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Synthesis and Liquid Crystal Properties of Novel Ethylene Derivatives: α-3-[-4′-n-Alkoxy Cinnamoyloxy] phenyl β-4′′-methoxy Benzoyl Ethylenes

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Eleven members of a novel homologous series of α-3-[-4′-n-alkoxy cinnamoyloxy] phenyl β-4′′-methoxy benzoyl ethylenes were synthesized. The methyloxy, ethyloxy, butyloxy, and hexadecyloxy homologues are nonmesomorphic, while all the other homologues are mesomorphic. The mesomorphic homologues are enantiotropically smectogenic in combination with nematogenic character, except for the propyloxy homologue, which shows only nematogenic character. A phase diagram of the series shows the expected mesomorphic behavior. Transition temperatures of this series are observed through an optical polarizing microscope equipped with a heating stage. An odd–even effect is observed for nematic–isotropic transition curve. Analytical data supports the structures of the molecules. Mesomorphic temperature range varies from 23°C to 51°C. Liquid crystal properties of this series are compared with a structurally similar homologous series. The smectic and nematic thermal stability of the series are 138.8°C and 165.7°C, respectively. The nematic phase shows a threaded or schlieren texture, and the smectic phase is a smectic A phase.

Keywords Liquid crystal; mesophase; monotropy; nematic; smectic

Introduction

Suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of molecular rigidity and flexibility can favorably induce a physically distinct state of a substance between the crystalline solid and the isotropic liquid states, called the liquid crystal state. Many homologous series with varying molecular rigidity and flexibility have been reported [1–3]. Normally structures consist of two or more rings (aromatic, alicyclic, or heterocyclic) and central linking groups comprise the rigidity and lateral or/and terminal groups act as the flexible part of the molecule. The present series involves three phenyl rings bridged through a cinnamoyoxy group (–CH=CH–COO–) and a cinnamoyl group (–CH=CH–CO–) to give the rigid section, and terminal n-alkoxy (–OR) groups as the

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Table 1. Elemental analysis for ethoxy, butyloxy, and hexadecyloxy derivatives

		Elements % found (compared with% calculated)	
	Molecular formula	C	H
1	$C_{27}H_{24}O_5$	75.70 (75.67)	5.61 (5.59)
2	$C_{29}H_{28}O_5$	76.32 (76.34)	6.14 (6.17)
3	$C_{41}H_{52}O_5$	78.85 (78.86)	8.33 (8.35)

flexible parts of the molecule. The resultant magnitudes of molecular rigidity and flexibility induce the liquid crystal in seven homologues of the eleven investigated.

Experimental

Characterization

The materials were characterized for the molecular structure by IR (infra red) and ^{1}H NMR (proton nuclear magnetic resonance) techniques. Microanalysis was performed using a Perkin Elmer PE 2400 CHN analyzer. IR spectra were recorded on a Perkin-Elmer spectrum GX, and ^{1}H 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.

Synthesis

4-Methoxyacetophenone, 3-hydroxybenzaldehyde, ethanol, potassium hydroxide, pyridine, thionyl chloride, malonic acid, piperidine, and n-alkyl halides were used as received. Thionyl chloride was freshly distilled. 4-n-Alkoxycinnamic acids and 4-n-alkoxycinnamoyl chlorides (A) were synthesized by the modified method of Dave and Vora [4]. α-3-Hydroxy phenyl β-4′-methoxy benzoyl ethylene (B) was prepared by the known method [4,5]. α-3-[4′-n-alkoxy cinnamoyloxy] phenyl β-4′-methoxy benzoyl ethylenes were synthesized by condensing 4-n-alkoxy cinnamoyl chloride (A) with α-3-hydroxy phenyl β-4′-methoxy benzoyl ethylene (B) in dry cold pyridine [6]. Final products of the series were decomposed, filtered, washed, dried, and crystallized from alcohol until constant transition temperatures were obtained. Analytical data were found satisfactory as shown in Table 1. The synthetic route to the series is outlined as shown in Scheme 1.

