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Synthesis and Mesomorphic Properties of Novel Ethylene Derivatives

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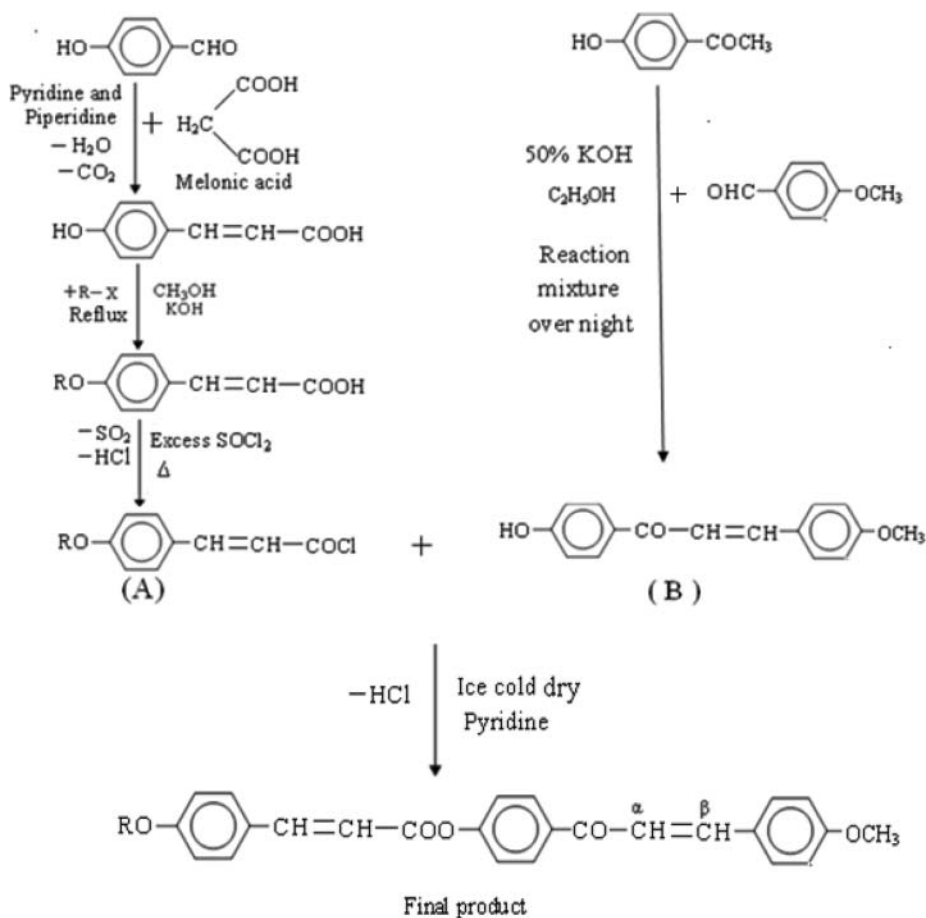
A novel homologous series, α -4-[-4'-n-alkoxy cinnamoyloxy] benzoyl- β -4'-methoxy phenyl ethylenes, has been synthesized, which consists of 12 homologues. The pentyl to tetradecyl homologues are enantiotropically mesomorphic, and the rest of the homologues are nonmesomorphic. The pentyl to octyl derivatives exhibit smectogenic character in addition to nematogenic character, but the decyl to tetradecyl homologues exhibit only nematogenic character without the exhibition of a smectic phase. A phase diagram of three transition curves shows a normal phase behavior. Analytical and spectral data confirm the molecular structure of the homologues. The optical microscopic textures are threaded or Schlieren for the nematic phase and the normal smectic A type, respectively. Liquid crystal properties and transition temperatures were determined using a hot stage polarizing microscope. The smectic and nematic thermal stabilities are 159.7°C and 174.1°C, respectively. Thus, the present novel series is predominantly nematogenic and partly smectogenic in nature and is compared with other structurally similar homologous series.

Keywords Enantiotropy; ethylene derivatives; liquid crystal; nematic; smectic

Introduction

Molecular structure consists of different atoms making a variety of skeletons whose rigidity and flexibility [1–3] vary from molecular skeleton to skeleton. Thus, suitable magnitudes of anisotropic intermolecular forces of the end to end and lateral attractions also vary to facilitate or to induce liquid crystal properties. Thus, the present study is planned with a view to understand and establish the relationship between liquid crystal properties [4] and the molecular structure by constructing a new skeleton of ethylene derivatives by linking three phenyl rings through two central bridges $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ in which two terminal end groups of $-\text{OR}$ and $-\text{OCH}_3$ are attached at the $p'-p''$ positions without any lateral substitution.

