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Synthesis and Evaluation of a Novel Liquid Crystalline Homologous Series: α-4-[4'-n-Alkoxy Cinnamoyloxy] Benzoyl-β-3",4"-Dimethoxy Phenyl Ethylenes

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The synthesis and evaluation of a novel series of 12 homologues is presented. Enantiotropic nematogenic mesomorphism is exhibited from the pentyl to hexadecyl homologues. The other homologues are not liquid crystalline. Smectic mesomorphism is absent in all homologues. Transition temperatures were determined using an optical polarizing microscope equipped with a heating stage. The transition curves of a phase diagram behave in a normal manner. An odd–even effect is observed for the N-I transition curve. The textures of the nematic phase are of the threaded or Schlieren type. Mesomorphic–isotropic transition temperatures range from 152°C to 178°C. The nematogenic phase length varies between 24°C and 51°C. The nematic thermal stability is 163.1°C. Thus, the novel homologous series is entirely nematogenic without the exhibition of smectogenic character, and is of a middle ordered melting type. Analytical and spectral data support the molecular structures. Liquid crystal (LC) properties of the novel series are compared with structurally similar homologous series.

Keywords Liquid crystal; mesomorphism; nematic; smectic; thermotropic

Introduction

The exhibition of liquid crystal properties by any substance is related directly to the molecular structure. Molecular structure [1] includes aspects of geometrical shape, size, number of phenyl rings, molecular aromaticity, polarities of the central, lateral and terminal end groups, and the molecular width. Molecular polarity, polarizability, steric hindrance, and electronic interactions are also significant factors. Overall favorable molecular rigidity and flexibility [2–4] enable suitable magnitudes of anisotropic intermolecular forces of attractions; which maintain ordered molecular arrangement [1] facilitating mesomorphism. The molecular geometry in this novel series consists of three phenyl rings bridged through

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-CH = CH-COO- and -CO-CH = CH- central groups, with -OR and $-OCH_3$ terminal end groups, and a $-OCH_3$ lateral group positioned at the ortho position to the right handed terminal end group on the third phenyl ring. Thus, the effect of molecular structure on liquid crystal properties in terms of broadening the molecule with a highly polar $-OCH_3$ group is discussed.

Experimental

Synthesis

4-Hydroxycinnamic acid was alkylated with suitable alkylating agents (R-X) and cis-4-*n*-alkoxycinnamic acids formed were converted to the corresponding 4-*n*-alkoxycinnamoyl chlorides (A) using freshly distilled thionyl chloride by the modified method of Dave and Vora [5]. α -4-Hydroxy benzoyl β -3',4'-dimethoxy phenyl ethylene (B) was prepared by the usual established method [6]. Components (A) and (B) were condensed in dry cold pyridine. Final products were individually decomposed, filtered, washed, dried, and purified until they gave constant transition temperatures. The p-hydroxybenzaldehyde, malonic acid, pyridine, alkyl halides, MeOH, KOH, ethanol, thionyl chloride, p-hydroxy acetophenon, and 3,4-dimethoxy benzaldehyde required for synthesis were used as received except for solvents, which were dried and purified prior to use. The synthetic route to the series is shown below in Scheme 1.

Characterization

Some selected homologues of the novel series were characterized by elemental analysis, Infra red, and ¹HNMR spectroscopy techniques. Micro analysis of the compounds was performed on a Perkin–Elmer PE 2400 CHN analyzer with results shown in Table 1. Nuclear magnetic resonance (NMR) spectra were recorded using CDCl₃ as solvent and IR spectra

| * | | | | | | |
|----------|--|----|-------|-----------|--|--|
| Compound | <i>n</i> -Alkyl group | Sm | Ν | Isotropic | | |
| no. | $\mathbf{R} = \mathbf{C}_n \mathbf{H}_{2n+1} \left(n \right)$ | Sm | Ν | Isotropic | | |
| 1 | 1 | _ | _ | 200.0 | | |
| 2 | 2 | _ | _ | 206.0 | | |
| 3 | 3 | _ | _ | 190.0 | | |
| 4 | 4 | _ | _ | 201.0 | | |
| 5 | 5 | _ | 142.0 | 170.0 | | |
| 6 | 6 | _ | 124.0 | 160.0 | | |
| 7 | 7 | _ | 123.0 | 174.0 | | |
| 8 | 8 | _ | 110.0 | 169.0 | | |
| 9 | 10 | _ | 132.0 | 178.0 | | |
| 10 | 12 | _ | 120.0 | 166.0 | | |
| 11 | 14 | _ | 125.0 | 152.0 | | |
| 12 | 16 | _ | 132.0 | 156.0 | | |
| | | | | | | |

Table 1. Transition temperatures in °C of series-1

Note: Sm = Smectic; N = Nematic.



