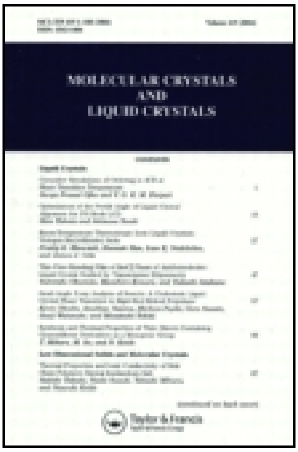

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Synthesis and Mesomorphism of Novel Liquid Crystalline: *p*-(*p*′-*n*-Alkoxy Benzoyloxy) Methyl Cinnamates

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A new homologous series p-(p′-n-alkoxy benzoyloxy) methyl cinnamates is synthesized with a view to understand and establish the relation between mesogenic properties and structure of molecules. Ethyl to octyl, decyl, dodecyl, tetradecyl, and hexadecyl homolgues are enantiotropically nematogenic, while the methyl homologue is nonmesogenic. None of the homologues exhibit a smectogenic mesophase. An odd–even effect is observed in the nematic–isotropic transition curve. The average thermal stability is 105.0°C and the nematogenic mesophase ranges from 11.0°C to 54.0°C. Thus, the series is of a middle ordered melting type with moderate nematogenic range. Analytical data confirm the structure of the compounds, and the mesomorphism was identified by optical microscopy. The mesogenic properties are compared with structurally similar compounds.

Keywords Liquid crystal; nematic; smectic

Introduction

A number of homologous series with two phenyl rings bridged through a variety of central linking groups, which causes variation in the molecular rigidity and flexibility, were reported earlier [1,2]. Such differences in the molecular rigidity cause a difference in the types and degrees of mesomorphism exhibited by the substance. The ester homologous series formed by −COO− and −CH=CH−COO− linking groups considerably affect molecular rigidity. Liquid crystals are important materials in several different fields, particularly display devices and in the medical fields. Therefore, the present homologous series was designed and synthesized with a vinylcarboxylate linking group, and its effects on the type of mesophase and degree of mesomorphism were determined. Thus, the present study is aimed at developing structure–property relationships in liquid crystals.

Experimental

Characterization

Some representative homologues were selected for full characterization by elemental analysis, IR, and ^{1}HNMR. ^{1}HNMR was recorded using $CDCl_3$ as solvent. Thermodynamic

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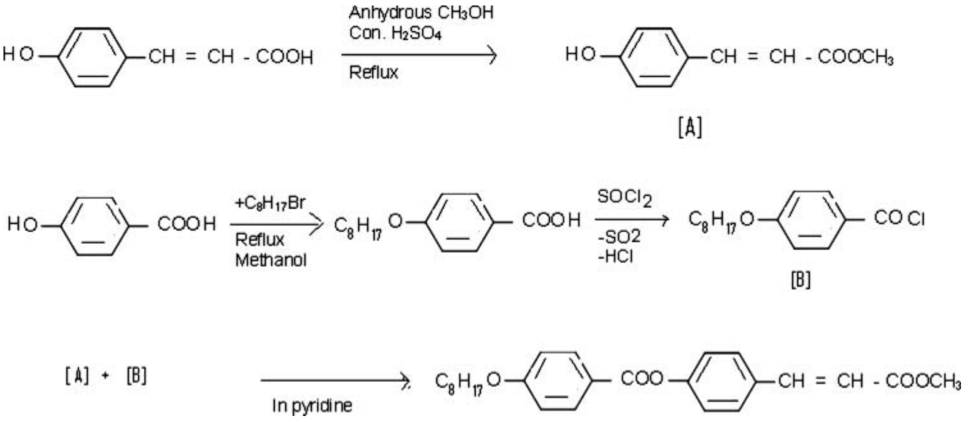
treatment related to thermal stability is qualitatively discussed by enthalpy (ΔH) entropy (ΔS) concept. Mesomorphic properties were investigated by optical polarizing microscopy.

Synthesis

4-Hydroxy cinnamic acid, methanol, pyridine, thionyl chloride, 4-hydroxy benzoic acid, and *n*-alkyl halides were used as received. The synthetic route to the present series is reported here by selecting the octyloxy homologue of the series as outlined in Scheme 1; other homologues were similarly prepared.



Scheme 1.

4-Hydroxy methyl cinnamate was synthesized by using a known method [4]. 4-*n*-Alkoxy benzoic acids and 4-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora [3]. The 11 esters of the series were synthesized by condensing equimolar amounts of 4-*n*-alkoxy benzoyl chlorides with *p*-hydroxy methyl cinnamate (A) in pyridine. Final products were recrystallized from alcohol until constant transition temperatures were obtained [7,9,10].