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α -4-[4'-n-Alkoxy cinnamoyloxy] benzoyl- β -4''-methoxy phenyl ethylenes

Scheme 1. Synthetic route to the series.

Experimental

Synthesis

4-*n*-Alkoxy cinnamic acids were prepared using suitable alkylating agents and 4-hydroxyl cinnamic acid. *cis*-4-*n*-Alkoxy cinnamic acids were converted to the corresponding acid chlorides (A) using thionyl chloride by the modified method of Dave and Vora [5]. α -4-Hydroxy benzoyl β -4'-methoxy phenyl ethylene (B) was prepared by usual established method [6]. Components (A) and (B) were condensed in dry cold pyridine [7]. Final products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained. 4-Hydroxy benzaldehyde, malonic acid, piperidine, pyridine, alkyl halide, MeOH, KOH, EtOH, thionyl chloride were used as received, and solvents were dried and purified prior to use. The synthetic route to the series is under mentioned as Scheme 1.

Where $R = C_nH_{2n+1}$, $n = 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16$.

Table 1. Elemental analysis for methoxy, ethoxy, butoxy, and pentyloxy derivatives

Sr. no.	Molecular formula	Elements % found (% Calculated)	
		C	H
1	C ₂₆ H ₂₂ O ₅	75.41 (75.36)	5.38 (5.31)
2	C ₂₇ H ₂₄ O ₅	75.80 (75.70)	5.78 (5.60)
3	C ₂₉ H ₂₈ O ₅	76.64 (76.31)	6.37 (6.14)
4	C ₃₀ H ₃₀ O ₅	75.75 (75.59)	6.49 (6.38)

Characterization

Selected members of the novel homologous series were characterized by elemental analysis (Table 1), infrared (IR) spectroscopy, and ¹HNMR spectroscopy techniques. Microanalysis was performed on a Perkin-Elmer PE2400 CHN analyzer. IR spectra were recorded on a Perkin-Elmer spectrum GX, and ¹HNMR spectra were recorded on a Bruker instrument using CDCl₃ as the solvent. The mesogenic properties of the novel series were determined using polarizing microscopy. The textures of nematic and smectic mesophases were determined by a miscibility method.

Texture Determination

Dodecyl-Threaded nematic

Octyl-Schilieren nematic

Hexyl-Smectic-A

Analytical Data

Spectral Data

NMR in ppm for the decyloxy derivative: 0.910 (—CH₃ of —OC₁₀H₂₁ group), 1.245 (—(CH₂)_n— polymethylene group of —OC₁₀H₂₁), 3.670 (triplet) (—OCH₂—CH₂— of —OC₁₀H₂₁), 6.625 and 6.987 (—CH=CH—CO— group), 7.277, 7.390, and 7.717 (*p*-substituted phenyl ring). NMR supports the molecular structure.

NMR in ppm for the dodecyloxy derivative: 0.946 (—CH₃ of —OC₁₂H₂₅ group), 1.421 (—(CH₂)_n— polymethylene group of —OC₁₂H₂₅), 4.007 (triplet) (—OCH₂—CH₂— of —OC₁₂H₂₅ group), 6.898 and 6.920 (—CH=CH—CO— group), 7.899, 7.920, and 7.980 (*p*-substituted phenyl ring). NMR supports the molecular structure.

IR in cm⁻¹ for the hexyloxy derivative: 740 polymethylene —(CH₂)_n— group of —OC₆H₁₃, 815 *p*-substituted phenyl ring, 1180 C—O of —OC₆H₁₃ group, 1220 and 1600 —COO ester group, 930 —CH=CH— group. IR supports the molecular structure.

IR in cm⁻¹ for octyloxy derivative: 680 polymethylene —(CH₂)_n— group of —OC₈H₁₇, 830 *p*-substituted phenyl ring, 1140 C—O of —OC₈H₁₇ group, 1250 and 1600 —COO ester group, 960 —CH=CH— group. IR supports the molecular structure.

