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Synthesis and Liquid Crystalline Properties of Novel Ethylene Derivatives

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A novel homologous series of liquid crystals, viz., α -4-[4'-n-alkoxy cinnamoyloxy] benzoyl - β -4''-chloro phenyl ethylenes, has been synthesized. The series consists of twelve homologs. The methyl to butyl derivatives are not liquid crystalline and the rest of the homologs are enantiotropic liquid crystals. The octyl to dodecyl derivatives of the series are enantiotropically smectogenic in addition to nematogenic in character, but the pentyl, hexyl, heptyl tetradecyl, and hexadecyl homolog derivatives of the series are only nematogenic without the exhibition of a smectic phase. The transition temperatures of the novel substances were determined by optical polarizing microscopy equipped with a heating stage. A plot of transition temperatures versus the number of carbon atoms present in the n-alkoxy terminal chain represents the phase behavior of the series. An odd-even effect is observed for the nematic-isotropic transition curve. The textures of the nematic phase are of a threaded or Schlieren type and those of the smectic A and smectic C phases are typical. Analytical and spectral data agree with the molecular structures. The smectic and nematic thermal stabilities are 132.6°C and 156.7°C, respectively. The smectic phase commences from the octyloxy homolog. Smectogenic phase lengths vary from 26°C to 33°C and the nematogenic phase lengths vary from 6°C to 70°C. The series is predominantly nematogenic and partly smectogenic with considerable mesophase length and a middle-ordered melting type. The liquid crystal properties of the present series are compared with structurally similar homologous series.

Keywords Liquid crystal; smectic; nematic; mesomorphic; thermotropic

Introduction

The unique properties of the liquid crystalline state of a substance is exploited in varying fields of application in present era. Therefore, it is interesting to study the relationship between molecular structure and the liquid crystal state of a substance through homologous series, whose molecular rigidity and flexibility [1–3] dictate the formation of mesomorphism. Liquid crystal phases are formed as a consequence of suitable magnitudes of anisotropic intermolecular forces of attraction [4], and as a consequence of favorable molecular rigidity and/or flexibility. The novel series under investigation has a molecular structure based on three phenyl rings linked through $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ central

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linking groups, two terminal end groups of $-OR$ and $-Cl$, hence the structures are linear with no lateral substituents.

