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Synthesis and Mesomorphism of Novel Liquid-Crystalline Isobutyl-p-(p'-n-Alkoxy Cinnamoyloxy) Cinnamates

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A new homologous series viz. Isobutyl-p-(p'-n-alkoxy cinnamoyloxy) cinnamates consisting of 11 homologs has been synthesized with an isobutyl cinnamate end group and a further cinnamate moiety as a linking group. The methyl to butyl homologs are nonmesomorphic, and the pentyl to hexadecyl derivatives are enantiotropic nematogens without exhibition of any smectic phases. The average thermal stability for the nematic phase is 138.1°C with a middle ordered melting point. The structures of the novel materials were confirmed by spectroscopic techniques. The liquid crystal phase type was determined by optical polarizing microscopy and all textures are of the threaded type. The mesomorphic behavior of the series is compared with a structurally similar homologous series.

Keywords Liquid crystals; mesomorphic; nematic

Introduction

The number of liquid crystals compounds consisted of rigid part as two or three phenyl rings bridged through central bridge or bridges and flexible part as varying left polar terminal, alkyl or alkoxy [1–12] end group keeping right terminal end group intact of fix polarity with or without lateral substitution [5,8]. In continuation of the same, presently a homologous series with two phenyl rings bridged through vinyl carboxylate linkage and isobutyl vinyl carboxylate fixed end group with n-alkoxy as left terminal end group, is synthesized to investigate the effect of varying molecular structure by varying molecular rigidity and flexibility on mesogenic property.

The present investigation is planned with a view to establish and to understand the effect of molecular structure on liquid crystalline behavior of a substance.

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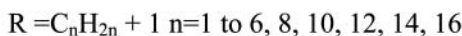
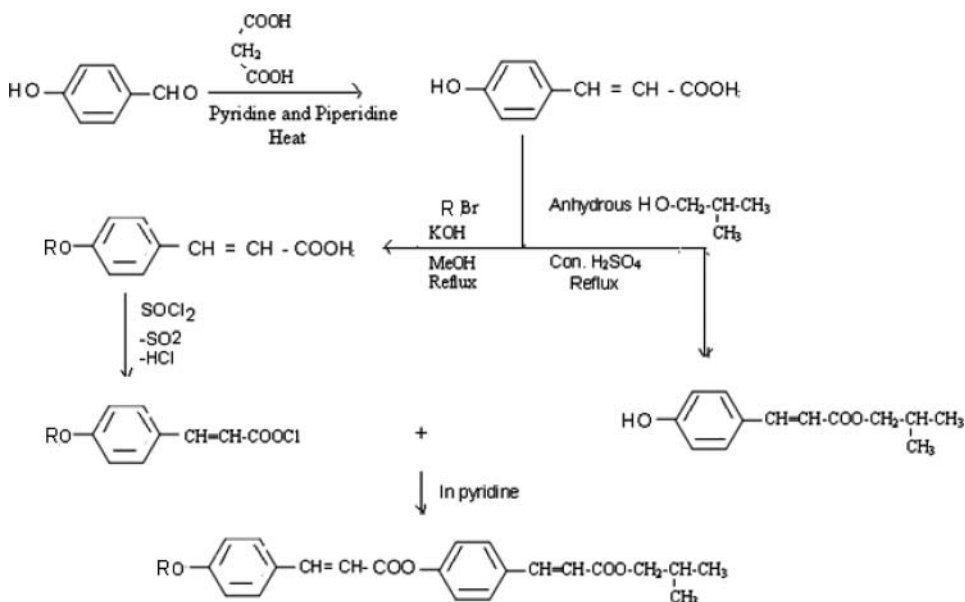
Experimental

Characterization

Some homologs as representative members of the series were selected for characterization of their structures by IR and ^1H NMR techniques. IR spectra were recorded on Perkin Elmer spectrum GX and NMR were recorded using CDCl_3 as solvent. Microanalysis was performed on Perkin Elmer PE 2400 CHN analyzer as shown in Table 1. Transition and melting temperatures and liquid crystal properties were investigated by using optical polarizing microscopy.

Synthesis

p-Hydroxy cinnamic acid was synthesized from p-hydroxy benzaldehyde and malonic acid, and the hydroxy group is alkylated by suitable corresponding alkylating agent. Constituent chemicals were used as received.