Results and Discussion

The novel homologous series consists of 12 homologues. The methyl to butyl and the hexadecyl homologues are not liquid crystalline, the pentyl to octyl homologues are enantiotropically smectogenic in addition to nematogenic, and the decyl to tetradecyl

Homologous Series: α -4-[4'-*n*-Alkoxy Cinnamoyloxy] benzoyl- β -4''- methoxy phenyl ethylenes

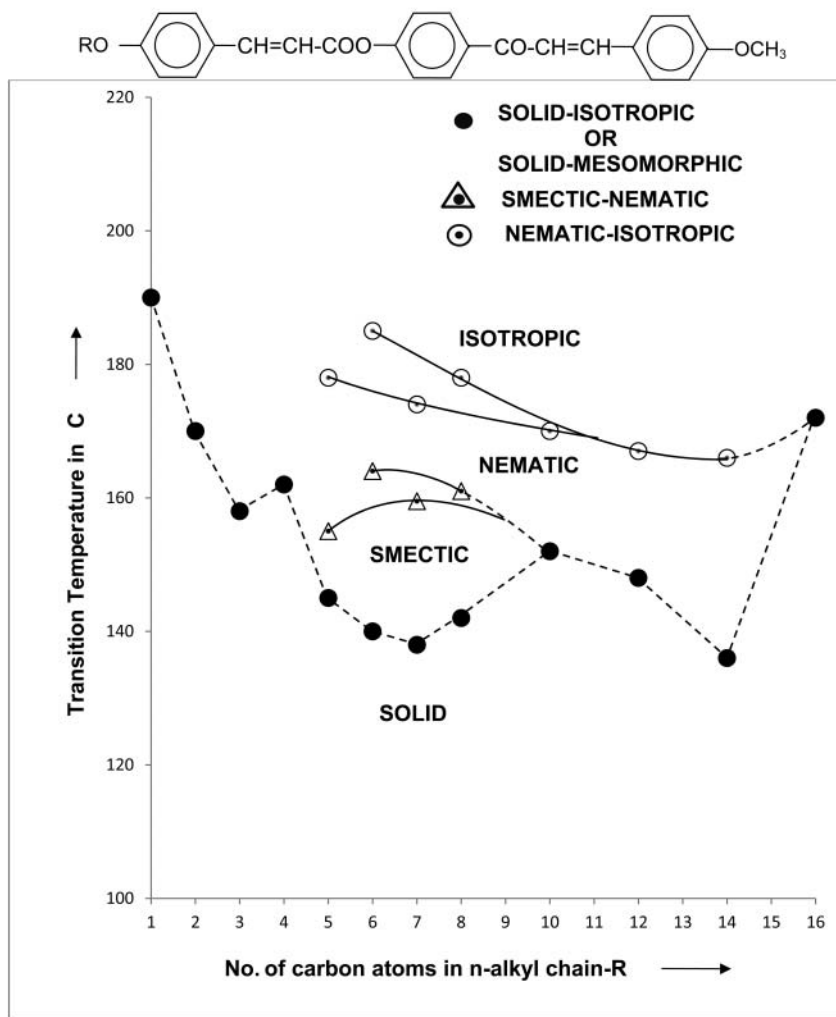


Figure 1. Phase behavior of a series.

homologues are only enantiotropically nematogenic. Acid chlorides (A) and the ethylenic component (B) forming the final homologue derivatives are nonmesomorphic. However, the resulting final homologues from pentyl to tetradecyl derivatives are mesomorphic with the exhibition of either the smectic and/or the nematic mesophase. A phase diagram (Fig. 1) of the series is drawn for the number of carbon atoms present in the *n*-alkyl chain versus the transition temperatures (Table 2) as determined from an optical polarizing microscope equipped with a heating stage. The solid-mesomorphic or isotropic curve adopts a zigzag path of rising and falling values with an overall falling tendency and behaves in a normal manner. The smectic-nematic transition curve initially rises, passes through maxima, and then descends with the exhibition of an odd-even effect and merges into the solid-nematic transition temperature of decyloxy homologue, which indicates that, from and beyond, the

Table 2. Transition temperatures of series in °C

Compound no.	<i>n</i> -Alkyl group -C _n H _{2n+1} (<i>n</i>)	Transition temperatures in °C		
		Sm	Nm	Isotropic
1	1	—	—	190.0
2	2	—	—	170.0
3	3	—	—	156.0
4	4	—	—	162.0
5	5	145.0	155.0	178.0
6	6	140.0	164.0	185.0
7	7	138.0	159.0	174.0
8	8	142.0	161.0	178.0
9	10	—	152.0	170.0
10	12	—	148.0	168.0
11	14	—	136.0	166.0
12	16	—	—	172.0

