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Physical study of new mesogenic homologous series: Methyl -p-(p¹-n-alkoxycinnamoyloxy) cinnamate

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ABSTRACT

Titled homologous series, Methyl-p(p¹-n-alkoxy cinnamoyloxy) cinnamates is synthesized and studied with a view to understand the relation between molecular structure and mesogenic property. First and second member of the series are nonmesomorphic. Third, fourth, fifth, sixth, eighth, tenth, twelfth, fourteenth and sixteenth members of the series are enantiotropic nematic without exhibition of any smectic property even in the monotropic condition. Odd-even effect is not appeared in nematic-isotropic transition curve. Solid-isotropic or solid-nematic transition curve falls from first to fourth member of the series and follows zig-zag path of rising and falling up to fourteenth homologue and further falls to the sixteenth member of the series. Nematic - isotropic transition curve initially rises and then falls in a normal manner. Transition temperatures are observed through hot stage polarizing microscope. Nematic mesophase is of threaded, type of texture in all the derivatives. Average thermal stability is relatively higher and series is of middle orderad melting type. Mesomorphic properties are compared with structurally similar homologous series. Analytical data support the structure of the molecules.

Key words : liquid crystals, Nematic, Smectic, Mesogens.

INTRODUCTION

Number of ester homologous series are reported with -COO- and -CH = CH-COO- as central bridge by different groups of researchers in order to understand the relation between mesomorphic properties and molecular structure. In present investigation, attempt is made to synthesize a homologous series with -CH = CH-COO- as a central bridge and same as terminal end group without any lateral substitution, with a view to understand the relation between mesogenic properties and terminally substituted unsaturated end group in combination with a same functional group as a central bridge linking two phenyl rings. Also the utility of liquid crystalline materials in electronic display devices to be operated at desired and / or required

temperatures and many other fields of applications, inspired to synthesize new mesogenic materials.

MATERIALS AND METHODS

Experimental :

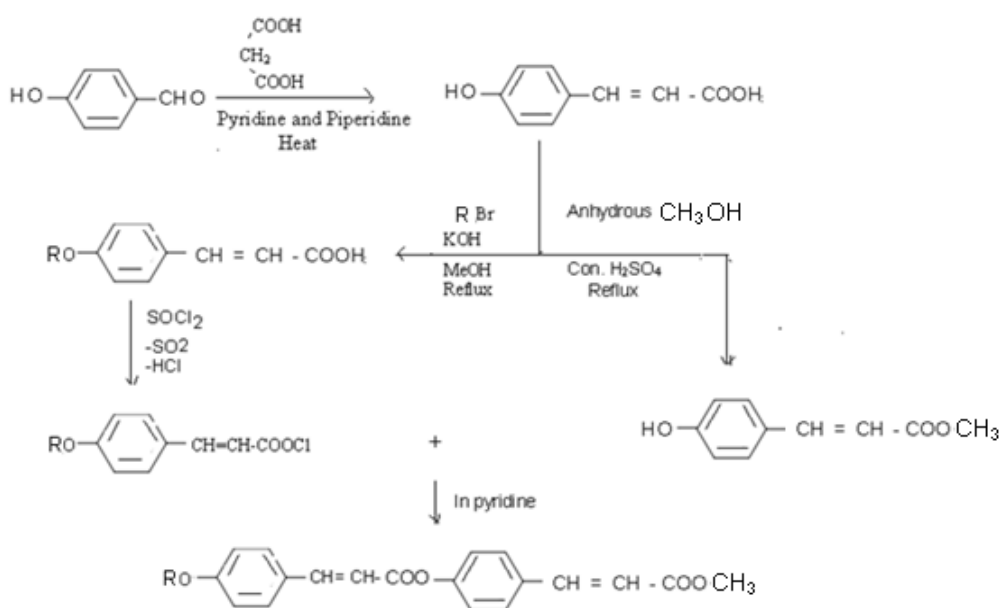
(i) Equimolar proportion of p-hydroxy cinnamic acid and absolute methanol shaken well in presence of two drops of concentrated H_2SO_4 and reaction mixture was refluxed for three hours. Then reaction mixture was decomposed in ice cool water, and allowed it to settle. Solid substance p-hydroxy methyl cinnamate is obtained. Product was filtered, washed, dried and then purified by alcohol. Fine crystals are obtained M.P. $117^\circ C$, yield 69 % (6)

(ii) Preparation of p-n-alkoxy cinnamoyl chloride.:

p-n-Alkoxy cinnamic acids are refluxed with excess of freshly distilled thionyl chloride till evolution of SO_2 ceases. Excess of thionyl chloride is distilled off, (1 to 5, and 10, 13) leaving behind p-n alkoxy cinnamoyl chloride and preserved carefully in moisture free atmosphere without further purification.