Scheme 1. Synthetic route to the series.

p-Hydroxy isobutyl cinnamate (A) was synthesized by an established method of esterification [6]. p-n-Alkoxy cinnamic acids and p-n-alkoxy cinnamoyl chlorides were synthesized by a modified method of Dave and Vora [3]. The eleven esters of the series were synthesized by condensing equimolar amounts of the p-n-alkoxy cinnamoyl chloride and p-hydroxy isobutyl cinnamate (A) in pyridine. The esters were crystallized from alcohol until constant transition temperatures were obtained.

Table 1. Elemental analysis for decyloxy and dodecyloxy derivatives

Molecular formula	Elements% found (% calculated)	
	C	H
$C_{32}H_{42}O_5$	76.02 (75.89)	8.30 (8.45)
$C_{34}H_{46}O_5$	76.69 (76.40)	8.87 (8.61)

Analytical Data

NMR: in ppm. Hexadecyl. 1.25 – $-CH_3$, 3.98 – $O-CH_2$, 4.01 – $O-CH_2$ of $O-CH_2-CH_2-CH_3$, 4.44 and 4.02 – $CH=CH-$, 6.89, 6.92, 8.00, and 8.03 –p-sub.phenyl two p-sub.benzene, 7.24 and 8.02 – p-subphenyl two p-subbenzene,

Octyl. 0.83 – CH_3 , 1.21 – CH_2 , 2.49 – OCH_2-CH_2- , 3.5 – $O-CH_2$ of – $COOC_4H_9$, 3.31 – $O-CH_2$ of C_8H_{17} , 4.41 – $CH=CH-$, 6.80 and 6.83 two p-subphenyl ring, 7.75 and 7.78, two p-subphenyl ring.

IR in cm^{-1} . Tetradecyl. 2850 alkyl group, 1080,1150, and 1700 – $COO-$ group, 660 cis – $CH=CH-$ group, 860 p-subphenyl ring, 3000 aromatic ring, 750 polymethylene of $C_{14}H_{29}$

Hexyl. 2850.0 alkyl group, 1050,1150, and 1710 – $COO-$ group, 660 cis – $CH=CH-$ group, 850 p-subphenyl ring, 3000 aromatic ring, 750 polymethylene of C_6H_{13} ,

Results and Discussion

The homologous series isobutyl p-(p'-n-alkoxy cinnamoyloxy) cinnamates is presently synthesized and studied for 11 homologs, which were evaluated for their mesomorphic characteristics. The transition temperatures of the homologous series under discussion are recorded in Table 2. The pentyl to hexadecyl members of the series showed a threaded or Schlieren texture on heating the crystalline solid reversibly on heating and cooling to isotropic liquid, while the methyl to butyl homologs are nonmesomorphic. Thus, the

Table 2. Transition temperatures of the series

Compound no.	$R = C_nH_{2n+1}$	S_m .	N_m .	I
1	1	—	—	200.0
2	2	—	—	210.0
3	3	—	—	144.0
4	4	—	—	125.0
5	5	—	132.0	165.0
6	6	—	97.0	136.0
7	8	—	110.0	125.0
8	10	—	105.0	130.0
9	12	—	115.0	142.0
10	14	—	110.0	143.0
11	16	—	105.0	129.0