Sm, smectic; Nm, nematic.

decyloxy to tetradecyloxy homologues, the smectic mesophase formation ceases to appear and only the nematogenic mesophase occurs. Thus, the smectic–nematic transition curve behaves in the usual established manner. The nematic–isotropic transition curve follows a descending tendency as the series is ascended with the exhibition of an odd–even effect and merges into the isotropic point of the hexadecyloxy homologue showing that the nematogenic mesophase formation ceases to appear beyond the tetradecyloxy homologue, and so the hexadecyloxy homologue is nonmesomorphic. Thus, nematic–isotropic transition curve behaves in a normal manner. The smectogenic phase length varies from a minimum of 10°C at the pentyloxy homologue to maximum of 24°C at the hexyloxy homologue. The nematogenic mesophase length varies from a minimum of 15°C at the heptyloxy homologue to maximum of 30°C at the tetradecyloxy homologue. The smectic and nematic thermal stabilities are 159.7°C and 174.1°C, respectively. Thus, the novel homologous series is predominantly nematogenic and partly smectogenic with a middle ordered melting type. The mesomorphic properties vary from homologue to homologue in the same series. The curves for the odd and the even homologues for smectic and nematic merge into each other at the 9th and 11th homologues, respectively. Thus, the odd–even effect diminishes as series is ascended for higher homologues, which is because the longer *n*-alkyl chain may coil, bend, flex, or couple to lie on the major axis of the core [4,8]. The smectic and nematic mesophase formation commences from the pentyloxy homologue. The members of the novel homologous series are synthesized from two nonmesomorphic components (A) and (B). The mesomorphic property induces from the pentyl to the tetradecyl homologues because of suitable magnitudes of molecular rigidity and flexibility enables the molecules to float in an ordered two-dimensional array causing formation of either smectic and/or nematic mesophase. The molecules of the pentyl to octyl homologues show a lamellar packing in their crystal lattices, which generates the smectic mesophase. However, on continued heating the lamellar packing gives way to simply a statistically parallel orientational order of the molecules, which generates the nematic mesophase. Thus, the smectic mesophase and the nematic mesophase occur for the pentyl to octyl homologues. The octyl to tetradecyl

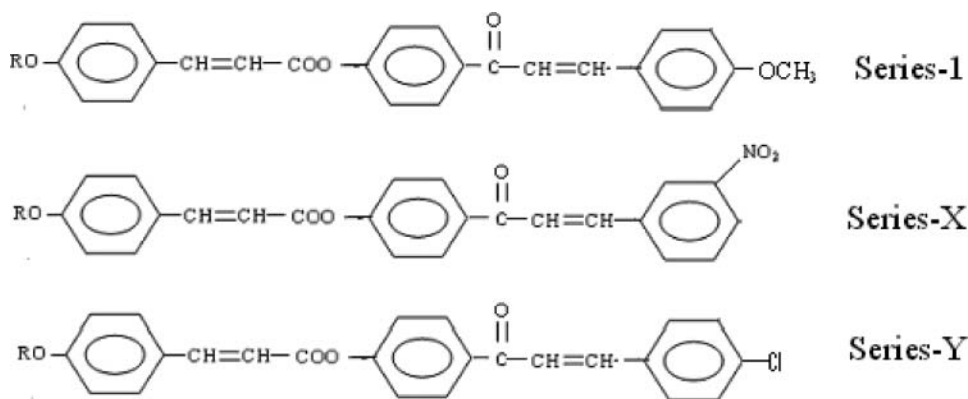


Figure 2. Structurally similar homologous series.

derivatives do not show a lamellar packing of the molecules, but the end to end intermolecular attractions are sufficient to induce nematogenic character in these homologues. The observed odd–even effect and variations in mesomorphic properties from homologue to homologue in the same series is attributed to the sequentially added methylene unit [4, 8] in the *n*-alkoxy terminal chain. The nonmesomorphic nature of the methyl to butyl and the hexadecyl homologues is attributed to the high crystallizing tendency arising from unsuitable magnitudes of anisotropic intermolecular forces of attraction giving an unfavorable combination of molecular rigidity and flexibility [1,2,3]. The mesomorphic properties of the series (1) under discussion are compared with other homologous with similar molecular structure, series X [9] and Y [10] as shown in Fig. 2.

