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Dependence of Molecular Structure on Mesomorphic Behavior with Special Reference to Central Bridge

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A novel homologous series of liquid crystalline 4-(4'-n-alkoxy cinnamoyloxy)-4"methoxy benzyl cinnamates was synthesized and studied with a view to understand and establish the effects of molecular structure on liquid crystal behavior. The series consists of eleven members of the series. None of the homologue derivatives are either nonliquid crystal or smectogenic, i.e. all the eleven members of the novel homologous series are enantiotropcially nematogenic only. Transition and melting temperatures as well as textures of the nematic mesophase were determined on an optical polarizing microscope equipped with a heating stage. The transition curves of the phase diagram show phase behavior in a normal expected manner. An odd-even effect is observed for the nematic-isotropic transition curve. The textures of the nematic mesophase are threaded or Schlieren as determined a by miscibility method. Analytical and spectral data confirm the molecular structures of the homologues. The average thermal stability for nematic is 213.8°C. The isotropic temperatures vary between 190°C and 240°C. The nematogenic mesophase length varies from 17°C to 102°C. Thus, the novel homologous series is entirely nematogenic without the exhibition of smectogenic character. The liquid crystal (LC) properties of the present novel series are compared with structurally similar other known homologous series.

Keywords Enantiotropy; liquid crystal; nematic; smectic; thermotropic

Introduction

Thermotropic liquid crystals show their an intermediate state of existence between crystalline solid state and isotropic liquid state between two temperatures and are essentially free from solvent [1, 2] have more scientific, biological and pharmaceutical, technological and industrial importance [3–5]. Kazuki Iwahata et al. [6] studied applications of biomaterials to chemically synthesized thermotropic liquid crystals. Such study covers the improvement of the performance of liquid crystal displays using LC physical gels consisting of a liquid crystal admixed with amino acid based gelator and some other functionalization like electro optical measurements, electronic device industry and refining of industrial products. The

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derivatives of benzoic acids and cinnamic acids are biologically active molecules giving rise to exhibit liquid crystal property and are useful to the pharmaceutical, medicinal, electronic etc fields of applications which require LC materials workable at desired temperatures [7,8]. The LC materials workable at low or desired temperature requires imagination of constructing a molecule of conventional or unconventional LC substances with proper central, terminal and lateral groups substituted at appropriate position or positions of phenyl rings [9, 10]. Proposed investigation is planned with a view to construct a molecules consisting of three phenyl rings bonded through -CH=CH-COO- and -CH=CH-COO-CH₂central bridges, $-OC_nH2_{n+1}$ and $-OCH_3$ terminal end groups without any lateral substitution as long linear molecule. Present study will include only construction of novel LC molecules, their synthesis, their characterization by elemental analysis IR, ¹HNMR, mass spectra, microscopic examination texture determination and comparative study of LC properties with structurally similar known substances. Thus, the present proposed investigation is aimed with a view to understand and establish the effects of molecular structure [11, 12] on liquid crystal behavior dependence on central group as a consequence of molecular rigidity and flexibility [13-17].

Experimental

Synthesis

4-Hydroxy cinnamic acid was converted to 4-n-alkoxy cinnamic acids using suitable alkylating (R-X) agents by modified method of Dave and Vora [18]. 4-Hydroxy cinnamic acid was converted to 4-hydroxy-4"-methoxy benzyl cinnamate by the modified method of European patent EP0117502B1 [19]. 4-n-alkoxy cinnamic acids were individually condensed with 4-hydroxy-4"-methoxy benzyl cinnamate (m.p. 204°C, yield is 35%) in pyridine through their acid chlorides in dry cold pyridine [20–22]. Final products were individually decomposed, filtered, washed dried and purified in ethanol till constant transition temperatures obtained. Transition and melting temperatures were determined by an optical hot stage polarizing microscopy.

The chemicals 4-hydroxy cinnamic acid, 4-methoxy benzyl alcohol, dibutyltin oxide, pyridine, alkyl halides, MeOH, EtOH, thionyl chloride, HCl, KOH etc. were used as received, except solvents, which were dried and distilled prior to use. The synthetic route to the series is shown in Scheme 1.

