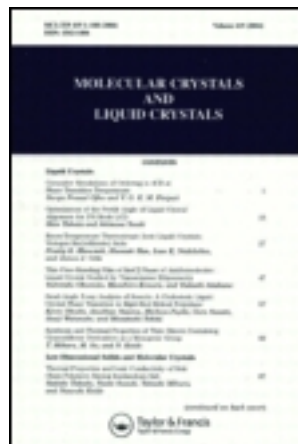


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# Study of the Effect of Molecular Structure on Mesomorphic Properties Through a Novel Homologous Series $\alpha$ -3-[4'-n-Alkoxy cinnamoyloxy] Phenyl- $\beta$ -4''-nitro Benzoyl Ethylenes

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*Eleven members of a novel homologous series  $\alpha$ -3-[4'-n-Alkoxy Cinnamoyloxy] phenyl- $\beta$ -4''-nitro benzoyl ethylene are synthesized and evaluated for their mesomorphic properties. Seven members of the series are enantiotropically nematogenic without exhibition of smectogenic character, and the other four members are non-mesomorphic in character. Mesomorphic behavior from a phase diagram for solid to nematic and for nematic to isotropic transitions shows the normal behavior. The nematic to isotropic transition curve shows an odd–even effect. Analytical data support the structures of molecules. Nematogenic phase length ranges from 30°C to 62°C. Nematic-isotropic thermal stability is 175.7°C. The mesomorphic properties of the series are compared with the structurally similar isomeric series. Thus, the series is predominantly mesomorphic (nematogenic) and partly non-mesomorphic with middle-order melting points. Transition temperatures and other liquid crystal properties were determined by optical polarizing microscopy with a heating stage.*

**Keywords** Enantiotropy; liquid crystal; mesomorphism; nematic; smectic

## Introduction

Some compounds exhibit an intermediate state of matter between the crystalline solid and the isotropic liquid, such phases of matter are called liquid crystals (LCs), and are often termed as mesophases. This sort of physically distinct state of matter depends upon suitable magnitudes of anisotropic intermolecular forces of attraction as a consequence of favorable molecular rigidity and flexibility [1–3]. In present series, the molecular rigidity is due to three phenyl rings linked through two central groups  $-\text{CH}=\text{CH}-\text{COO}-$  and  $-\text{CH}=\text{CH}-\text{CO}-$  for all the members of the series, but flexible part of the molecule (n-alkoxychain) varies in length. The effect of nonlinear broad shape molecular structure

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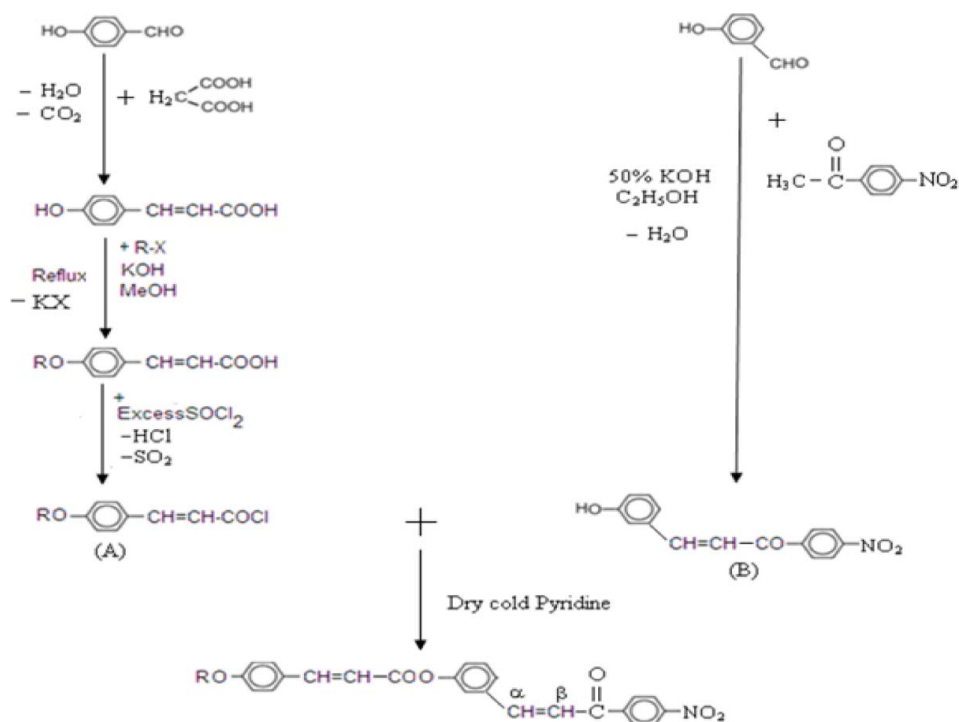
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on liquid crystallinity will be discussed in terms of molecular polarity, polarizability, rigidity, and flexibility.