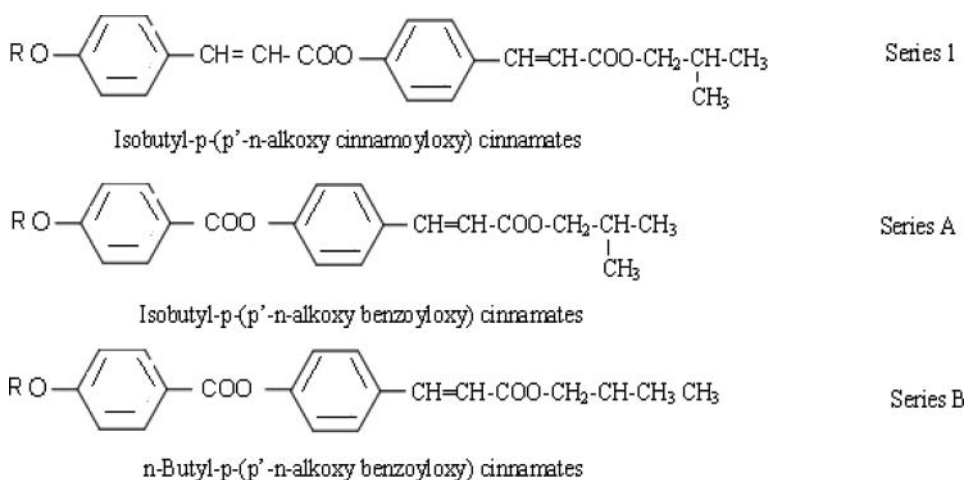


Figure 1. Structurally similar homologous series.

pentyl to hexadecyl homologs are enantiotropically nematogenic without exhibition of any smectogenic character.

Table 2 shows the dependence of transition temperatures on the number of carbon atoms in the terminal chain.

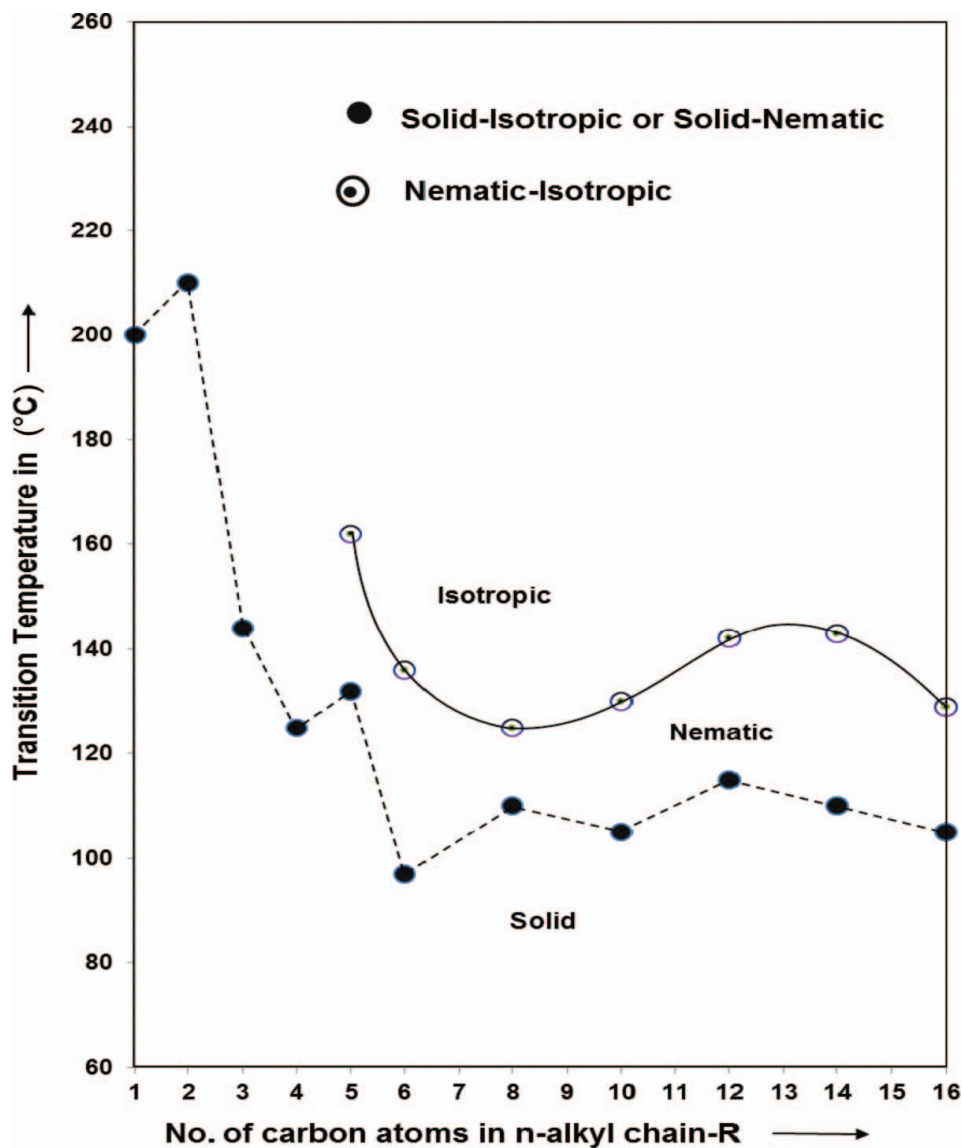
The average thermal stability and other mesomorphic behavior of titled homologous series 1 are compared with the structurally similar homologous series A and series B, as shown in Fig. 1.