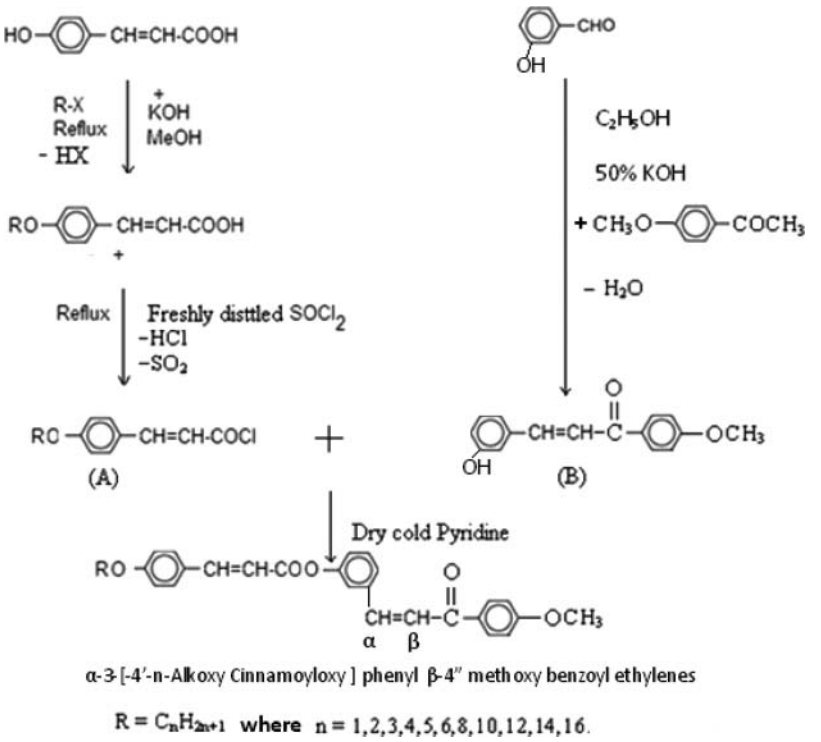
Analytical Data for Series 1

Analytical data for series 1 is given in Table 1.

Spectral Data for Series 1

NMR in PPM (parts per million) for the hexyloxy derivative: 0.868 (–CH_3 of –OC_6H_{13}), 1.245 (–CH_2– of –OC_6H_{13}), 4.07 (triplet) (–OCH_2–CH_2 of –OC_6H_{13}), 6.98 (broad) –CH=CH, 7.15 and 7.27 (–CH=CH–CO–), 6.9–8.6 (phenyl ring) NMR confirms the structure.

NMR in PPM for the octyloxy derivative: 0.88 (–CH_3 of –OC_8H_{17}), 1.308 and 1.77 (triplet) (–CH_2– of –OC_8H_{17}), 4.02 (triplet) (–OCH_2–CH_2) of –OC_8H_{17}), 7.00 (broad) −CH=CH, 6.9–8.6 (phenyl ring) NMR confirms the structure.



Scheme 1. Synthetic route to the series.

IR in cm^{-1} for pentyloxy derivative: 700 (polymethylene of $-OC_5H_{11}$), 840 (phenyl ring), 940 (–CH=CH–), 1170 of $-OC_5H_{11}$, 1250, 1600, and 1680 , (–COO group), 650 and 770 (phenyl ring), IR supports the structure.

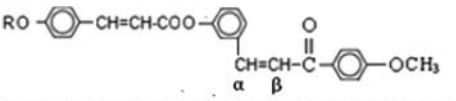
IR in cm^{-1} for dodecyloxy derivative: 680 polymethylene of $OC_{12}H_{25}$, 720 and 770 (phenyl ring), 840 (phenyl ring). 1160 (C–O of $-OC_{12}H_{25}$), 1220, 1260, and 1605 (–COO group), IR supports the structure.

Miscibility Method

Derivative	Texture
• Propyloxy derivative	Nematic threaded type
• Octyloxy derivative	Nematic schlieren type
• Pentyloxy derivative	Smectic A type
• Decyloxy derivative	Smectic A type

Results and Discussion

4-n-Alkoxycinnamic acids and the corresponding acid chlorides and α-3-hydroxy phenyl β-4′-methoxy benzoyl ethylene are all nonmesomorphic. However, on condensing, both of them can turn to liquid crystalline materials, and in this study, seven members of the titled series of eleven members thus found to have liquid crystalline characteristic. The propyloxy