(iii) Synthesis of Methyl-p-(p¹-n-alkoxy cinnamoyloxy) cinnamates:

Homologues of the titled homologous series are prepared by usual established method, by reacting carefully corresponding acid chloride (step-(ii)) with pre ice cooled solution of p-hydroxy methyl cinnamate (step-(i)) dissolved in pyridine drop wise and then subsequently warming the reaction mixture for half an hour after complete addition of a solution of p-hydroxy methyl cinnamate and further treatment followed to get final product in pure state after 24 hours.



SCHEME-1 Synthetic route to the series

(iv). Transition temperatures are determined by polarizing microscope with heating stage as recorded in table -1

(v). Analytical data supported the structure of molecules.

Table-1: Homologous series: Methyl-p-(p/n-alkoxy cinnamoyloxy) cinnamates

| Sr.No. | n-Alkyl group | Transition temperatures in °C | | |
|--------|---------------|-------------------------------|---------|-----------|
| | | Smectic | Nematic | Isotropic |
| 1 | Methyl | - | - | 178.0 |
| 2 | Ethyl | - | - | 170.0 |
| 3 | Propyl | - | 124.0 | 140.0 |
| 4 | Butyl | - | 115.0 | 128.0 |
| 5 | Pentyl | - | 118.0 | 125.0 |
| 6 | Hexyl | - | 112.0 | 128.0 |
| 7 | Octyl | - | 125.0 | 150.0 |
| 8 | Decyl | - | 120.0 | 166.0 |
| 9 | Dodecyl | - | 135.0 | 175.0 |
| 10 | Tetradecyl | - | 132.0 | 163.0 |
| 11 | Hexadecyl | - | 130.0 | 138.0 |

Analytical data :

Methyl -p-(p/n-alkoxy cinnamoyloxy) cinnamates.

Table-2: Elemental Analysis

| Sr. No | R=n-alkyl chain | Molecular Formula | Calculated % | | Observed % | |
|--------|-----------------|--|--------------|------|------------|------|
| | | | C | H | C | H |
| 1. | Methyl | C ₂₀ H ₁₈ O ₅ | 71.10 | 5.33 | 71.18 | 5.38 |
| 2. | Butyl | C ₂₃ H ₂₄ O ₅ | 72.63 | 6.32 | 72.67 | 6.25 |
| 3. | Hexyl | C ₂₅ H ₂₈ O ₅ | 73.53 | 6.86 | 73.45 | 6.98 |
| 4. | Dodecyl | C ₃₁ H ₄₀ O ₅ | 75.61 | 8.13 | 75.50 | 8.35 |

NMR: in ppm**Propyl**

1.84 – CH₂-CH₂-CH₃, 3.806 – O-CH₃, 4.00 – O-CH₂ of O-CH₂-CH₂-CH₃, 4.44 & 4.02 – CH=CH-, 6.43 & 6.94, 6.97 & 7.20 – P-sub.phenyl two p-sub.benzene, 7.23 & 7.55, 8.09 & 8.12 – P-sub.phenyl two p-sub.benzene,

Octyl

1.81– O-CH₂-CH₂-(CH₂)₅-CH₃, 3.8 – O-CH₃, 4.034 – O-CH₂ of (O-CH₂-(CH₂)₆-CH₃), 4.41– CH=CH-, 6.38 & 6.43, 7.23 & 7.24 – Two p-sub.phenyl ring, 7.55 & 7.58, 8.09 & 8.12 – Two p-sub.phenyl ring,

IR: in cm⁻¹**Pentyl**

720.0 Poly –CH₂ (Long methyle chain), 1050.0 –CO- group of ester, 820.0 p-sub. Phenyl ring, 1250.0 >C=O bend, 698.2 cis –CH=CH- group, 1750.0 >C=O of ester, 3000.0 >C-H of aromatic,

Tetradecyl

1050.0 >C-O of ester group, 650.0 cis –CH=CH- group, 1250.0 >C=O of ester group, 840.0 p-sub. Phenyl ring, 750.0 poly –CH₂- of n-octyl, 1750.0 >C=O of ester group, 1250 >C=O of ester group, 3000.0 Confirms =C-H of aromatic group,

