1} for the Octyloxy Derivative. 696 (mono-substituted phenyl ring), 831 (*p*-substituted phenyl ring), 1217 (ether linkage of -$C_8H_{17}O$-C_6H_4), 1171, 1285, 1676 (—COO—ester group), 982 (*trans* —CH═CH— group).

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

		Elements % found (% calculated)	
Sr. no.	Molecular formula	C	H
1	$C_{26}H_{22}O_5$	75.06 (75.36)	5.14 (5.31)
2	$C_{27}H_{24}O_5$	75.58 (75.70)	5.62 (5.60)
3	$C_{28}H_{26}O_5$	75.98 (76.01)	5.71 (5.88)

Table 2. Transition temperatures of series in °C

Compound no.	n-alkyl group ($-C_nH_{2n+1}$) (n)	Transition temperature in °C Sm	 Nm	 Isotropic
1	1	—	—	198.0
2	2	—	—	199.0
3	3	—	202.0	248.0
4	4	—	166.0	242.0
5	5	—	162.0	221.0
6	6	160.0	166.0	220.0
7	8	158.0	164.0	200.0
8	10	161.0	180.0	202.0
9	12	159.0	192.0	216.0
10	14	170.0	182.0	215.0
11	16	—	188.0	210.0

Note: Sm: smectic, Nm: nematic.

IR in cm^{-1} for the Dodecyloxy Derivative. 694 (mono-substituted phenyl ring), 828 (p-substituted phenyl ring), 981 (*trans* $-CH{=}CH-$ group), 1217 (ether linkage of $-C_{12}H_{25}O-C_6H_4$), 1173, 1288, 1677 ($-$COO- ester group), 1217 (ether linkage of -$C_{12}H_{25}O$-C_6H_4 group).

Mass Spectra

Mass spectra for the butoxy derivative:

Molecular formula is $C_{29}H_{28}O_5$, calculated molecular weight is 456. Practical mass observed by mass spectroscopy is 456.

Texture of Nematic Phase by Miscibility Method

Pentyloxy derivative ——————→Threaded nematic
Hexadecyloxy derivative ————→Schlieren nematic
Hexyloxy derivate ———————→Threaded nematic and smectic A

Results and Discussion

4-Hydroxy benzyl cinnamate (m.p. 150°C) and 4-n-alkoxy cinnamic acids are non-mesomorphic, but on linking them through their corresponding acid chlorides, they yielded mesomorphic homologs from the third member of the novel homologous series of 4-(4′-n-alkoxy cinnamoyloxy) benzyl cinnamates. The methoxy and ethoxy homologs are non-mesomorphic. The propoxy to hexadecyloxy homologs are nematogenic only or are nematogenic with smectogenic behavior. The hexyloxy to tetradecyloxy homologs exhibit a smectogenic mesophase prior to nematogenic mesophase formation. Transition temperatures (Table 2) of the homologs are plotted versus the number of carbon atoms present in