Characterization

Some selected members of a present novel series were characterized by elemental analysis, Infra red spectra, ¹HNMR spectra and mass spectra. Micro analysis was performed by Perkin-Elmer PE 2400 CHN analyser, ¹HNMR spectra were recorded on a Bruker spectrometer using DMSO solvent. Infra red spectra were recorded on a Perkin Elmer spectrum GX spectrometer. Transition temperatures and the textures of nematic mesophases are determined by amiscibility method, which was characterized by an optical polarizing microscope equipped with a heating stage. Thermodynamic quantity enthalpy change (Δ H) and entropy change (Δ S = Δ H/T) are qualitatively discussed instead of DSC scane.

Analytical Data

Spectral Data. ¹HNMR in ppm for the Decyloxy Derivative: 0.84-1.68 (H of $C_{10}H_{21}$), 2.52 ($-O-CH_2-CH_2$ of $-OC_{10}H_{21}$), 3.76 ($-OCH_3$), 5.06 (-CH=CH-), 6.51 (p-substituted benzene ring), 6.9–7.7 (indicates presence of more than one benzene).

Sr. no.	Molecular formula	Elements % found (% calculated)		
		С	Н	
1	$C_{27}H_{24}O_{6}$	72.74 (72.97)	5.28 (5.40)	
2	$C_{28}H_{26}O_{6}$	73.10 (73.36)	5.47 (5.67)	
3	$C_{29}H_{28}O_6$	73.58 (73.72)	5.68 (5.93)	

Table 1. Elemental analysis for methyloxy, ethyloxy, and propyloxy derivatives

¹HNMR in ppm for the Dodecyloxy Derivative: 0.84-1.69 (H of C₁₂H₂₅), 3.77 ($-OCH_3$), 2.53 ($-OCH_2$ of $-OC_{12}H_{25}$), 5.07 (-CH=CH-), 6.31 (p-substituted benzene ring), 6.9-8 (presence of more than one benzene rings).

IR in cm⁻¹ for tetradecyloxy Derivative: 830 para-substituted phenyl ring, 1218 ether linkage of $(-C_{14}H_{29}-O-C_{6}H_{4})$, 1171, 1286, 1679 (-COO-ester group), 982 (trans -CH=CH-)

IR in cm⁻¹ for Hexadecyloxy Derivative: 830 para-substituted phenyl ring, 1217 ether linkage of $(-C_{16}H_{33}-O-C_{6}H_{4})$, 1171, 1286, 1680 (-COO-ester group), 982 (trans -CH=CH-)



Where $R = C_n H_{2n+1}$; n = 1,2,3,4,5,6,8,10,12,14,16

Scheme 1. Synthetic route to the series. Series: 4-[4'-*n*-alkoxy cinnamoyloxy]-4''-methoxy benzyl cinnamates.

Mass Spectra. Mass spectra for butyloxy derivative:

Molecular formula $C_{30}H_{30}O_6$ Calculated Molecular weight 486. Practical mass observed by Mass spectroscopy 486.

Texture of Nematic by Miscibility Method

Results and Discussion

Cis-4-n-alkoxy cinnamic acid and 4-hydroxy-4"-methoxy benzyl cinnamate (m.p. 204°C) are nonliquid crystal (NLC) components. But the liquid crystal property is induced from the first to the last member of the novel series as an enantiotropic nematic phase without exhibition of any smectogenic mesophase. The homologous series consists of eleven members (C_1 to C_6 , C_8 , C_{10} , C_{12} , C_{14} , and C_{16}), which are all liquid crystals of considerable nematogenic phase length. Transition temperatures (Table 2) of the homologues were plotted for the number of carbon atoms present in n-alkyl chain of the left terminal end group bonded to the phenyl ring through oxygen atom. The solid-nematic and nematic-isotropic transition curves drawn by linking like or related points constitute a phase diagram (Fig. 1) showing the phase behavior of the presently investigated novel series of cinnamate diesters of unchanged methoxy group as the right handed terminal end group. An odd-even effect for nematic-isotropic transition curve and alternation of transition temperatures is observed for the novel series. The solid-nematic transition curve follows a zigzag path of rising and falling values and behaves in the usual established manner. The nematic-isotropic transition curve continuously descends as series is ascended with an overall falling tendency from the first (methoxy) to the last (hexadecyloxy) homologue with the exhibition of an odd-even effect. The nematic-isotropic curves for odd and even homologues merge into each other