## Experimental

### Synthesis

4-Hydroxycinnamic acid and the 4-n-alkoxycinnamic acids, as well as the corresponding acid chlorides (A), were prepared using the appropriate n-alkyl halides and subsequently using thionyl chloride by the modified method of Dave and Vora [4].  $\alpha$ -3-Hydroxy phenyl  $\beta$ -4'-nitro benzoyl ethylene (B) was prepared by an established method [5c]. Components (A) and (B) were condensed in dry cold pyridine to obtain final products. 4-hydroxybenzaldehyde, 3-hydroxybenzaldehyde, malonic acid, piperidine, pyridine, thionylchloride, alkyl halides, methanol, KOH, ethanol, and 4-nitroacetophenone required for synthesis were used as received. The final products were all purified and crystallized from alcohol until they gave constant transition temperatures. The synthetic route to the novel series is outlined in Scheme 1.



Where  $\text{R} = \text{C}_n\text{H}_{2n+1} = 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16$

**Scheme 1.** Synthetic route to the novel series.

### Characterization

Some selected representative members of the series were characterized by Infrared (IR) and Hydrogen-1 Nuclear Magnetic Resonance ( $^1\text{H}$ NMR) spectra, and elemental analysis. The

**Table 1.** Elemental analysis (CHN) for ethyloxy, butyloxy, dodecyloxy, and andhexadecyloxy derivatives

No.	Molecular formula	Elements found % (calculated %)		
		C	H	N
1.	C <sub>26</sub> H <sub>21</sub> NO <sub>6</sub>	70.38 (70.42)	4.79 (4.74)	3.10 (3.16)
2.	C <sub>28</sub> H <sub>25</sub> NO <sub>6</sub>	71.29 (71.34)	5.35 (5.31)	2.94 (2.97)
3.	C <sub>36</sub> H <sub>41</sub> NO <sub>6</sub>	74.12 (74.10)	7.10 (7.03)	2.36 (2.40)
4.	C <sub>38</sub> H <sub>45</sub> NO <sub>6</sub>	74.69 (74.63)	7.29 (7.36)	2.34 (2.29)

IR spectra were recorded on a Perkin Elmer spectrum GX and the <sup>1</sup>HNMR spectra were recorded on a Bruker instrument using CDCl<sub>3</sub> as solvent. Microanalysis was performed on a Perkin Elmer PE 2400 CHN analyzer (Table 1). Transition temperatures and LC properties were investigated using optical polarizing microscopy equipped with a heating stage. Thermodynamic quantities enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) are qualitatively discussed. The texture of the nematic mesophase was determined by the miscibility method using polarizing microscopy.

### Analytical Data

#### Spectral Data

##### NMR in ppm for the octyloxy derivative.

0.993 (—CH<sub>3</sub> of OC<sub>8</sub>H<sub>17</sub>), 1.173((—CH<sub>2</sub>—)<sub>n</sub> of —OC<sub>8</sub>H<sub>17</sub>), 3.718 (—OCH<sub>2</sub> of —OC<sub>8</sub>H<sub>17</sub>), 3.223 (—CH=CH—), 6.611 (—CH=CH—CO—), 6.633 (p-substituted phenyl ring) 7.60 and 7.734 (m-substituted phenyl ring). NMR supports the structure.

##### NMR in ppm for the tetradecyloxy derivative.

0.872 (—CH<sub>3</sub> of —OC<sub>14</sub>H<sub>29</sub>), 1.253((—CH<sub>2</sub>—)<sub>n</sub> of —OC<sub>14</sub>H<sub>29</sub>), 4.00 (—OCH<sub>2</sub> of —OC<sub>14</sub>H<sub>29</sub>), 4.289&4.30 (—CH=CH—CO—), 6.88 and 7.931 (p-substituted phenyl ring), 6.90 (m-substituted phenyl ring). NMR supports the structure.