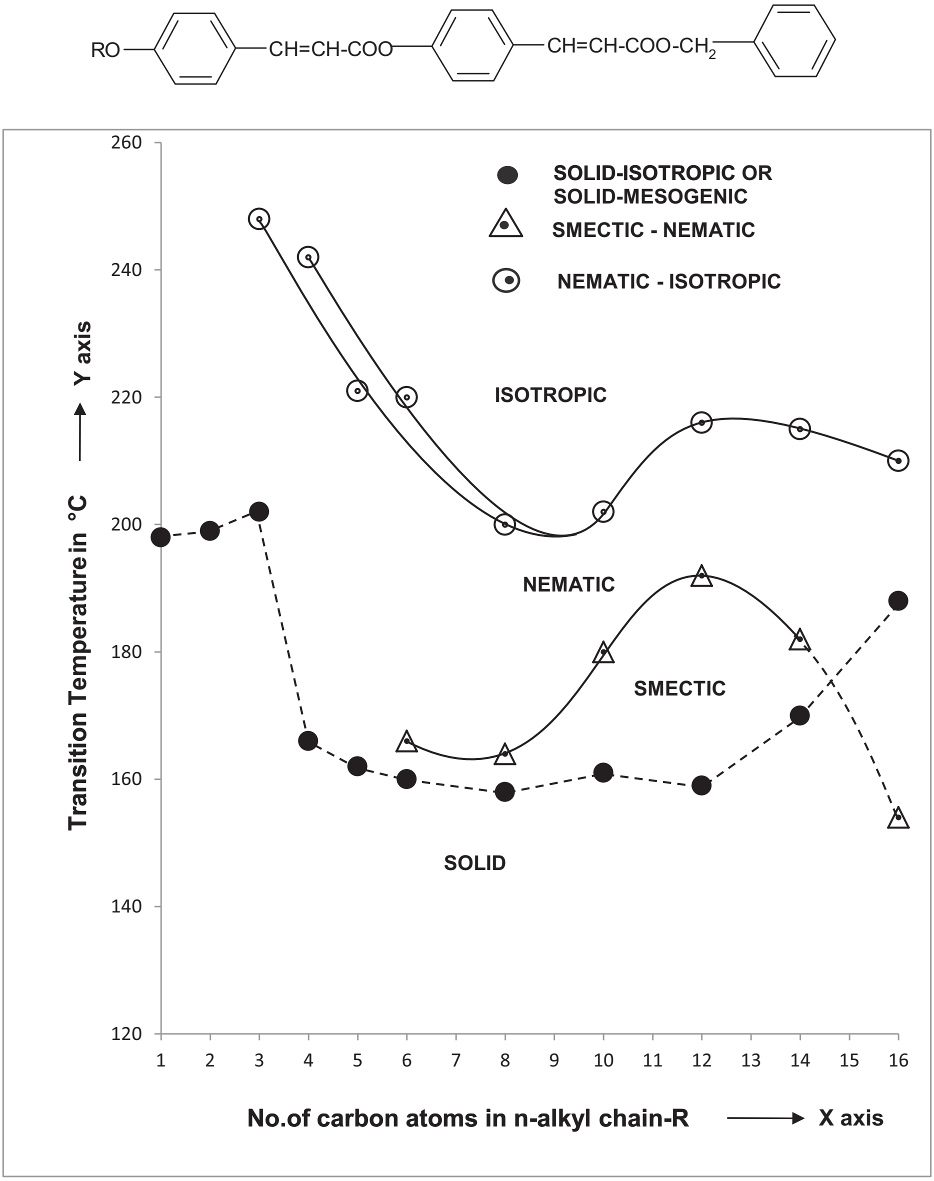


Figure 1. Phase behavior of series.

n-alkyl chain of the left *n*-alkoxy terminal end group. A phase diagram (Fig. 1) showing phase behavior is obtained by joining like or related points. The solid-isotropic or mesomorphic transition curve adopts a zigzag path of rising and falling values with a drastic rise from and beyond the dodecyloxy homolog to the hexadecyloxy homolog. Thus, it behaves in a normal manner. The smectic-nematic transition curve commences from the hexyloxy homolog and initially rises, passes through maxima, and then descends as series is ascended up to the tetradecyloxy homolog. The Sm-Nm transition curve is smoothly extrapolated [10] to predict the latent transition temperature (LTT) following the trend of the curve to determine the probable latent ability to form the smectic mesophase, which indicates the LTT to be 154°C below (monotropic) the solid-nematic transition temperature. However, LTT is not realizable due to the high crystallization tendency of the hexadecyloxy homolog. Thus, the smectic-nematic transition curve perfectly behaves in the usual established manner without the exhibition of an odd–even effect. The nematic-isotropic transition curve commences from propoxy homolog to the hexadecyloxy homolog. Initially, it descends from the propoxy to decyloxy homolog and then it descends for the tetradecyloxy and the hexadecyloxy homologs after a 14°C rise at the dodecyloxy homolog. Thus, it generally behaves in a normal manner except for the slight abnormality from and beyond the decyloxy homolog derivative. An odd–even effect is observed for the Nm-I transition curve. Both curves, for the odd and even merge into each other at the nonyloxy homolog and then the effect diminishes and disappears. The Sm-Nm mesophase length varies between 6°C and 33°C, Nm-I mesophase length varies between 22°C and 54°C, and the total mesophase length varies between 22°C and 76°C. Thus, the present novel series bears rich mesomorphism at relatively high temperatures. Hence, the present series is a high melting series whose melting temperatures are varied between minimum of 198°C at the first homolog to maximum of 242°C at the third homolog, from which mesomorphism commences enantiotropically. The average thermal stabilities for smectic and nematic phases are 176°C and 219.3°C, respectively. The novel series under discussion is predominantly nematogenic and partly smectogenic whose mesomorphic behavior varies from homolog to homolog, with changing molecular length by the methylene unit at the left *n*-alkoxy terminal end group. The mesomorphic behavior is induced on linking two non-mesomorphic components, viz., 4-*n*-alkoxy cinnamic acid and 4-hydroxy benzyl cinnamate, because the molecular rigidity is strengthened by increasing the number of phenyl rings to the acid molecule. Hence, the molecular aromaticity length to breadth ratio, molecular polarity is enhanced to create suitable magnitudes of anisotropic forces of intermolecular attractions, which can resist exposed thermal vibrations to cause mesomorphism from third member (propoxy homolog) of the series under discussion. The methoxy and ethoxy homologs are non-mesomorphic because of their high crystallizing tendency arising from imbalanced intermolecular attractions as combined effect of suitable magnitudes of molecular rigidity and flexibility, which induces an inability of molecules concerned to resist or withstand exposed thermal vibrations from thermodynamic surroundings. Therefore, molecules of the methoxy and ethoxy homologs are transformed into the isotropic liquid state directly from the crystalline solid state without passing through mesomorphic states. Molecules of the homologs from and beyond the propoxy homolog resist enough externally exposed thermal vibrations and are disaligned to take on a floating surface at an angle of less than 90° within a definite range of temperature. The molecules of the methoxy and ethoxy derivatives due to relatively shorter *n*-alkyl chain length in left *n*-alkoxy terminal end group show an inability to disalign to set on the surface at an angle of less than 90° against exposed thermal vibrations. Therefore, they neither acquire statistically parallel orientational ordered arrangement of molecules nor ordered sliding layered arrangement of molecules in floating condition to exhibit either nematic or smectic mesophase or mesophases. The propoxy to hexadecyloxy homologs under the influence of exposed thermal vibrations acquire suitable magnitudes of anisotropic forces of intermolecular end to end attractions to maintain statistically parallel orientational order of molecules with or without prior sliding layered arrangement of molecules to cause nematic and/or smectic mesophase formation. Thus, the propoxy, butoxy, pentyloxy, and hexadecyloxy homologs are only nematogenic without exhibition of any smectogenic character, but the hexyloxy to tetradecyloxy homologs exhibit