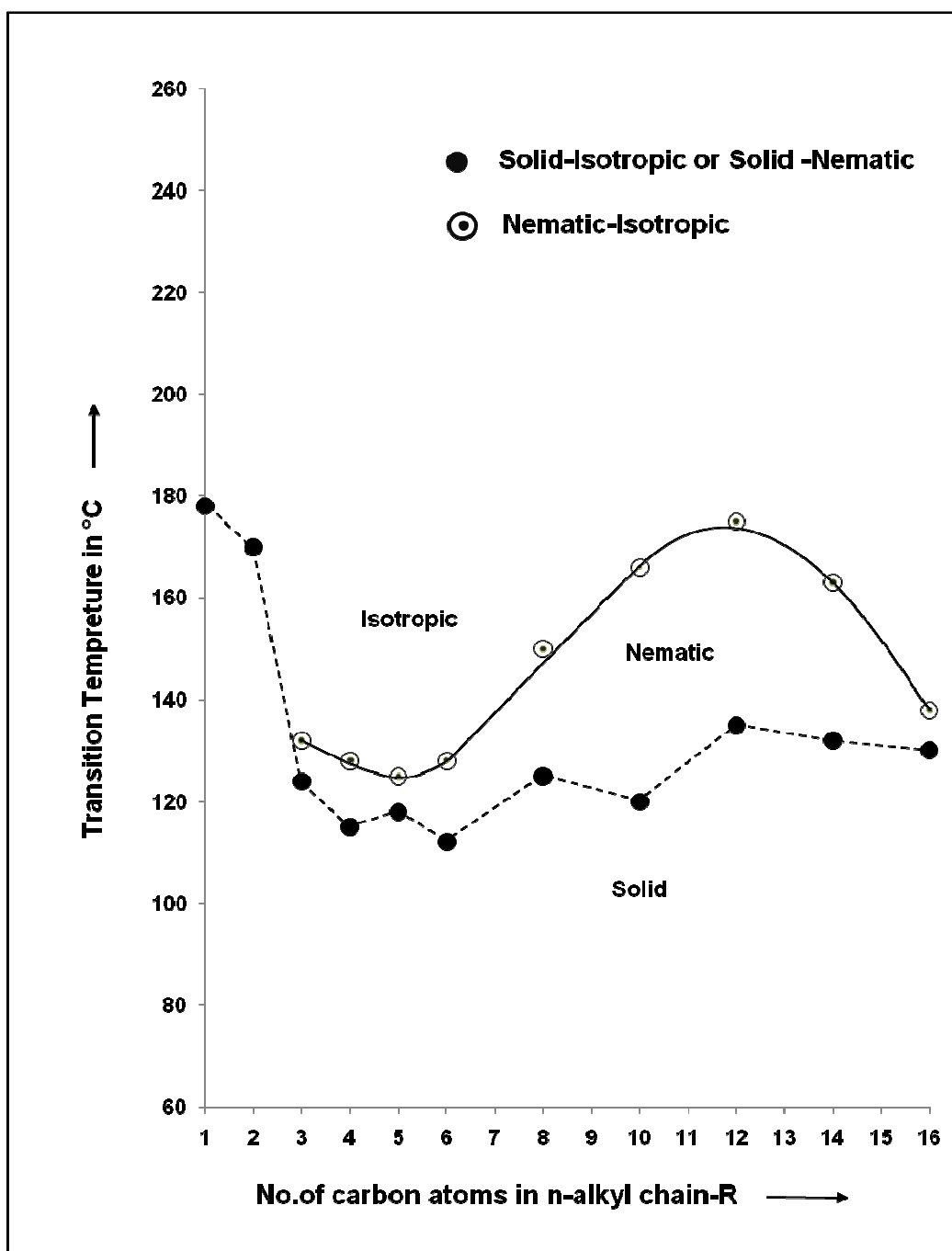


Fig-I, Homologous Series: Methyl p- (p' n-Alkoxy Cinnamoyloxy) Cinnamates

RESULTS AND DISCUSSION

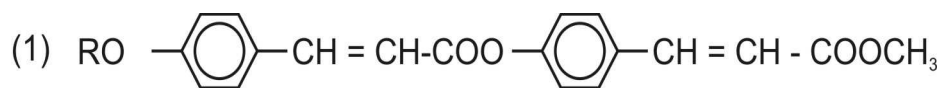
Methyl and ethyl derivatives of titled homologous series are nonmesomorphic, while propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl derivatives are enantiotropic nematic. None of the homologues is smectogenic even in the monotropic condition. Number of carbon atoms in the n-alkyl chain of left n-alkoxy end group are plotted versus the transition temperatures of homologues from table-1. Smooth curves are drawn through the like points and phase diagram (figure I) is obtained. Careful observation of phase diagram (Figure I) shows that, solid-isotropic or solid-nematic transition curve directly falls from first to the fourth and then follows zigzag path of rising and falling upto fourteenth homologue and then, instead of