Scheme 1. Synthetic route to the series.

were recorded using a Perkin–Elmer GX spectrometer. The liquid crystal properties, transition temperatures, and melting temperatures were investigated by using optical polarizing microscopy.

The optical texture of the nematic mesophase were determined by the miscibility method. Pentyloxy homologue shows athreded type nematic texture and tetradecyloxy homologue ahows a schlieren type texture.

Analytical Data

NMR in ppm for Hexyloxy Derivative. 0.88 (–CH₃ of –OC₆H₁₃ group), 1.28 (–CH₂–)_n Polymethylene group of –OC₆H₁₃, 4.08 (–OCH₂–CH₂– of –OC₆H₁₃), 3.88 (–OCH₃), 4.74 broad (–CH = CH– group), 6.90 & 6.92 (–CO–CH = CH–group), 7.90, 7.92, & 8.08 (substituted phenyl ring). The NMR data supports the molecular structure.

NMR in ppm for Decyloxy Derivative. 0.87 ($-CH_3$ of $-OC_{10}H_{21}$ group), 1.25 ($-CH_2-$)_n Polymethylene group of $-OC_{10}H_{21}$, 4.00 ($-OCH_2-CH_2-$ of $-OC_{10}H_{21}$), 3.86 ($-OCH_3$),

| Sr. no. | Molecular formula | Elements % found (% calculated) | | |
|---------|---------------------|---------------------------------|-------------|--|
| | | С | Н | |
| | | 73.78 (73.73) | 5.83 (5.93) | |
| 2 | $C_{30}H_{30}O_6$ | 74.19 (74.07) | 6.35 (6.17) | |
| 3 | $C_{34}H_{38}O_{6}$ | 75.38 (75.28) | 6.92 (7.01) | |
| 4 | $C_{38}H_{46}O_{6}$ | 76.40 (76.25) | 7.78 (7.69) | |

Table 2. Elemental analysis for propoxy, butoxy, octyloxy, and dodecyloxy derivatives

4.696 broad (-CH = CH-group), 7.04 & 7.22 (-CO-CH = CH-group), 6.90, 7.88, & 7.90 (substituted phenyl ring). The NMR data supports the molecular structure.

IR in cm⁻¹ for Ethyloxy Derivative. 690 (polymethylene – $(CH_2)n$ – group of $-OC_2H_5$), 1170 (>C = O group), 1260, 1605 (–COO ester group), 990 (–CH = CH– group), 770 (1,2,4-trisubstituted phenyl ring). The IR data supports the molecular structure.

IR in cm⁻¹ for Dodecyloxy Derivative. 720 (polymethylene $-(CH_2)n$ - group of $-OC_{12}H_{25}$), 765 (p-substituted phenyl ring), 1165 (>C = O group),1260, 1600 (-COO ester group), 960 (-CH = CH- group), 845 (1,2,4-trisubstituted phenyl ring). The IR data supports the molecular structure (Table 2).