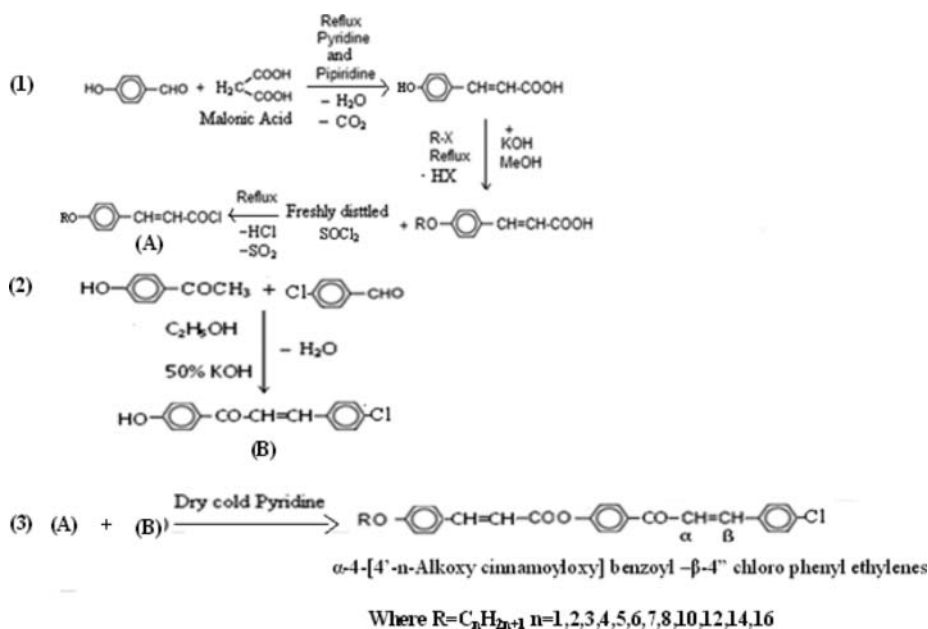
Experimental

Synthesis

4-Hydroxy benzaldehyde was treated with malonic acid in pyridine to prepare 4-hydroxy cinnamic acid. 4-Hydroxy cinnamic acid was alkylated by suitable alkylating agents $[R-X]$ and then, the corresponding *cis* *n*-alkoxy cinnamic acids were converted to their acid chlorides $[A]$ using freshly distilled thionyl chloride by modified method of Dave and Vora [5]. The second reacting component $[B]$, i.e., α -4-hydroxy benzoyl $-\beta$ -4'-chloro phenyl ethylene was prepared by the combination of 4-hydroxy acetophenone with 4-chloro benzaldehyde by an established method [6]. Components $[A]$ and $[B]$ were condensed in dry cold pyridine [7]. The Final products of series were individually filtered, washed, dried, and purified until they gave constant transition temperatures. The chemicals required for synthesis, viz., 4-hydroxy benzaldehyde, pyridine, malonic acid, alkyl halides, 4-hydroxy acetophenone, 4-chloro benzaldehyde, MeOH, EtOH, KOH, were used as received except solvents which were dried and purified before use. The synthetic route to the series is illustrated below in Scheme 1.

Characterization

Some of the selected homologs of the novel series were characterized for the determination of molecular structures by elemental analysis, infra red [IR] and 1H NMR (Nuclear Magnetic Resonance) techniques. Microanalysis was performed using a Perkin Elmer PE 2400



Scheme 1. Synthetic route to the novel series.

CHN analyzer. IR spectra were recorded on a Perkin-Elmer spectrum GX, and ^1H NMR spectra were recorded on a Bruker instrument using CDCl_3 as a solvent. The mesogenic properties and transition temperatures of the series were investigated using an optical polarizing microscope equipped with heating stage. The textures of the smectic and nematic mesophases were determined by miscibility methods.

Analytical Data

Spectral Data

NMR in ppm for Pentyloxy Derivative. 0.88 ($-\text{CH}_3$ of $-\text{OC}_5\text{H}_{11}$ group), 1.20 ($-\text{CH}_2-$) $_n$ polymethylene group of $-\text{OC}_5\text{H}_{11}$, 4.02 (triplet) ($-\text{OCH}_2-\text{CH}_2-$ of $-\text{OC}_5\text{H}_{11}$), 3.954 ($-\text{Cl}$ group), 7.77 ($-\text{CO}-\text{CH}=\text{CH}-$ group), 6.87 to 8.08 (p-substituted phenyl ring). The NMR data are consistent with the molecular structure.

NMR in ppm for Dodecyloxy Derivative. 0.87 ($-\text{CH}_3$ of $-\text{OC}_{12}\text{H}_{25}$ group), 1.26 ($-\text{CH}_2-$) $_n$ polymethylene group of $-\text{OC}_{12}\text{H}_{25}$, 4.01 (triplet) ($-\text{OCH}_2-\text{CH}_2-$ of $-\text{OC}_{12}\text{H}_{25}$), 4.41 ($-\text{Cl}$ group), 7.88 ($-\text{CO}-\text{CH}=\text{CH}-$ group), 6.90 to 8.13 (p-substituted phenyl ring). The NMR data are consistent with the molecular structure.

NMR in ppm for Tetradecyloxy Derivative. 0.87 ($-\text{CH}_3$ of $-\text{OC}_{14}\text{H}_{29}$ group), 1.25 ($-\text{CH}_2-$) $_n$ polymethylene group of $-\text{OC}_{14}\text{H}_{29}$, 4.01 (triplet) ($-\text{OCH}_2-\text{CH}_2-$ of $-\text{OC}_{14}\text{H}_{29}$), 4.29 ($-\text{Cl}$ group), 7.83 ($-\text{CO}-\text{CH}=\text{CH}-$ group), 6.81 to 8.13 (p-substituted phenyl ring). The NMR data are consistent with the molecular structure.