subsequent rising, it falls to the hexadecyl derivative and behaves in a normal manner. Nematic-isotropic transition curve falls by five degree centigrade and then rises and again falls smoothly as series is ascended with normal behavior. Odd-even effect is not observed in nematic-isotropic transition curve. Transition temperatures and melting temperatures are relatively high as compared to other homologous series with -COO- central bridge. Nematogenic mesophase range varies from 7.0°C to 46.0°C. Thus Nematogenic phase length is minimum of 7.0°C at the pentyl derivative and maximum of 46.0°C at the decyl derivative. Nematic-isotropic temperatures are minimum 125.0°C at the fifth homologue and maximum 175.0°C at the twelfth homologue. Thus homologous series under discussion is of higher middle ordered melting type with absence of smectogenic character. The texture of nematic mesophase is of threaded type as judged directly by observing, the field of view of polarizing microscope. Analytical data conforms the structure of molecules. The mesomorphic behavior of titled homologous series is compared with structurally identical homologous series (A) and (B).

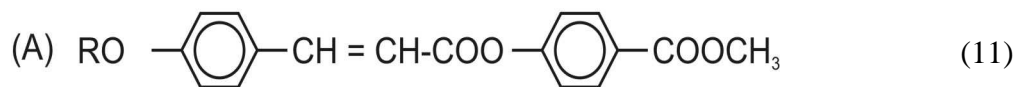
First and second homologues of the homologous series, Methyl-p-(p^l-n-alkoxy cinnamoyloxy) cinnamate are nonmesomorphic and directly and smoothly passes into isotropic liquid from crystalline solid state without passing through an intermediate state of existence, called liquid crystalline state or mesomorphic state or mesogenic state or nonamphiphilic state. This type of nonmesomorphic behavior is attributed to the high crystallizing tendency of molecules arising out of strong intermolecular forces of attractions due to the presence of shorter methyl and ethyl groups linked through $\text{-}\ddot{\text{O}}\text{-}$ with left phenyl ring and -CH=CH-COOCH_3 right terminal end group. Stronger intermolecular forces of attractions abruptly breaks the crystal structure on heating. The adhering forces of attractions are unable to maintain two dimensional array of molecules in floating condition. Thus first and second members of the series smoothly pass into isotropic liquid or molecules are randomly oriented without display of any kind of mesophase.

Nematogenic mesophase commences from third member of series enantiotropically and it continue upto sixteenth homologue without exhibition of any smectic character even in the monotropic condition. On heating the samples of homologues from and beyond propyl derivative of the series under discussion, the intermolecular forces are strong enough to resist thermal vibrations so that the statistically parallel orientational order of molecule is maintained as a result of two dimensional array of molecules in floating condition within definite range of temperature at constant pressure. This has resulted finally into exhibition of only nematogenic character from propyl to hexadecyl derivatives. However intermolecular forces of attractions of homologues of series under discussion are not capable enough to maintain two dimensional array of sliding layered arrangement of molecules. As a result of this, smectogenic character is totally absent in the series.

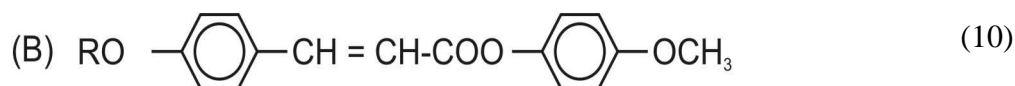
Absence of odd-even effect in nematic isotropic transition curve is attributed to the commencement of mesophase from third homologue or absence of mesophase in methyl and ethyl derivative. Moreover longer n-alkyl chain of left n-alkoxy group of rest of the homologues may coil or couple to lie in the line with major axis of core and bend in such a manner that, end to end contact would then ultimately be the same for odd and even homologus. Thus, it cannot contribute to odd and even effect. Moreover hexyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl derivatives are of even numbered carbon of the n-alkyl groups. Average thermal stability and mesogenic properties of the titled homologous series (1) are compared with structurally similar homologous series (A) and (B) as under.



Methyl-p-(p^l-n-alkoxy cinnamoyloxy) cinnamates



Methyl-p-(p^l-n-alkoxy cinnamoyloxy) benzoates



Methyl-p-(p^l-n-alkoxy cinnamoyloxy) anisole

Figure II

Average thermal stabilities for series (1), (A) and (B) are recorded in table -3 as under.