Results and Discussion

Cis-4-n-Alkoxycinnamic acids and α -4-hydroxy benzoyl β -3',4'-dimethoxy phenyl ethylene (B) are not liquid crystals. However, liquid crystalline properties are induced on linking ethylene derivative (B) to the corresponding acid chlorides of 4-n-alkoxycinnamic acids. The methyl to butyl homologues are not liquid crystals, while the pentyl to hexadecyl homologues of the series are enantiotropic liquid crystals with nematogenic character only, without the exhibition of smectogenic properties even in the monotropic condition. Thus, 8 out of 12 homologues of the series are liquid crystalline. A plot of a phase diagram drawn for transition temperatures versus the number of carbon atoms present in the left nalkoxy terminal end group consists of two transition curves. The solid-isotropic or nematic transition curve adopts a zigzag path of rising and falling values as the series is ascended with an overall descending tendency and behaves in normal manner. The nematic-isotropic transition curve initially rises up to the decyl homologue and then descends as the series is ascended with exhibition of an odd-even effect and a negligible rise of few degrees at the hexadecyl homologue. Thus, the N-I transition curve behaves in the usual established manner. The N-I transition curves for the odd and even members of the series merge into each other at the nonyl homologue of the series. The odd-even effect diminishes as series is ascended for higher homologues because the longer *n*-alkyl chains may coil, bend, flex, or couple to lie with the major axis of the core. The texture of the nematic mesophase is threaded or Schlieren. The maximum nematogenic mesophase length is 59°C at the octyl homologue and the minimum mesophase length is $24^{\circ}C$ for the hexadecyl homologue. The thermal stability for nematic mesophase is 163.1°C. Thus, the presently investigated novel homologous series is entirely nematogenic without exhibition of smectogenic character and is of a middle ordered melting type. The mesomorphic (LC) properties vary from homologue to homologue in the same series.

Homologous Series: α-4-[4'-n-Alkoxy Cinnamoylokxy] benzoyl-β-3"- 4"-dimethoxyphenyl ethylenes



Figure 1. Phase behavior of series.

The occurrence of a liquid crystalline state from and beyond the pentyl homologue is attributed to the occurrence of suitable magnitudes of anisotropic intermolecular forces of end-to-end attractions as a consequence of favorable molecular rigidity and flexibility [1–4]. The molecules forming the nematogenic mesophase resist thermal vibrations imposed upon them and set themselves at an angle of less than 90° on the plane of a surface at a particular temperature t_1 and continue up to temperature t_2 ; between t_1 and t_2 the molecules float with a statistically parallel orientation ordered. The temperature difference, $t_2 - t_1$, is called phase length or range of liquid crystallinity (nematic). The temperature above t_2 converts the sample into the isotropic state, at which point the molecules are randomly

oriented in all possible directions in disordered manner. Thus, suitable magnitudes of anisotropic intermolecular forces of adhesion [1] as a consequence of favorable rigidity and flexibility [2–4] maintain ordered molecular arrangement in a floating condition. The nonliquid crystalline behavior of the methyl to butyl homologues is attributed to their high crystallizing tendency, which arises from their unsuitable magnitudes of intermolecular forces of attraction. Therefore, the molecules concerned transform sharply into the isotropic state from the solid state without passing through a liquid crystalline state. The absence of smectogenic character indicates absence of lamellar packing of molecules in their crystal lattices. The shape of either the nematic–isotropic transition curve or solid-nematic or isotropic curve adopts the path of their propagation in a phase diagram according to the resultant molecular rigidity and/or flexibility. The odd–even effect and the variations in mesomorphic properties from homologue to homologue in the same series is due to the sequentially added methylene unit of the left *n*-alkoxy terminal end group [1–4]. The liquid crystal properties of the presently investigated novel homologous series 1 are compared with the other structurally similar homologous series X [7] and Y [8] as shown in Fig. 2.

Homologous series X and Y chosen for comparison and the novel homologous series 1 as shown in Fig. 2 are similar in respect of three phenyl rings bridged through two identical central groups -CH = CH-COO- and -CO-CH = CH- as well as commonly substituted left *n*-alkoxy (-OR) terminal end group. However they differ in respect of the groups in the terminal and/or lateral positions in the right phenyl ring, as can clearly be seen in Fig. 2. Therefore, the observed variations in their mesomorphic properties and the degree of mesomorphism can be attributed to the differing features of series 1, X and Y [1–4].

The length to breadth ratio, intermolecular end-to-end and lateral attractions, molecular polarizability due to molecular width by laterally substituted $-OCH_3$ and $-NO_2$ groups contributing to the magnitudes of anisotropic intermolecular forces of adhesion considerably differ, based on molecular rigidity and flexibility [1–4]. Similarly, series 1 and Y differ in respect of only one of the $-OCH_3$ groups substituted at the lateral position (3"), i.e., two $-OCH_3$ groups present on 3"-4" position of series 1 and only one $-OCH_3$ group present on 4" position of series Y; or 3" $-OCH_3$ group is missing in series Y, which results in a linear shape of series Y and a nonlinear shape of series 1. Thus, the magnitudes of anisotropic intermolecular closeness, molecular polarity and polarizability as a consequence of the resultant rigidity and flexibility. Table 3 shows the thermal stability of mesophases, commencement of mesophase, type of mesophase exhibition, as shown below.