α-3-[-4′-n-Alkoxy Cinnamoyloxy] phenyl β-4″ methoxy benzoyl ethylenes

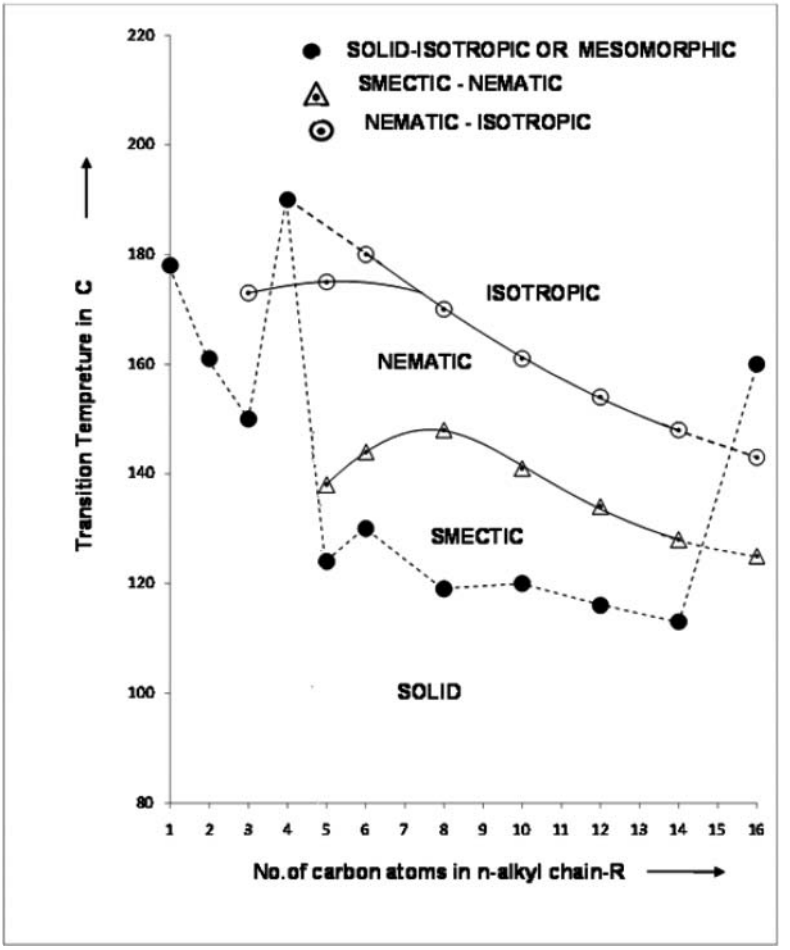


Figure 1. Phase behavior of the series.

homologue exhibits only nematogenic character, while the pentyloxy to tetradecyloxy homologues exhibit enantiotropic nematogenic character in addition to smectogenic character. The methyloxy, ethyloxy, butyloxy, and hexadecyloxy homologues are nonmesomorphic. A phase diagram (see Fig. 1) is plotted for the transition temperature of homologues as recorded in Table 2 versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group. A solid mesomorphic transition curve follows a zigzag path of rising and falling values, as the series is ascended with an overall falling tendency, except for the hexadecyloxy homologue. The smectic–nematic transition curve initially rises, passes through maxima, and smoothly adopts a descending tendency as the series is ascended and behaves in an expected manner, without showing an odd–even effect. The nematic–isotropic transition curve adopts a descending tendency as the series is ascended with an odd–even effect and behaves in the usual expected manner. The nematic–isotropic

Table 2. Transition temperatures of the series in °C

Compound no.	n-alkyl group, C_nH_{2n+1} (n)	Transition temperatures in °C		
		Sm	N	Isotropic
1	1	–	–	178.0
2	2	–	–	161.0
3	3	–	150.0	173.0
4	4	–	–	190.0
5	5	124.0	138.0	175.0
6	6	130.0	144.0	180.0
7	8	119.0	148.0	170.0
8	10	120.0	141.0	161.0
9	12	116.0	134.0	154.0
10	14	113.0	128.0	148.0
11	16	–	–	160.0

Note: Sm: Smectic; N: Nematic.

transition curve is extrapolated to the solid-isotropic transition temperature of the nonmesomorphic butyloxy homologue, following the trends of the nematic–isotropic transition curve, and clearly coincides with the nematic–isotropic transition temperature.

Thus the predicted latent transition temperature (LTT) for the nematic–isotropic transition for the butyloxy homologue is 190°C, but the melting point is 190°C, so no mesophase exists. Similarly, the nematic–isotropic and smectic–nematic transition curves are extrapolated for the nonmesomorphic hexadecyloxy homologue following the trend of the respective curves. This suggests that the probable predicted LTT for nematic and smectic phases should be 142°C and 125°C, respectively. Mesophase temperature ranges vary between a minimum of 23°C and a maximum 51°C. The odd–even effect diminishes from the heptyloxy homologue by merging both curves because the longer n-alkyl chain may coil or couple to lie in the line with the major axis of core and bend in such a manner that end-to-end contact would then be the same for odd and even homologues. Thus, higher homologues do not show an odd–even effect. The nonmesomorphic behavior of the methoxy, ethoxy, butyloxy, and hexadecyloxy homologues is due to their high crystallizing tendency arising from unsuitable magnitudes of anisotropic intermolecular forces of attractions related to molecular rigidity and flexibility [1–3]. Thus molecules of nonmesomorphic homologues are unable to resist thermal vibrations exposed upon them and melt sharply at their melting point from the crystalline state to the isotropic liquid state without passing through an intermediate liquid crystal or mesogenic state. The exhibition of a mesomorphic state by the seven homologues of the series either smectic and/or nematic is attributed to their molecular disalignment at an angle less than 90°C with the plane of the surface under the influence of exposed heat energy to a thermodynamic system (homologue) from surroundings. The molecules showing smectic or/and nematic mesophase or mesophases are capable of resisting exposed thermal vibrations and arrange themselves either (i) statistically parallel or/and (ii) in a sliding layered molecular order due to lamellar packing in their crystal lattices, as a consequence of molecular rigidity and flexibility [1–3], which causes suitable magnitudes of intermolecular anisotropic forces of attractions. An odd–even effect observed for the