Analytical Data for the Octyl Homologue

H NMR Spectra δ (ppm). 0.890 ($-C\underline{H}_3$ of $-C_8H_{17}$), 1.308 ($-C\underline{H}_2$ of $-C_8H_{17}$), 1.772 ($-OC\underline{H}_2-C\underline{H}_2$ of $-C_8H_{17}$), 3.816 ($-O-C\underline{H}_3$), 4.021 ($-O-C\underline{H}_2$- of $-O-C_8H_{17}$), 6.460 & 7.260 [$-O-$C6H4-CH$=$CH$-$CO$-$], 6.905 & 8.026 (*p*-sub. benzene ring).

IR Spectra (cm^{-1}). 2854.5 cm^{-1} – alkyl group, 1685.7 & 1168.8 cm^{-1} – $-$COO$-$ group and ether group, 844.8 cm^{-1} – *p*-sub. benzene ring, 721.3 cm^{-1} – polymethylene of C_8H_{17}, 698.2 cm^{-1} – *cis* – $-$CH$=$CH$-$ group (see Table 2).

Results and Discussion

The titled homologous series consists of 12 homologues. Eleven homologues (ethyl to octyl, decyl, dodecyl, tetradecyl, and hexadecyl) are liquid crystalline while the methyl homologue is nonmesogenic. All the liquid crystalline homologues are enantiotropic nematogenic in character with threaded type of texture. No smectic mesophase is exhibited by any of the homologues. Transition temperatures and melting temperatures were determined by optical

Table 1. Elemental analysis for hexyloxy and octyloxy derivatives

Molecular formula	Calculated% C	Observed% H
$C_{23}H_{26}O_5$	72.08 (72.25)	6.80 (6.80)
$C_{25}H_{30}O_5$	74.92 (75.0)	7.56 (7.50)

polarizing microscopy, and the results are recorded in Table 2. Transition temperatures are plotted versus the number of carbon atoms in *n*-alkyl chain of the left *n*-alkoxy terminal end group. A phase diagram (Fig. 1) is obtained by joining like or related points. Careful observation of the phase diagram indicates that the solid–isotropic or solid–mesomorphic transition curve falls steeply from the methyl to propyl homologue and then follows a partly zigzag path of rising and falling as series is ascended. The nematic–isotropic transition curve behaves in a normal manner with an odd–even effect observed initially, but has disappeared at the seventh homologue. The nematic mesophase temperature range stretches from 11° to 54° at ethyl and pentyl derivatives of the series, respectively. Thus, the mesophase range is of a moderate type. The mesomorphism of the titled homologous series – 1 is compared with the other structurally similar homologous series A (11), B (6), and C (5), respectively.

4-*n*-Alkoxy benzoic acids are dimeric in structure linked through hydrogen bonding. On esterification by 4-hydroxy methyl cinnamate, the hydrogen bonding is not present and the resultant esters are obtained with lower transition temperatures with exhibition of mesogenic character. The methyl homologue is nonmesogenic and melts sharply from solid crystalline state to isotropic liquid. Exhibition of nematogenic character by ethyl to hexadecyl homologues is attributed to the anisotropic intermolecular forces of attraction of suitable magnitude arising from aligned molecules at an angle less than 90° on the plane of surface resisting thermal vibrations imposed upon them. This situation does not restrict statistically parallel orientational order of molecules, maintaining two-dimensional array in floating condition causing occurrence and appearance of nematic mesophase within definite range of temperature. Absence of smectic mesophase is attributed to the absence of lamellar packing of molecules in their crystal lattices. The odd–even effect in the

Table 2. Transition temperatures in °C

Sr. No.	R = *n*-alkyl group	Smectic	Nematic	Isotropic
1.	Methyl	—	—	143.0
2.	Ethyl	—	96.0	107.0
3.	Propyl	—	68.0	108.0
4.	Butyl	—	78.0	118.0
5.	Pentyl	—	62.0	98.0
6.	Hexyl	—	58.0	110.0
7.	Heptyl	—	62.0	102.0
8.	Octyl	—	66.0	105.0
9.	Decyl	—	65.0	103.0
10.	Dodecyl	—	83.0	109.0
11.	Tetradecyl	—	79.0	99.0
12.	Hexadecyl	—	79.0	96.0