IR in cm^{-1} for Propoxy Derivative. 750 polymethylene ($-\text{CH}_2-$) $_n-$ group of $-\text{OC}_3\text{H}_7$, $-\text{Cl}$ group, 885 p-substituted phenyl ring, 1160 ($-\text{CO}-$ of $-\text{OC}_3\text{H}_7$ group), 1200, 1260 and 1600 ($-\text{COO}-$ ester group), 1000 ($-\text{CH}=\text{CH}-$ group). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Octyloxy Derivative. 770 (polymethylene ($-\text{CH}_2-$) $_n-$ group of $-\text{OC}_8\text{H}_{17}$), 640 $-\text{Cl}$ group, 845 (p-substituted phenyl ring), 1160 ($-\text{CO}-$ of $-\text{OC}_8\text{H}_{17}$ group), 1260 and 1605 ($-\text{COO}-$ ester group). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Dodecyloxy Derivative. 740 (polymethylene ($-\text{CH}_2-$) $_n-$ group of $-\text{OC}_{12}\text{H}_{25}$), 685 $-\text{Cl}$ group, 840 (p-substituted phenyl ring), 1160 ($-\text{CO}-$ of $-\text{OC}_{12}\text{H}_{25}$ group), 1210, 1260 & 1600 ($-\text{COO}-$ ester group). The NMR data are consistent with the molecular structure.

Results and Discussion

Cis 4-n-Alkoxy cinnamic acids and α -4-hydroxy benzoyl β -4' chloro phenyl ethylene [B] are nonmesomorphic. However, on condensing the two nonmesomorphic components through acid chlorides [A], the resultant homologous ethylene derivatives from pentyloxy to hexadecyloxy give rise to mesomorphic behaviour. The methyl to butyl homologs are nonmesomorphic. The octyloxy, decyloxy, and dodecyloxy homologs are enantiotropically smectogenic in addition to nematogenic in character and the rest of the homologs are enantiotropic nematic only (Table 1). The transition and melting temperatures of all the homologs were determined on an optical polarizing microscope equipped with a heating

Table 1. Elemental analysis for ethoxy, hexyloxy, and decyloxy derivatives

| No. | Molecular formula | Elements% found (% Calculated) | |
|-----|---|--------------------------------|-------------|
| | | C | H |
| 1 | C ₂₆ H ₂₁ O ₄ Cl | 72.00 (72.10) | 5.03 (4.86) |
| 2 | C ₃₀ H ₂₉ O ₄ Cl | 73.70 (73.52) | 5.84 (5.94) |
| 3 | C ₃₄ H ₃₇ O ₄ Cl | 74.38 (74.49) | 6.62 (6.80) |

stage, and are shown in Table 2. A plot of the transition temperatures versus number of carbon atoms present in n-alkoxy terminal chain shows the phase behavior of the series (Fig. 1). An odd-even effect is observed for a nematic-isotropic transition curve, but the effect is missing in the smectic-nematic transition curve. The smectic-nematic transition curve initially rises, passes through maxima and then descends as series is ascended up to the dodecyloxy homolog. The same curve is extrapolated [8] following the trend of the curve up to the tetradecyloxy homolog to predict a latent smectic-nematic transition temperature [LTT], which merges into the solid-nematic transition temperature 111.0°C. Thus, the smectic mesophase formation should occur at 111.0°C. However, practically it is a solid-nematic transition temperature, which suggests that the smectic mesophase ceases to form and only the nematic mesophase forms. The nematic-isotropic transition curve descends as the series is ascended and behaves in normal manner. The curves for the odd and the even homologs merge into one nematic-isotropic curve at the eleventh homolog. Thus, the odd-even effect diminishes as the series is ascended for higher homologs from and beyond eleventh homolog. The solid mesomorphic or isotropic curve follows a zigzag path of rising and falling values as the series is ascended with an overall falling tendency. Thus, all the three transition curves behave in normal manner. The texture of the nematic

Table 2. Transition temperatures of series in °C

| Compound no. | n-alkyl group —C _n H _{2n+1} (n) | Transition temperatures in °C | | |
|--------------|---|-------------------------------|-------|-----------|
| | | Sm | Nm | Isotropic |
| 1 | 1 | — | — | 215.0 |
| 2 | 2 | — | — | 182.0 |
| 3 | 3 | — | — | 180.0 |
| 4 | 4 | — | — | 185.0 |
| 5 | 5 | — | 143.0 | 178.0 |
| 6 | 6 | — | 115.0 | 185.0 |
| 7 | 7 | — | 123.0 | 155.0 |
| 8 | 8 | 108.0 | 134.0 | 182.0 |
| 9 | 10 | 105.0 | 138.0 | 151.0 |
| 10 | 12 | 98.0 | 128.0 | 144.0 |
| 11 | 14 | — | 111.0 | 132.0 |
| 12 | 16 | — | 119.0 | 125.0 |

Sm—smectic; Nm—nematic.