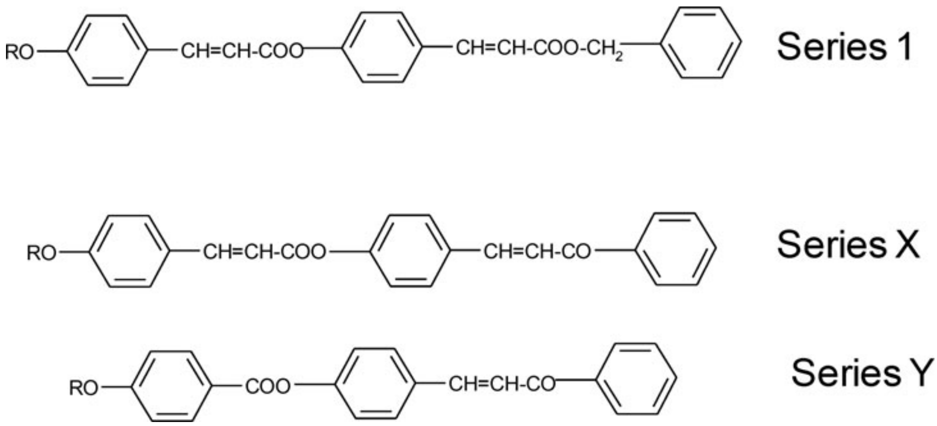


Figure 2. Structurally similar homologous series.

nematogenic mesophase formation in addition to smectogenic mesophase formation. Smectogenic mesophase formation occurs due to the lamellar packing of molecules in their crystal lattices and the resistivity of exposed thermal vibration is high enough to maintain a sliding layered arrangement of molecules in a floating condition within definite temperature range and then, on further heating, the sample substance loses intermolecular attractions, but at this stage intermolecular end to end attractions are still strong enough to maintain a relatively less ordered statically parallel orientational order of molecules to enable nematic mesophase formation. An odd–even effect of alternation in transition temperatures and changing mesomorphic behavior from homolog to homolog is attributed to the sequentially and progressively added methylene group to the *n*-alkyl terminal end group, which causes variations in molecular flexibility with stronger molecular rigidity as a result of three phenyl rings and two central bridges bearing the linking group $-CH=CH-$. The disappearance of the odd–even effect from and beyond nonyloxy homolog in Nm-I transition curve is attributed to the coiling or bending or flexing or coupling of the longer *n*-alkyl chain with the major axis of the core of left *n*-alkoxy terminal end group. High thermal stabilities for mesophases and a high degree of mesomorphism are attributed to the stronger intermolecular attractions as a consequence of relatively higher molecular rigidity and flexibility induced by longer molecules with $-CH=CH-COO-$ and $-CH-CH-COO-CH_2-$ central bridges. The mesomorphic behavior of present novel series-1 is compared with structurally similar other known series X [11] and Y [7], as shown in Fig. 2.