	n-alkyl group	Transition temperature in $^{\circ}C$		
Compound no.	$(-\mathbf{C}_{n}\mathbf{H}_{2n+1})(n)$	Sm	Nm	Isotropic
1	1		155.0	240.0
2	2		160.0	238.0
3	3		119.0	221.0
4	4		153.0	227.0
5	5		173.0	214.0
6	6		127.0	219.0
7	8		161.0	210.0
8	10		167.0	203.0
9	12	_	150.0	198.0
10	14		152.0	192.0
11	16		173.0	190.0

Table 2. Transition temperatures of series in °C

Sm: Smectic; Nm: Nematic.



Figure 1. Phase behavior of series.

at the nonyloxy homologue and then they adopt a single curve for higher homologues. Liquid crystal behavior varies from homologue to homologue in the present series of ester derivatives. The entire novel series is nematogenic and a high melting type. The mesomorphic phase length varies from a minimum of 17° C at the hexadecyloxy homologue to a maximum of 102° C at the propyloxy homologue. The nematogenic mesophase length alternates up to the hexy n-alkyl chain and then gradually diminishes up to the hexadecyl variation at the fifth and twelfth homologues respectively.

The introduction of mesomorphism to a molecule formed by linking two nonmesomorphic (NLC) components through acid chlorides of corresponding cis n-alkoxy cinnamic acids, which increases molecular length, polarity and polarizability, length to breadth ratio, dispersion forces including the presence of the highly polar methoxy end group and the conjugated double bonds. Such an environment raises the suitable magnitudes of anisotropic forces of end to end intermolecular attractions as a result of favourable molecular rigidity and flexibility for all the members of the present homologous series. The molecules of all the members of the series individually disalign at an angle less than ninety degree with the plane of a floating surface under the influence of externally exposed thermal vibrations. Molecules of all novel homologues individually on their microscopic examination travel in two dimensional ordered array with statistically parallel orientational order against exposed thermal energy or by resisting exposed thermal vibrations for definite range of temperature. termed the nematogenic mesophase length of the homologue. The absence of smectogenic character of all the homologues of a present series is attributed to the absence of lamellar packing of molecules in their crystal lattices due to the cis configuration of n-alkoxy cinnamic acids from which final products are synthesized. Thus the suitable magnitudes of anisotropic forces of intermolecular attractions are adequate to induce nematic mesophase but inadequate to induce smectic mesophase formation. The exhibition of odd-even effect for nematic-isotropic transition curve is attributed to the alternation of transition temperatures for odd-even homologues. The odd-even effect for nematic-isotropic transition curve diminished from and beyond the nonyloxy derivative of the present series because longer n-alkyl chains may coil, bend, flex or couple to lie with major axis of a core structure. High magnitudes of thermal resistivity by the molecular structure of homologues with absence of lamellar packing, led to nematogenic mesophase formation at high transition temperature and relatively high mesomorphic phaselength. "Cinnamoyloxy mesomorphic derivatives are generally nematogenic" [23]. This early statement is very well supported by present investigation. The liquid crystal behavior of the present novel series-1 is compared with structurally similar known series X [24] as shown in Fig. 2.