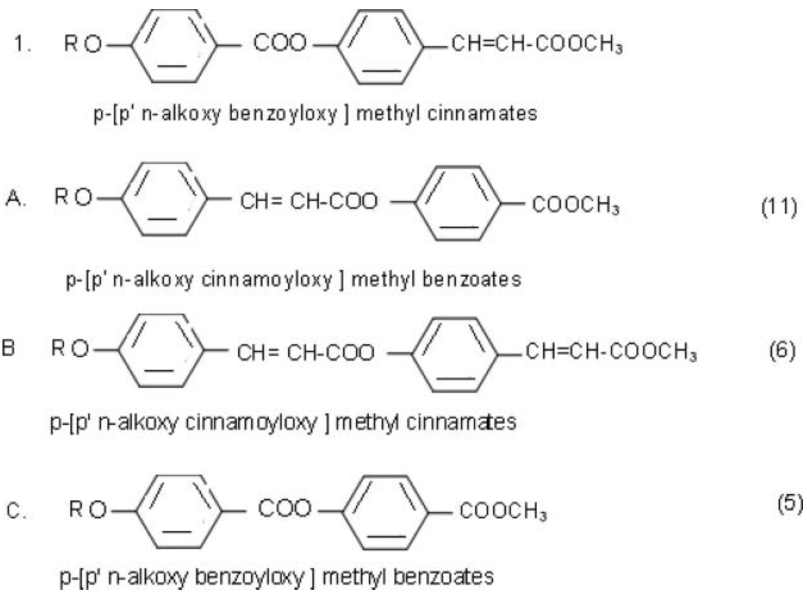


Figure 1. *p*-(*p*′-*n*-alkoxy benzoyloxy) methyl cinnamates.

nematic–isotropic transition curve observed up to seventh homologue is due to sequential addition of methylene unit at the flexible left *n*-alkoxy terminal end group. In case of higher homologues, the longer left *n*-alkyl chain of *n*-alkoxy group may be coiled or coupled to lie in line with the major axis of core. Thus, end-to-end contact would then ultimately be the same for odd- and even-numbered homologues beyond the seventh homologue [5,6,11].

The mesogenic characteristics of titled homologous series 1 are compared with structurally similar homologous series as under (Fig. 2).

The average thermal stability and commencements of smectic/nematic mesophase are given in Table 3 as under.

Table 3 indicates that homologous series 1 and B are entirely nematogenic, series C is entirely smectogenic, and series A is partly smectogenic and partly nematogenic. In all of the homologous series under comparison, two phenyl rings linked through central bridge and left *n*-alkoxy terminal are the common identical features. Only terminal end groups

Table 3. Average thermal stability

Series	(1)	(A)	(B)	(C)
Nematic–isotropic	105.0 (C2–C16)	138.25 (C3–C6)	145.88 (C3–C16)	—
Commencement of nematic mesophase	C2	C3	C3	—
Smectic–isotropic or Smectic–nematic	—	135.9 (C7–C12)	—	118.75 (C6–C12)
Commencement of smectic mesophase	—	C4		C5