##### IR in cm<sup>-1</sup>for the hexyloxy derivative.

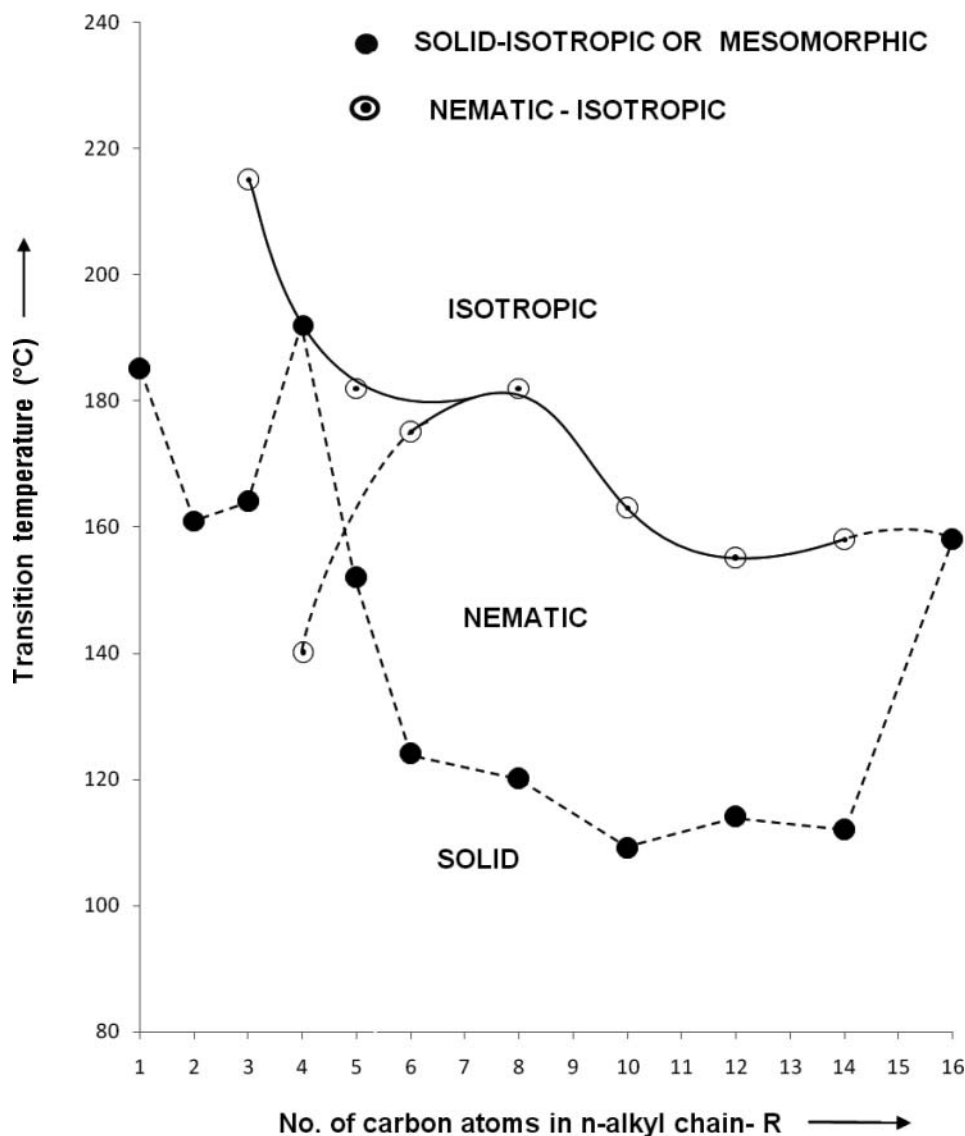
625 (—(CH<sub>2</sub>)<sub>n</sub>— group of OC<sub>6</sub>H<sub>13</sub>), 760 (m-substituted phenyl ring), 1160 (>C=O), 1230, 1600, and 1680(—COO—), 1415 (—NO<sub>2</sub> group), 930 (—CH=CH—). IR supports the structure.

##### IR in cm<sup>-1</sup>for the decyloxy derivative.

625 (—(CH<sub>2</sub>)<sub>n</sub>— group of OC<sub>10</sub>H<sub>21</sub>), 820 (p-substituted phenyl ring), 770 (m-substituted phenyl ring), 1160 (>C=O), 1230, 1600, and 1680 (—COO—), 1415 and 1430 (—NO<sub>2</sub>), 930 (—CH=CH—). IR confirms the structure.

#### Texture by miscibility method.

Pentyloxy homologues shows a threaded type texture and dodecyloxy shows a schlieren type texture.



**Figure 1.** Phase behavior of the novel series 1. Homologous series:  $\alpha$ -3-[4'-n-alkoxy cinnamoyloxy] phenyl- $\beta$ -4''-nitrobenzoyl ethylenes.