The novel homologous series-1 and a known series-X are identical in all respects except for the central bridge linking middle and third phenyl rings $-CH=CH-COO-CH_2$ and -CH=CH-CO- respectively. Thus molecular flexibility varies from homologue to homologue in the same series but it remains unchanged for the same homologue from series to series because of the common $-OCH_3$ terminal end group in both series under comparison. The molecular rigidity remains unchanged from homologue to homologue in the same series, but it varies for the same homologue from series to series due to changing length and polarity of the differing central groups. The combined effects of molecular rigidity and flexibility are operative to the mesophase formation as a consequence of favourable molecular rigidity and flexibility, which cause suitable or unsuitable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions depending upon intermolecular closeness for the same homologue from series to series under comparison. Thus, liquid crystal behavior and the degree of mesomorphism are dependent upon the differing features of two series under comparison. Table 3 shows the thermal stabilities of the mesophase, commencement of mesophase etc. for series 1 and X.



Figure 2. Structurally similar homologous series.

Series→	Series 1	Series X
Smectic-Nematic		
Or		
Smectic-isotropic		_
Commencement of		
Smectic phase		
Nematic-Isotropic	235.2	164.6
Commencement of	$(C_1 - C_{16})$	$(C_5 - C_{14})$
Nematic phase	C_1	C_5

Table 3. Average thermal stability in °C

Table 3 indicates the following.

- Homologous series 1 and X are nematogenic only without exhibition of any smectogenic character.
- The nematic thermal stability of series-1 is greater than a series-X under comparison by 70.6°C.
- Liquid crystal nematogenic mesophase commences from very first member of a series-1, while it commences from a fifth member of a series-X.
- Isotropic temperatures of series-1 are varied between 190°C and 240°C by hexadecyloxy and methoxy derivatives of LC homologues, while, the same are varied between 160°C and 170°C among LC homologues as well as it vary between 160°C LC and 205°C NLC homologue of series-X.
- Mesogenic temperatures are varied from 119°C to 173°C for series-1, while, it vary from 110°C to150°C.
- Nematogenic mesophase length vary from 17°C to 102°C in case of series-, while, it varied from 10°C to 58°C in case of series-X.

Thus, all above points of thermometric data indicate that, presently investigated homologous series-1 possess richer degree of mesomorphism and relatively higher values of thermometric data. Hence molecular rigidity induced by $-CH=CH-COO-CH_2$ - central group (series-1) is more than a central group -CH=CH-CO- (series-X) for the same homologue from series-1 to series-X. Hence, the molecules tend to pack more efficiently in case of series 1 with higher thermal stability. The central bridge $-CH=CH-COO-CH_2$ of series-1 and -CH=CH-CO- in case of series-X under comparison are closely similar to each other. Both these central bridges are comparable, though the vinyl carboxylate with methylene unit $-CH=CH-COO-CH_2-$ has relatively greater length and causes more non coplanarity due to the unequal twist obtained as the oxygen atoms of the vinyl carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic phenyl ring. On account of this difference the nematogenic thermal stabilities and thermometric data of series-1 are relatively greater than a series-X, under comparison.

Conclusions

• Homologous series 4-(4'-*n*-alkoxy cinnamoyloxy)-4"-methoxy benzyl cinnamates is entirely nematogenic without exhibition of smectogenic character with wide range of liquid crystallinity and high melting type.

- Mesomorphic properties varies from homologue to homologue in the same series and they vary from series to series for the same homologue due to only one differing feature (one of the central bridges) keeping the rest of the molecular parts unchanged.
- The group efficiency order derived on the basis of (i) thermal stability and (ii) the early commencement of mesophase for nematic are as under.
- (i) Nematic: $-CH=CH-COO-CH_2 > -CH=CH-CO-$ Smectic: $-CH=CH-COO-CH_2=CH=CH-CO = zero$
- (ii) Nematic: $-CH=CH-COO-CH_2 > -CH=CH-CO-$ Smectic: $-CH=CH-COO-CH_2 - =CH=CH-CO- = Zero$
- Molecular rigidity and flexibility are very sensitive and susceptible to mesophase formation, the degree of mesomorphism and the commencement of the smectic or/and nematic mesophase.
- Molecular rigidity and flexibility are susceptible to molecular structure only.
- Early statement that "Vinyl carboxy group is nematogenic" is very well supported by present investigation and raised the reliability and credibility to the conclusions drawn earlier.

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