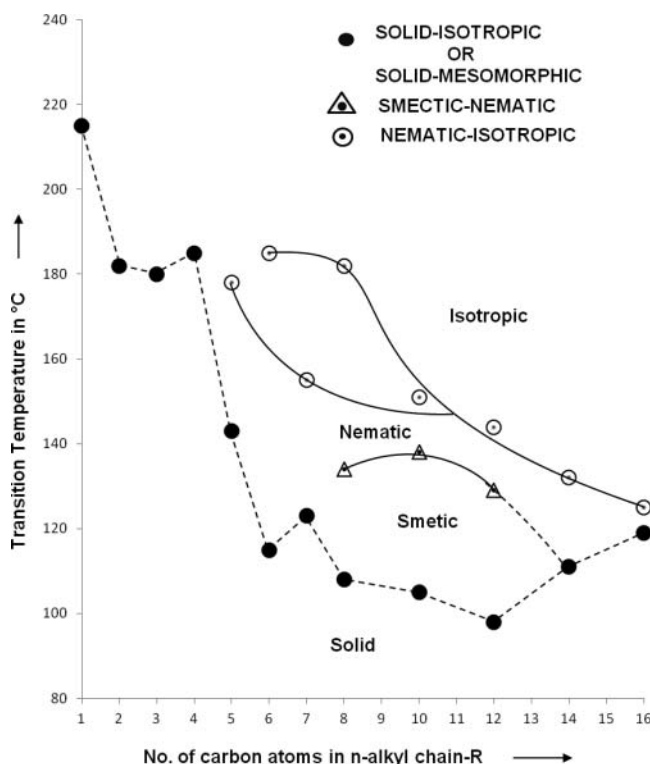


Figure 1. Phase behavior of the series.

mesophase is threaded or Schlieren and that of a smectic mesophase is of the typical A or C type. The smectic mesophase varies from a minimum of 26°C at the octyloxy homolog to a maximum of 33°C at the decyloxy homolog. The nematic mesophase length varies from a minimum of 6°C at the hexadecyloxy homolog and maximum of 70°C at the hexyloxy homolog. The present series is predominantly nematogenic and partly smectogenic with a middle-ordered melting type. The smectic and nematic mesophases commence from the octyl and pentyl homolog derivatives, respectively.

The pentyl to hexadecyl homologs are mesomorphic due to their suitable magnitudes of rigidity and flexibility. The octyloxy, decyloxy, and dodecyloxy homologs generate a lamellar packing of the molecules at a transition temperature t_1 , and then adopt a statistically parallel orientational order from and beyond a higher temperature t_2 . However, on further continued heating of the sample, the molecules randomly orient in all possible directions without any molecular ordering at a higher temperature t_3 . Thus, the samples under microscopic examination exhibit and show a smectic mesophase between t_1 and t_2 , and then a nematic mesophase between t_2 and t_3 , and an isotropic liquid beyond temperature t_3 . Mesomorphic molecules of homologs other than octyloxy to dodecyloxy exhibit only nematogenic mesomorphism. The methyl to butyl homologs of the series are unable to withstand exposed thermal vibrations due to the unsuitable magnitudes of anisotropic intermolecular forces of attraction as a consequence of unfavorable molecular rigidity and flexibility [1–4]. The odd-even effect diminishes for higher homologs, because longer n-alkyl chain from and beyond dodecyloxy homolog may coil, bend, flex or couple to lie

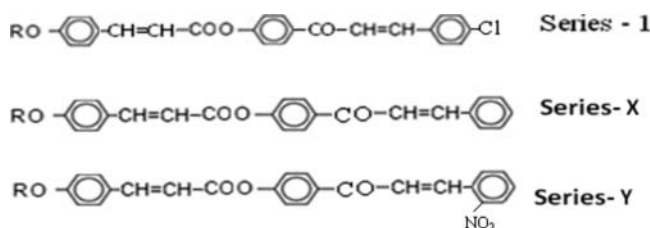


Figure 2. Structurally similar series.

with the major axis of the core [4, 9]. The degree of mesomorphism exhibited by the series is sufficiently high, because the series under discussion has sufficient lateral and terminal end-to-end attractions by the linear shape with two central groups bearing a conjugating double bond which strengthens rigidity of a molecule. The variation in mesomorphic property from homolog to homolog is attributed to the sequentially added methylene unit of the n-alkoxy terminal chain. The variation in mesomorphic properties is compared with other structurally similar homologous series X [10] and Y [11], as shown in Fig. 2.