## Results and Discussion

n-Alkoxy cinnamic acids and  $\alpha$ -3-hydroxyphenyl- $\beta$ -4'-nitrobenzoyl ethylenes are non-mesomorphics. However, mesomorphism is induced in seven final products of the novel series. The other four members (methyl, ethyl, butyl, and hexadecyl derivatives) are non-mesomorphics. The mesomorphic homologues exhibit enantiotropic nematogenic mesomorphism only with absence of smectogenic character. A phase diagram (Fig. 1) shows the phase behavior, and indicates that the solid to isotropic or solid to nematic transition curve rises and falls in zigzag manner with an overall descending tendency. The nematic

**Table 2.** Transition temperatures in °C

Compound No.	R = C <sub>n</sub> H <sub>2n+1</sub> (n)	Sm	N	Isotropic
1	1	—	—	185.0
2	2	—	—	161.0
3	3	—	164.0	215.0
4	4	—	—	192.0
5	5	—	152.0	182.0
6	6	—	124.0	175.0
7	8	—	120.0	182.0
8	10	—	109.0	163.0
9	12	—	114.0	155.0
10	14	—	112.0	158.0
11	16	—	—	158.0

Sm = smectic; N = nematic.

to isotropic transition curve gradually falls as series is ascended with the exhibition of an odd–even effect. The transition curves of the phase diagram show the number of carbon atoms present in n-alkoxyterminal chain versus transition temperatures (Table 2) of homologues. The mesomorphic phase length varies from a minimum of 30°C for the pentyl derivative to a maximum of 62°C for the octyl derivative of the series. The nematic to isotropic transition curve is extrapolated [5c] for the non-mesomorphic homologues to predict their probable latent transition temperatures (LTT) keeping in mind the trend of the actual transition curve. The predicted LTT for nematic to isotropic transition is 140°C, and for butyl and hexadecyl derivatives, it is 158°C. The monotropic temperature of 140°C is not realizable because before the nematic phase appears, crystallization occurs. The LTT for nematic and solid to isotropic temperature coincided at 158°C. The nematic mesophase is induced in the novel series due to an increase in the number of phenyl rings from the two non-mesomorphic components (A) and (B), which increases molecular aromaticity, polarity, polarizability, and rigidity. Hence, the thermal vibrations give end-to-end intermolecular anisotropic forces of attraction such that the molecules possess a statistically parallel orientational order within definite range of temperature to form nematic mesophase [5, 6]. However, intermolecular forces of attraction are insufficient to cause lamellar packing of molecules, and hence the smectic phase is not exhibited by any member of the novel series. The non-mesomorphic behavior of methyl, ethyl, butyl, and hexadecyl derivatives of the series is attributed to their high crystallizing tendency arising from their shorter and longest n-alkyl terminal chains, which causes unsuitable magnitudes of anisotropic forces of intermolecular attractions. Hence, high degree of disorder, randomness, and entropy ( $\Delta S = \Delta H/T$ ) generated and molecules are sharply transformed into the isotropic liquid from crystalline solid state without passing through an intermediate LC state. Variations in LC properties from homologue to homologue in the same series and the observed odd–even effect are attributed to the sequentially added methylene unit in the n-alkoxy terminal chain. The odd–even effect diminishes as the series is ascended because n-alkoxy chain of higher homologues may coil, bend, flex, or couple to lie with major axis of the core. Thus, the series is predominantly nematogenic and partly non-mesomorphic with middle order melting point and a moderate range of mesomorphism. The LC properties of the novel series 1, including average thermal stability (Table 3) and commencement of mesomorphism, are

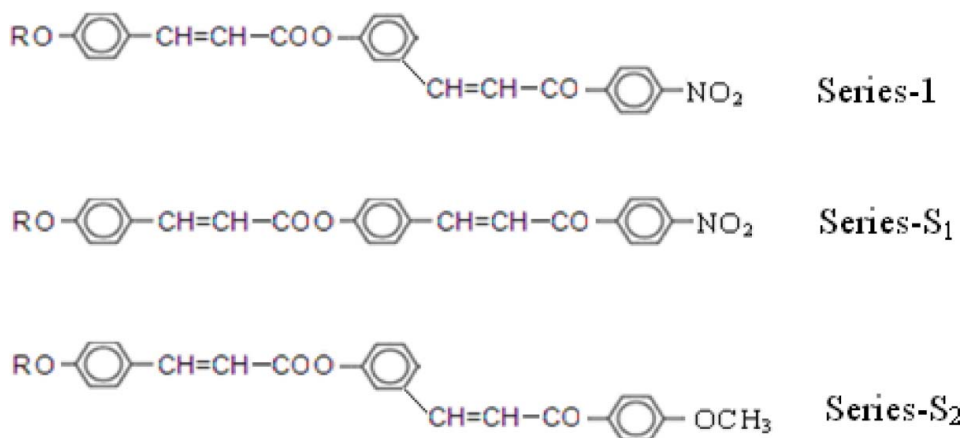
**Table 3.** Relative average thermal stability in °C