As can be seen from Fig. 2, homologous series 1, X, and Y (Fig. 2) are similar in structure with respect to three phenyl rings and left *n*-alkoxy terminal end group, but they differ with respect to their central bridges. The three phenyl rings and the differing linking bridge groups contribute to the total molecular rigidity, and changing *n*-alkyl chain of left *n*-alkoxy terminal end group contributes to the total molecular flexibility of each varying homologs of the series. However, the combined effect of molecular rigidity and flexibility controls the suitable magnitudes of anisotropic forces of intermolecular attractions through which mesomorphic behavior of a substance controlled. Varying suitable magnitudes of molecular rigidity and flexibility of present series-1 and the series X and Y chosen for

Table 3. Average thermal stability in °C

Series	Series 1	Series X	Series Y
Smectic-isotropic or smectic-nematic	176.0 (C_6–C_{14})	—	106.6 (C_{10}–C_{16})
Commencement of smectic phase	C_6		C_{10}
Nematic-isotropic	219.3 (C_3–C_{16})	144.5 (C_6–C_{16})	119.8 (C_8–C_{16})
Commencement of nematic phase	C_3	C_6	C_8

comparison cause variations in mesomorphic behavior and the degree of mesomorphism shown by homologous series-1 to X and Y.

Table 3 represents thermal stabilities for smectic and/or nematic, commencement of smectic and/or nematic mesophase formation, etc.

The thermal stability for nematic mesophase decreases from series-1 to X to Y (Table 3). The smectogenic thermal stability of series-1 is also greater than a series Y, whereas series X is non-smectogenic.

The commencement of nematic mesophase formation takes place earlier from the third member of a present series-1, but it commences from the sixth and eighth member of the series X and Y, respectively.

The molecular length of series-1 is longer than series X by the $-O-CH_2-$ unit of the second central bridge, $-CH=CH-COO-CH_2-$, of series-1. Therefore, length to breadth ratio and the ratio of the molecular polarity to polarizability as well as anisotropic intermolecular attractions differ between series-1 and X. This situation reflects the molecular rigidity of series-1 and the thermodynamic quantity, enthalpy change, and entropy change $\Delta S = \Delta H/T$ of the system, i.e., the resistivity to exposed thermal vibrations of the molecule is enhanced enabling two-dimensional order in a floating condition. The reasons for early or late commencement of the nematic mesophase formation is also related to the factors such as suitable magnitudes of anisotropic forces of intermolecular end to end attractions, as a consequence of more or less favorable molecular rigidity and/or flexibility [1–4]. Early or late commencement (including absence) of smectic mesophase appearance, i.e., lamellar packing of molecules in crystal lattices, depends upon favorable magnitudes of intermolecular attractions and the extent of non-coplanarity caused by the molecule.

The observed difference of mesomorphic behavior between a series-1 and Y is attributed to the above discussed reasons of molecular rigidity versus flexibility, and also to the differing central bridges $-CH=CH-COO-$ and $-COO-$, joining first and middle phenyl rings. Both these central bridges are comparable, though the vinyl carboxylate unit, $-CH=CH-COO-$, has a relatively greater length and causes more molecular non-coplanarity. On account of this difference, the smectic-isotropic or smectic-nematic thermal stability of series Y is relatively lower than the corresponding smectic thermal stability of a present investigated novel homologous series-1. Thus, variations in mesomorphic behavior for the same homolog from series to series are attributed to the differing central bridge or bridges.

Conclusions

1. Group efficiency order derived for smectic and nematic on the basis of thermal stabilities are as under.

   Smectic : – CH=CH–COO– > –COO– > –CH=CH–COO–
   with with with
   –CH=CH–COO – CH2– –CH=CH–CO– –CH=CH–CO–

   Nematic : – CH=CH–COO–CH2– > –CH=CH–CO– > –CH=CH–CO–
   with with with
   –CH=CH–COO– –CH=CH–COO– –COO–

2. Group efficiency order derived on the basis of early commencement of smectic and nematic phase are as under.

   Smectic : – CH=CH–COO–CH2– > –CH=CH–CO– > –CH=CH–CO–
   with with
   –CH=CH–COO– –COO–

   Nematic : – CH=CH–COO – CH2– > –CH=CH–CO– > –CH=CH–CO–
   with with
   –CH=CH–COO –COO–

3. Molecular rigidity and flexibility of favorable or suitable magnitudes can only induce mesomorphic property in a substance.
4. The -COO- group is generally smectogenic only, however, nematogenic character can be incorporated by introducing second central group like –CH=CH–CO–.
5. The –CH=CH–COO– group is generally nematogenic but smectic and nematic mesophases can be induced by high degree of mesomorphism and high melting type mesomorphism by introducing –CH=CH–COO–CH_2– as second central group with –CH=CH–COO– central group.
6. Mesomorphic behavior of a substance is very sensitive to molecular structural variation of a substance.
7. Mesomorphic behavior from homolog to homolog in the same series varies with the sequential addition of methylene unit or units.
8. Mesomorphic behavior of a same homolog from series to series varies with the varying molecular structure of the mesomorphic substances.
9. Mesomorphic behavior of any homologous series (including novel series-1) depends upon the varying positional substitution of same functional group or groups whose individual self-group polarity is same; especially in the case of isomeric series.
10. Presently investigated novel series is predominantly nematogenic and partly smectogenic, with exhibition of good degree of mesomorphism and high melting type.

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