Figure 2. Structurally similar series.

| Series | 1 | Х | Y |
|---|---|------------------------------------|---|
| Smectic-nematic or | _ | 141.0 | 159.7 |
| smectic–isotropic commencement of smectic phase | | $(C_5 - C_{10})$ C ₅ | $(C_5 - C_8)$ C_5 |
| Nematic–isotropic commencement of | 163.1 (C ₅ -C ₁₆) | 156.0 (C5-C16) | 174.1 (C ₅ -C ₁₄) |
| nematic phase | C ₅ | C_5 | C ₅ |

Table 3. Average thermal stability in °C

Table 3 shows that homologous series X and Y, selected for comparison, are smectogenic in addition to being nematogenic, but the novel series 1 does not exhibit smectogenic character at all. The intermolecular closeness due to the varying molecular width plays an important role to the net magnitudes of intermolecular anisotropic forces of attractions. The laterally substituted –OCH₃ and –NO₂ groups increase molecular width as compared to series Y, chosen for comparison. When molecular width increases, the intermolecular forces of attraction depend upon two opposing forces operating at a time. (1) As molecular width increases, the intermolecular distance increases or the intermolecular closeness reduces, consequently intermolecular attractions diminish. (2) Increased molecular width raises molecular polarizability, which results in an increase of intermolecular attractions [1]. The net resultant effect of intermolecular attractions depends upon the predominating effect out of two opposing effects (1) and (2) operating at the time. Thus, the (1) effect predominates for the nonlinear series 1 while; the (2) effect predominates for the nonlinear series X. The intermolecular distance is closest for a linear shaped series Y. Thus, suitable magnitudes of anisotropic intermolecular forces of attractions are favorable and sufficient to facilitate lamellar packing of molecules of series X and Y in their crystal lattices but it is insufficient, unfavorable, and unsuitable to facilitate lamellar packing of molecules in the crystal lattices of series 1. Hence, the statistically parallel orientation order of molecules is maintained by only end-to-end attractions, but the sliding layered arrangement of molecule is missing in the floating condition for the presently investigated series 1. Homologous series Y being linear induces the highest intermolecular closeness to exhibit smectic and nematic mesophase formation. The highest value of smectic and nematic thermal stability of series Y among the series under comparison is obvious from the point of view of intermolecular closeness and end group polarity. The nematic-isotropic thermal stability of series 1 is higher than the series X, because series 1 contains two highly polar groups $-OCH_3$, while series X contains only one polar group $-NO_2$. Thus only nematic thermal stability has occurred at the cost of the missing smectogenic mesophase. The ematic mesophase commences from the fifth homologue of all the series 1, X and Y, but the smectic phase does not occur or commence until the last hexadecyloxy homologue of series. However, smectic mesophase formation commences from the fifth member of the series X and Y. This difference of behavior is attributed to the different magnitudes of noncoplanarity caused [9] by the molecules of series 1, X, and Y, under comparison. Thus, the variations in mesomorphic properties for the same homologue from series to series is attributed to the unchanging lateral and/or terminal end group throughout the same series. The group efficiency order derived on the basis of thermal stability for smectic and nematic is mentioned in the conclusions below.

Conclusions





2. Group efficiency order for the nematic phase:

$$-\bigcirc$$
 $-\bigcirc$ $-\bigcirc$ $-\bigcirc$ $-\bigcirc$ $-\bigcirc$ $-H$
OCH₃ > $-\bigcirc$ $-H$
NO₂

- Molecular width plays an important role in inducing smectic and/or nematic mesophase.
- Molecular width variation by lateral substitution regulates the desired type mesophase formation.
- Molecular rigidity and/or flexibility is an important criteria to predict mesophase formation based on molecular shape, size, and the polarity of a substituted functional group.

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