Figure 2 shows the structurally similar series 1, X, and Y are identical in respect of three phenyl rings bridged through to central groups $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ with a common left terminal end group $-\text{OR}$. However, the uncommon part is a right-handed terminal end groups para $-\text{Cl}$, $-\text{H}$, and ortho $-\text{NO}_2$. Therefore, the molecular aromaticity and rigidity remains identical, but the molecular flexibility varies due to polarity and induced polarizability of laterally and terminally substituted group only on third phenyl ring, viz., $-\text{NO}_2$ and $-\text{Cl}$, $-\text{H}$. Thus, suitable magnitudes of anisotropic forces or intermolecular adhesion as a consequence of varying molecular flexibility differ accordingly. Thus, mesomorphic properties and the degree of mesomorphism vary with changing of the terminal end groups of series 1, X, and Y, respectively. Thermal stability of each series and commencement of mesophase are given in Table 3.

Table 3 indicates that present series-1 is smectogenic in addition to nematogenic character, while series X and Y chosen for comparison are nematogenic only without exhibition of any smectogenic character. The absence of smectogenic character in series X and Y chosen for comparison indicates the absence of lamellar packing of molecules in their crystal lattices. The commencement of smectogenic property takes place from the octyl homolog of series 1, but it does not commence until the last homolog of the series X and Y. This variation may be attributed to the extent of noncoplanarity [9] caused by the

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

| Series | Average transition temperatures in $^{\circ}\text{C}$ | | |
|--------------------------------------|---|---|---|
| | Series (1) | Series (X) | Series (Y) |
| Smectic-nematic or smectic-isotropic | 132.6 (C_8-C_{12}) | — | — |
| Commencement of smectic mesophase | C_8 | | |
| Nematic-isotropic | 156.7 (C_5-C_{16}) | 155.4 (C_5-C_{16}) | 171.5 (C_5-C_{16}) |
| Commencement of nematic mesophase | C_5 | C_5 | C_5 |

molecules concerned. The $-\text{Cl}$ terminal end group is more polar and monoatomic, which reduces the extent of molecular noncoplanarity than the differing end group $-\text{H}$ or lateral group $-\text{NO}_2$. Thus, suitable and favorable extent of molecular noncoplanarity facilitates lamellar packing of the molecules from the octyloxy to dodecyloxy homologs of series 1 but it does not facilitate for any homolog of series X and Y. The nematic mesophase formation commences identically from the pentyl homolog of all the series 1, X, and Y under comparison. This indicates that suitable magnitudes of anisotropic intermolecular forces of attraction, as emerging from molecular rigidity and flexibility, operate equally on end to end attractions, though the thermal stability of series Y is higher among those under comparison. Suitable magnitudes of anisotropic intermolecular forces of attraction facilitate a statistically parallel orientational order of the molecules which commences from the fifth homolog of series 1, X, and Y to generate the nematic mesophase. Thus the variation of mesomorphic properties for the same homolog from series to series is attributed to the unchanging terminal and/or lateral end group of each individual homologous series. The group efficiency order derived on the basis of (a) thermal stability and (b) early commencement of the mesophase is mentioned below in the conclusion.

Conclusions

- (a) Smectic group efficiency order: $-\text{Cl} > -\text{H}$ and $-\text{NO}_2$ [ortho]
- (b) Nematic group efficiency order: $-\text{NO}_2$ [ortho] $> -\text{Cl} > -\text{H}$

Smectic group efficiency order: $-\text{Cl} > -\text{H}$ and $-\text{NO}_2$ [ortho]

- 1. Nematic group efficiency order: $-\text{Cl} = -\text{H} = -\text{NO}_2$ [ortho]
- 2. Variations of mesomorphic properties from homolog to homolog in the same series depends upon the sequentially added methylene unit.
- 3. The novel series is predominantly nematogenic and partly smectogenic with middle ordered melting type.
- 4. Molecular rigidity and/or flexibility dictate the mesomorphic behavior of a substance.
- 5. Molecular structures that generate suitable magnitudes of anisotropic intermolecular forces of attraction as a consequence of molecular rigidity and flexibility generate mesomorphic properties in a substance.

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