The solid-nematic or isotropic transition curve follows a zigzag path of rising and falling tendency as the series is ascended. The plot of the phase diagram (Fig. 2) shows the absence of the odd-even effect in the nematic-isotropic transition curve, and then it falls up to the eighth homolog and then it rises up to the 14th homolog and finally falls off at the hexadecyl homolog by 14°. Thus, the behavior of nematic-isotropic transition curve of the present study suggests that, enthalpy change of the homolog from fifth to eighth homolog decreases and then increases up to the 14th homolog and then finally decreases. Hence, a low and a high value of enthalpy correspond to a low and a high amount of heat energy requirement (low and high temperature) from surrounding to system. The opposing effects to the molecular geometry of an isobutyl terminal group operates (1) an effect due to widening of the molecule causing a reduction in the intermolecular adhesion by increasing the intermolecular distance and on the other hand (2) increased molecular width, increases molecular polarizability causing an increase in the intermolecular adhesion. Thus, closeness of molecular packing depends upon the net resultant intermolecular forces of attractions, which depend upon the predominating effect out of two opposing effects (1) and (1). In the present study, the latter effect is a predominating effect. Table 3 summarizes the average thermal stabilities and molecular structure of the present series and other structurally related series A [6(i)] and series B [6(ii)] chosen for comparative study.

The molecular geometry of all the homologous series under comparison consists of two phenyl rings linked through a carboxy or a vinyl carboxy ester central linkage with n-alkoxy group at the left terminus and $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$ and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ at the right terminus for series [(1) and (A)] and (B) respectively. The variation in the mesomorphic characteristics can be attributed to the combined effect of the presence of

Table 3. Average thermal stabilities in °C

Series	(I)	(A)	(B)
Nematic isotropic	138.1 (C ₅ –C ₁₆)	110.0 (C ₆ –C ₁₄)	140.0 (C ₅ –C ₁₆)
Commencement of nematic phase	C ₅	C ₆	C ₅
Smectic isotropic	—	—	101.0 (C ₁₀ –C ₁₂)
Commencement of smectic phase	—	—	C ₁₀

**Figure 2.** Homologous series: Isobutyl-p- [p' n-alkoxy cinnamoyloxy] cinnamates. Phase behavior of series 1.

central ester and different right terminal groups, which have different molecular rigidity and flexibility related to molecular polarity and polarizability for the formation of mesophase [13,14].

On comparing the mesomorphic characteristics of series (1) with series A, it is observed that, the homologs of both the series differing in respect of central bridge only are enantiotropically nematogenic. Introduction of a polar isobutyl group at the terminal position in series 1 enable considerable and significant anisotropic [1] forces of attraction of suitable magnitude for pentyloxy to hexadecyloxy homologs, which serve to stabilize statistically parallel orientational order of molecules by end-to-end attractions conducive to the formation of a nematogenic mesophase. This effect persists even in the homologs with long n-alkoxy groups. Comparison of series 1 with series B indicates that the series 1 has an isobutyl group at the right terminal with a vinyl carboxy central group while series B has n-butyl terminal group with a carboxy central group. The flexible straight chained n-butyl group with —COO— central group in series B adds the formation of smectic mesophase due to enhanced lateral attraction in addition to terminal attractions, which facilitates lamellar packing required for the formation of smectic mesophase (1). Thus, series B exhibits smectogenic character in addition to nematogenic character. The nematic thermal stability of series A being lower than series B is understandable because of the difference in terminal attractions arising from the isobutyl and butyl groups.

Conclusion

The study suggests that a polar substituent at a terminal position in a homologous series with present molecular geometry gives rise to the exhibition of a nematogenic mesophase. Moreover, the presence of a vinyl carboxylate unit at a central and/or a terminal position favorably induce a nematogenic mesophase.

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