Table 3 Average thermal stability in

| Series | (1) | (A) | (B) |
|-------------------------------|---|--|---|
| Nematic - isotropic | 145.88 (C ₃ - C ₁₆) | 138.25 (C ₃ - C ₆) | 123.5 (C ₁ -C ₁₄) |
| Commencement of nematic phase | C ₃ | C ₃ | C ₁ |
| Smectic - Isotropic | - | 135.9 (C ₇ - C ₁₂) | 95.5 C ₈ -C ₁₈) |
| Commencement of Smectic phase | - | C ₇ | C ₈ |

Mesomorphic property and the degree of mesomorphism depend upon the magnitude of net intermolecular forces of attractions, (5,8) which depend upon geometrical shape, size, linearity, aromaticity, polarity and polarizability, length to breadth ratio, pi electron density, lateral substitution and many other untraced parameters of molecules contributing to the magnitude of net intermolecular adhering forces of attractions.

The molecular geometrical shapes of homologous series (i) (A) and (B) under comparison are identically rod like linear without any lateral substitution and with different right handed terminal end groups viz. -CH=CH-COOCH₃, -COOCH₃ and -OCH₃. Two phenyl rings and central bridge -CH=CH-COO- and left n-alkoxy terminal groups are same in case of same homologue from series to series but n-alkoxy left terminal group varies from homologue to homologue in the same series. Therefore uncommon part being the different terminals viz. -CH=CH-COOCH₃, -COOCH₃ and -OCH₃ and length to breadth ratio for the series under comparison which can cause difference in mesomorphic properties and degree of mesomorphism among the series (1), (A) and (B). The overall aromaticity, polarity and polarizability etc. remains same, for same homologue in series under comparison, but length to breadth ratio and different terminal end groups causes variation in polarity and polarizability of molecules. Consequently net intermolecular forces of attractions, which can directly cause variation in mesomorphic property and degree of mesomorphism from series to series and homologue to homologue in the same series.

Careful observation of table-3 indicate that average thermal stability for nematic of the series (B) is the lowest. Thus intermolecular forces of attractions for all the homologous series (1), (A) and

(B) are strong enough to resist the thermal vibrations maintaining statistically parallel orientations of molecules in floating condition. i.e. two dimensional array of molecules in floating condition is not disrupted. As a result of this, nematic mesophase is appeared by all the homologous series (1), (A) and (B). The commencement of nematic mesophase take place for homologous series (B) from very first member of the series but it takes place from third member of the series in case of series (1) and (A). Thus early commencement of nematogenic behaviour of series (B) is attributed to the higher polarity and polarizability of-OCH₃ terminal end group.

Absence of smectic character in series (1) as compared to series (A) and (B) is attributed to the weakest intermolecular forces of attractions , the magnitude of which fails to maintain two dimensional sliding layered arrangement of molecules in floating condition. However polarity (6,7,8)and polarizability of molecules causing resultant intermolecular adhering foci of attraction operate in such a manner and magnitude that, molecules maintain sliding layered arrangement in floating condition in series (A) & (B) while it fails in series (1) . Thus, smectogenic mesophase is exhibited by series (A) and (B) as compared to series (1) in addition to nematogenic mesophase. Early or late commencement of smectic mesophase depend upon the extent of noncoplanarity caused (5,12)by the molecule. Extent of noncoplanarity caused by the molecules for the series (B) and (A) varies depending upon their terminal end groups -COOCH₃ and -OCH₃. Thus smectic mesophase commences from seventh member of the series in case of series (A), while it commences from eight member of series (B) monotropically. The presence of -CH=CH-COOCH₃ longest terminal end group with double bond operates upon molecular planarity in such a manner that, molecules of titled homologous series (1) are unable to resist thermal vibrations even in case of higher members of the series and it disallows sliding layered arrangement of molecules in floating condition, excluding formation of ordered smectic mesophase on heating till the last homologue of the series(1). Thus, smectic and nematic group efficiency order derived for terminal end group on the basis of average thermal stability are as under.

Group efficiency order for nematic : -CH=CH-COOCH₃ > -COOCH₃ > -OCH₃

Group efficiency order for smectic : -COOCH₃ > -OCH₃ > -CH=CH-COOCH₃

CONCLUSION

Ester homologous series with -CH = CH-COO- central bridge and -CH=CH-COOR terminal end group are entirely nematogenic or predominantly nematogenic and partly smectogenic.

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