Table 3. Average thermal stabilities in °C

	Average transition temperatures in °C	
Series	Series 1	Series Y
Smectic–nematic or isotropic	138.8 (C_5–C_{14})	—
Commencement of smectic phase	C_5	
Nematic–isotropic	165.7 (C_3–C_{14})	144.5 (C_6–C_{16})
Commencement of nematic mesophase	C_3	C_6

nematic–isotropic transition curve and the variation in mesogenic character from homologue to homologue in the same series are attributed to the sequentially and progressively added methylene unit [7]. Thermal stabilities (see Table 3) and other liquid crystal properties of the present series 1 are compared with another structurally similar homologous series Y [5] as shown in Fig. 2.

Homologous series 1 and series Y are structurally similar with respect to three phenyl rings bridged through –CH=CH–COO– and –CH=CH–CO– central linking groups as the rigid section and the n-alkoxy end group as a common flexible part of the molecules. Therefore both series 1 and series Y are identical with respect to molecular rigidity, aromaticity, size, etc., but they differ in the flexible end groups $–OCH_3$ and –H, length-to-breadth ratio, molecular polarity and polarizability due to the $–OCH_3$ end group [7], end-to-end attractions, intermolecular distance, molecular planarity or extent of noncoplanarity, etc. Therefore observed variations in mesomorphic properties and thermal stabilities of mesophases are attributed to the structural differences mentioned above causing difference in the intermolecular forces of attractions between series 1 and series Y. Average thermal stability for smectic and nematic mesophases and commencement of mesophases are mentioned in Table 3.

From Table 3, it is clear that the average thermal stability for the smectic and nematic mesophases of series 1 is relatively higher than those of series Y. The higher values of thermal stabilities for series 1 suggest that heat content or enthalpy (ΔH) values of homologues of series 1 are relatively more than series Y. As temperature is raised for the homologue under observation, the quantum of heat required for the transition corresponds to the quantum of energy stored (ΔH value) by a molecule to stabilize at room temperature. Initially heat supplied to the system (homologue) with lamellar packing gives rise to the sliding layered arrangement of molecule under floating conditions at the solid-smectic

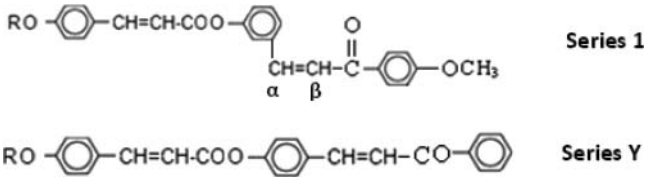


Figure 2. Structurally similar series.

temperature and then converted to maintain a statistically parallel orientational order of the molecules under floating conditions relatively at higher temperature to cause smectic and/or nematic mesophases, respectively. The difference of two temperatures for any mesophase is called a mesophase length and the ratio of enthalpy value to the corresponding temperature, that is, $\Delta H/T$ is called entropy (ΔS) value of a sample at a given temperature. The molecular width of series 1 is more than series Y. Hence molecular polarizability and molecular polarity [7] due to molecular breadth including the presence of the highly polar $-OCH_3$ end group is relatively more than –H, which raises intermolecular attractions for series 1 and results in higher values of thermal stability and phase length as compared with series Y. Early or late commencement of a smectic mesophase is related to the extent of noncoplanarity caused by a molecule [6,8]. Molecules of series 1 are less coplaner than the molecules of series Y, which results in early commencement of the smectic and nematic mesophases. The difference of mesomorphic properties for the same homologue from series to series is attributed to the varying end groups of fixed polarity (i.e., the polarity order is $-OCH_3 > -H$).

Conclusions

1 The group efficiency order derived on the basis of thermal stability for the smectic and nematic mesophases are $-OCH_3 > -H$.
2 The molecular flexibility and rigidity are important parameters to cause mesophase formation and mesophase length.
3 The results of the presently investigated series support the conclusions drawn and enhance the understanding of structure–property relationships in liquid crystals.

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