Homologous series 1, X, and Y are identical in all respects with three phenyl rings, two central groups $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ and an *n*-alkoxy ($-\text{OR}$) terminal chain. However, series 1, X, and Y differ with respect to terminal or lateral units of $-\text{OCH}_3$, $-\text{NO}_2$, and $-\text{Cl}$. Therefore, the observed differences in mesomorphic properties and the degree of mesomorphism can be linked to these differing structural features. Functional groups $-\text{OCH}_3$, $-\text{NO}_2$, and $-\text{Cl}$ have different polarities based upon their positional substitution on the third phenyl ring. Therefore, the molecular polarities and polarizability, length to breadth ratio based on linear (series 1 and Y) or nonlinear (series X) shape, electronic interactions, suitable magnitudes of anisotropic intermolecular forces of adhesion [4] cause the resultant molecular rigidity and flexibility to differ and generate different melting points and mesomorphism. Table 3 shows the thermal stability and the commencement of the mesophase.

Table 3. Average thermal stability in $^{\circ}\text{C}$

Series →	1	X	Y
Smectic–nematic or isotropic	159.7 (C_5-C_8)	141.0 (C_5-C_{10})	132.6 (C_8-C_{12})
Commencement of the smectic phase	C_5	C_5	C_8
Nematic–isotropic	174.1 (C_5-C_{14})	156.0 (C_5-C_{16})	156.7 (C_5-C_{16})
Commencement of the nematic phase	C_5	C_5	C_5

Table 3 indicates that all the series (1, X, and Y) under comparison are capable enough to induce smectic and nematic mesophases within definite range of temperature. However, they differ in the extent of smectic and nematic thermal stability. The smectic thermal stability decreases from series 1 to X to Y. Similarly, the nematic thermal stability of series 1 is the highest among the series under comparison. The thermal stability of series X and Y is almost equivalent ($56.0 \approx 56.7$). This suggests that the molecules of series 1 strongly resist the exposed thermal vibrations due to the highest magnitudes of anisotropic intermolecular forces of attractions facilitated by the highly polar $-\text{OCH}_3$ terminal end group of series 1. A gradual weakening of the intermolecular attractions may be due the lower polarity and polarizability of the $-\text{Cl}$ or $-\text{NO}_2$ terminal or lateral groups, respectively. The smectic mesophase commences from fifth member of the series 1 and X, but it commences later from the eighth member of series Y. The early or late commencement of a smectic phase depends upon [11] the extent of noncoplanarity caused by a molecular flexibility [1,2,3] because of the variation in the molecular structure arising from the $-\text{OCH}_3$, $-\text{NO}_2$, $-\text{Cl}$ flexible molecular parts. Thus, the observed variations of mesomorphic properties for the same homologue from series to series is attributed to the $-\text{OCH}_3$, $-\text{NO}_2$, and $-\text{Cl}$ group of series 1, X, and Y. However, the commencement of the nematogenic mesophase formation is unaffected by changing functional groups, which remains intact for each series. The group efficiency order derived on the basis of (a) thermal stability and (b) early commencement of smectic and nematic phases is mentioned below in the conclusions.

Conclusions

- (a) Smectic group efficiency order: $4''-\text{OCH}_3 > 3''-\text{NO}_2 > 4''-\text{Cl}$
 Nematic group efficiency order: $4''-\text{OCH}_3 > 4''-\text{Cl} \approx 3''-\text{NO}_2$
 (b) Smectic group efficiency order: $4''-\text{OCH}_3 \approx 3''-\text{NO}_2 > 4''-\text{Cl}$
 Nematic group efficiency order: $4''-\text{OCH}_3 = 3''-\text{NO}_2 = 4''-\text{Cl}$
- The novel series is predominantly nematogenic and partly smectogenic with a middle-ordered melting type and low mesomorphic range.
- Favorable molecular rigidity and flexibility of suitable magnitudes can facilitate mesophase formation.
- Variations in mesomorphic properties from homologue to homologue in the same series and from series to series for the same homologue are attributed to the progressively added methylene unit and unchanging terminal or lateral group of each series, respectively.

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