Series	1	S <sub>1</sub>	S <sub>2</sub>
Smectic to nematic or smectic to isotropic	–	132.25 (C <sub>5</sub> –C <sub>10</sub> )	138.8 (C <sub>10</sub> –C <sub>14</sub> )
Commencement of smectic phase		C <sub>5</sub>	C <sub>5</sub>
Nematic to isotropic	175.7 (C <sub>3</sub> –C <sub>14</sub> )	171.5 (C <sub>5</sub> –C <sub>10</sub> )	165.7 (C <sub>3</sub> –C <sub>14</sub> )
Commencement of nematic phase	C <sub>3</sub>	C <sub>5</sub>	C <sub>3</sub>

compared with other structurally similar (Fig. 2) homologous series S<sub>1</sub> and S<sub>2</sub> as mentioned below.

The three homologous series (Fig. 2) under comparison commonly contain three phenyl rings bridged through  $-\text{CH}=\text{CH}-\text{COO}-$  and  $-\text{CH}=\text{CH}-\text{CO}-$  central groups, and an n-alkoxy terminal chain. However, they differ in their geometrical shape, size, linearity of molecules, and right terminal end group. Therefore, observed variations in their mesomorphic properties and degree of mesomorphism, including thermal stability, are attributed to the differing magnitudes of molecular polarity, polarizability [7], molecular rigidity, and flexibility [1–3] as well as intermolecular anisotropic forces of attraction. The relative average thermal stability and commencement of mesophase or phases of series 1, S<sub>1</sub> [8], and S<sub>2</sub> [9] are mentioned in Table 3.

Table 3 indicates that the nematic to isotropic thermal stability shows a descending order, i.e., series 1 > S<sub>1</sub> > S<sub>2</sub>, and the smectic order of thermal stability is series S<sub>2</sub> > S<sub>1</sub> > 1. Series 1 and S<sub>2</sub> are nonlinear whereas series S<sub>1</sub> is linear, i.e., series 1 and S<sub>2</sub> are wider than series S<sub>1</sub>. An increase of molecular width increases intermolecular distance, and hence reduces intermolecular attractions and increases molecular polarizability. Thus, on one hand intermolecular anisotropic forces of attraction are reduced due to increased molecular width, while on the other hand, increased molecular polarizability enhances intermolecular cohesive forces. Therefore, these two opposing effects are operating for series 1 and S<sub>2</sub>.

**Figure 2.** Structurally similar homologous series.

In such a case of molecular broadening or widening, the resultant net magnitudes of intermolecular cohesion depend upon the predominating effect [7]. Series  $S_1$  being linear, the intermolecular distance is smaller, and hence the intermolecular anisotropic forces of attraction are relatively more than the isomeric series 1 of the present investigation, which causes lamellar packing of molecules in their crystal lattices and causes sliding layered arrangement of molecules in a floating condition under the influence of heat. The absence of smectogenic character in series 1 indicates the absence of lamellar packing due to intermolecular widening, which reduced intermolecular cohesive forces. The para-substituted  $-\text{NO}_2$  and  $-\text{OCH}_3$  end groups of series 1 and series  $S_2$  are respectively bonded with the phenyl ring in which nitrogen and oxygen atoms are directly linked with the carbon atom of the phenyl ring. The electronegativity of oxygen atom is greater than the nitrogen atom. Therefore,  $\text{C}-\text{O}$  bond polarity will be greater than the  $\text{C}-\text{N}$  bond polarity, and hence the ratio of the molecular polarity to polarizability differs accordingly. Thus, lamellar packing of molecules in case of series  $S_2$  is supported whereas it is not facilitated in the novel series 1.

## Conclusions

- (1) The novel series 1 is predominantly nematogenic without exhibition of smectogenic character.
- (2) Lamellar packing of molecules is facilitated more by  $-\text{OCH}_3$  terminal than  $-\text{NO}_2$  in equishaped molecules.
- (3) The group efficiency order derived for smectic and nematic on the basis of thermal stability are as under.

Nematic:  $-\text{NO}_2 > -\text{NO}_2 > -\text{OCH}_3$

(nonlinear) (linear)

( $S_1$ ) ( $S_2$ )

Smectic:  $-\text{OCH}_3 > -\text{NO}_2 > -\text{NO}_2$

(linear)(nonlinear)

( $S_2$ ) ( $S_1$ ) (1)

- (4) Molecular rigidity and flexibility depend upon the molecular shape, size, polarity of terminal end group, and electron–electron interactions, and facilitates or hinders the mesophase formation accordingly.

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