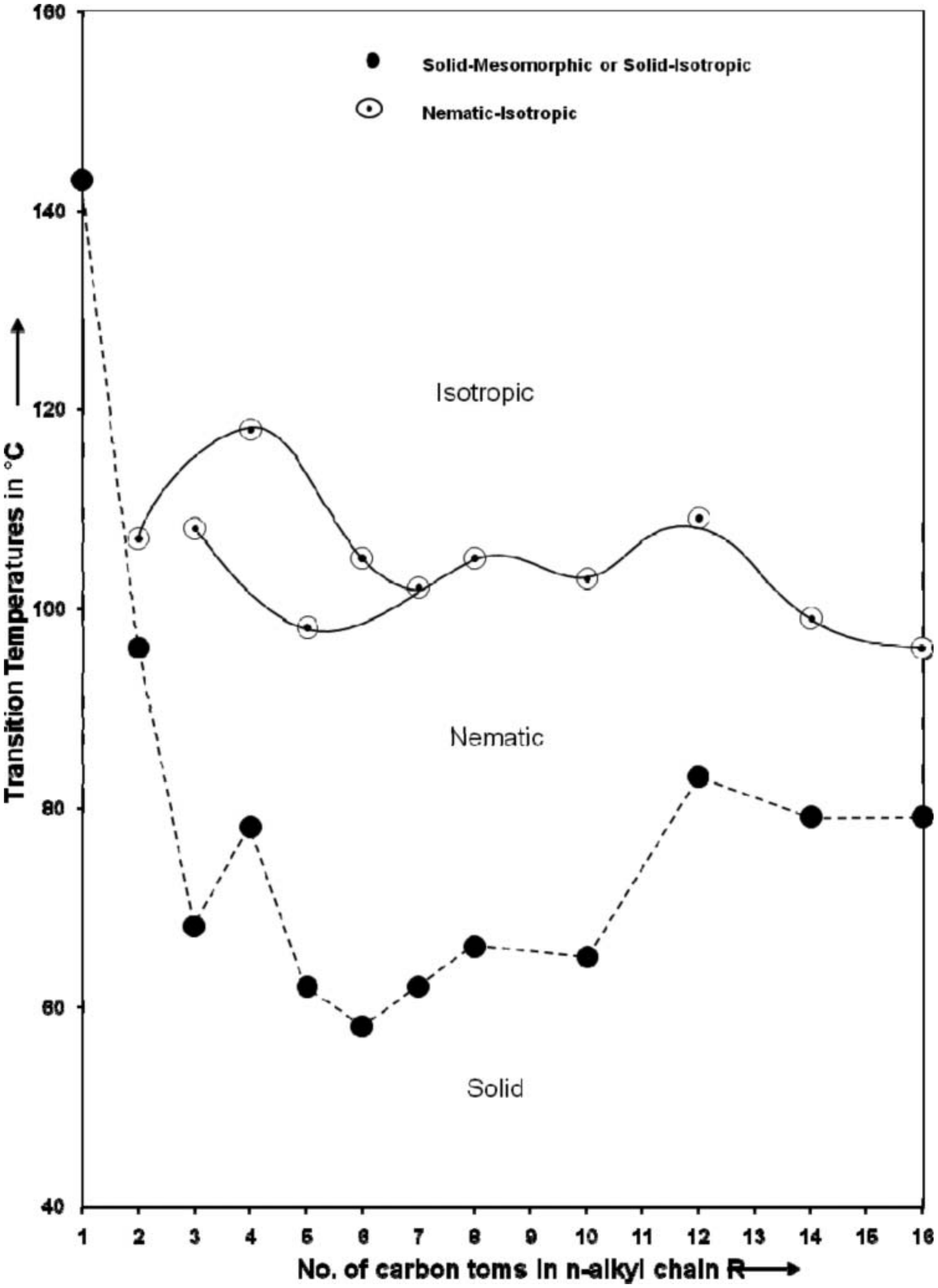


Figure 2. Phase diagram.

differ. Therefore, neglecting the effect of the central group, the degree of liquid crystallinity and thermal stability, etc., vary with the magnitude of polarity and polarizability of the terminal end groups for same homologue from series to series, and sequential addition of methylene unit in left *n*-alkoxy terminal end group causes variation in length to breadth ratio which results in a variation in mesogenic properties from homologue to homologue in the same series. Variation in length to breadth ratio can vary between —COO— and —CH=CH—COO— by the difference —CH=CH—, and hence, intermolecular forces of attraction undergo variation [12–14].

The commencement of the smectic mesophase does not occur until the last hexadecyl homologue of the series 1 and B. The early commencement of the smectic mesophase is related with less noncoplanarity of a molecule. Central bridge vinyl carboxylate —CH=CH—COO— has relatively greater length than the central bridge —COO— unit. Longer length of central bridge causes more noncoplanarity due to a twist attained as the oxygen atoms of the vinyl carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic phenyl rings in series A and B. Similarly, the oxygen atom of the central carboxy —COO— group in the molecules of series 1 and C will be bumping into the nonbonded sides of the adjacent hydrogens of aromatic ring which causes considerable strain on the molecule. Consequently, a twist around the C—O bond occurs, forcing the phenyl ring out of the plane of the molecule. Thus, the coplanarity of the molecule is reduced to some extent making a molecule thick, and contributing to the variation in commencement of smectic phase. Thus, smectic mesophase commences from butyl and pentyl homologue in series A and C, respectively, while the smectic phase does not occur or commence till the last homologue (hexadecyl) of the series 1 and B [15–17].

Conclusion

The present study of homologous series *p*-(-*p*′-*n*-alkoxy benzoyloxy) methyl cinnamates leads to the following conclusions.

i. The homologous series with a vinyl cinnamate terminal end group induces nematogenic character more favorably as compared to smectogenic character as induced by the benzoate terminal end group, irrespective of any central bridge.
ii. The homologous series with a —CH=CH—COO— as central and terminal group (series-B) is only nematogenic while a series with a —COO— as central and terminal end group is only smectogenic (series-C).
iii. The present homologous series (series-1) with a —CH=CH—COO— terminal end group is entirely nematogenic.
iv. The vinyl carboxylate group containing a —CH=CH— unit of conjugated double bond stabilizes the rigid core of a molecule and consequently, statistically parallel orientations of molecules are relatively favored more than the sliding layered arrangement of molecules in floating condition. Also, the increase in rigidity simultaneously increases the molecular thermal stability of the mesophase. The vinyl carboxylate unit in a molecule hinders lamellar packing of molecules in crystal lattices. Thus, the present investigation supports earlier research [8] and raises credibility to the conclusions.

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