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Mesomorphism dependence on terminal end groups

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ABSTRACT

A novel homologous series of liquid crystals (LC) 4-(4'-n-alkoxy cinnamoyloxy)-4"-bromobenzylbenzoate was synthesized and studied with a view to understanding and establishing the relation between LC properties and the molecular structure. The novel series comprises 11 members, and all the members exhibit mesomorphism as enantiotropic smectic. None of the homologues are nematogenic, even in the monotropic condition. Transition temperatures were determined by an optical polarizing microscope equipped with a heating stage. The textures of smectic phase are of the type A or C. The transition curves Sm-I and Cr-Sm behave in a normal manner in the phase diagram. An oddeven effect is exhibited by the Sm-I transition curve. Thermal stability for smectic is 102.6°C. Mesomorphism commences from the very first member of the series. The series is entirely smectogenic and of middle-order melting type whose mesomorphic phase length ranges from 7.4°C to 60.9°. Analytical and spectral data confirmed the molecular structures of homologues. The mesomorphic properties of the present series are compared with structurally similar homologous series.

KEYWORDS

Mesomorphism; enantiotropic; liquid crystals; nematic; smectic

Introduction

A common man is familiar with the word LCD in the present era, which is an abbreviation for liquid crystal display. Hence, the liquid crystalline state of matter has maintained its importance in the various fields of applications since its discovery in 1888 [1]. The scientific and technological communities are working extensively on liquid crystals (LCs) [2–12]. The present investigation is aimed to synthesize novel LC compounds through an homologous series of binary systems with a view to understanding and establishing the relationship between mesomorphism and molecular structure [13–15]. Therefore, the novel LC materials may be useful for researchers in branches of science and technology, other than chemistry, particularly applications. A large number of homologous series and binary or ternary systems have been reported [16–20]. The proposed investigation aims to synthesize a novel structure containing three phenyl rings bonded through two central bridges, viz. -CH=CH-COO- and -COO-, and two terminal end groups, viz. $-OC_nH_{2n+1}$ and -Br polar groups. The effect of central and terminal groups on LC properties with reference to molecular rigidity and flexibility [21–24] will be discussed in a comparative manner with structurally similar LC materials.

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Experimental

Synthesis

4-Hydroxy cinnamic acid was alkylated by suitable alkylating agent R-X to form n-alkoxy cinnamic acid by the modified method of Dave and Vora [25] as a main component of series. 4-Hydroxy-4'-bromobenzyl benzoate (m.p.: 115–122°C) was prepared from 4-bromobenzyl bromide and 4-hydroxy benzoic acid by applying the method of US patent No. 0053964 and European patent and the modified method of Doshi et al. [26]. n-Alkoxy cinnamic acids, through their corresponding acid chlorides, and 4-hydroxy-4'-bromobenzylbenzoate condensed in dry pyridine to form final products by an established method [27–29]. The final esterified products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained.

4-Hydroxy cinnamic acid, alkyl halides, methanol, KOH, 4-bromobenzyl bromide/alcohol, N,N-dimethyl formamide, NaHCO₃, HCl, dry pyridine, thionyl chloride, EtOH, etc. required for the synthesis were used as received, except solvents which were dried and purified prior to synthesis. Synthetic route to the series is mentioned below as Scheme 1.



R = CnH2n+1, where- n = 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16.

Scheme 1. Synthetic route to the series: 4-[4'-n-Alkoxy cinnamoyloxy]-4''-bromobenzyl benzoates.

		% Elements calculated (Experimental%)		
Sr. No.	Molecular formula	С	Н	Br
1.	C ₂₄ H ₁₉ BrO ₅	61.67 (59.88)	4.06 (4.28)	17.13(17.77)
2.	$C_{26}H_{23}BrO_{5}$	63.03 (64.22)	4.64 (4.60)	16.16 (16.00)
3.	$C_{27}H_{25}BrO_5$	63.65 (65.01)	4.91 (4.80)	15.71 (15.51)
4.	$C_{28}H_{27}BrO_{5}$	64.24 (64.55)	5.16 (5.20)	15.29 (14.89)

Table 1. Elemental ana	lysis for methoxy	, propyloxy, b	utyloxy, and p	pentyloxy derivatives.
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Characterization

The selected members of a novel homologues series were characterized and analyzed by elemental analysis and the structure elucidation by infra-red (IR) spectra, ¹H NMR spectra, and mass spectra. Textures and transition temperatures of homologues as well as related materials were determined by an optical polarizing microscope, equipped with a heating stage. Elemental analysis was performed on Perkin-Elmer PE 2400 CHN analyzer (Table 1). The percentage of halide content was determined by the usual analytical method. IR spectra were recorded on Perkin-Elmer spectrum GX. ¹H NMR spectra were determined on Bruker spectrometer using CDCl₃ solvent. Textures of smectic mesophase of some homologues were recognized either directly from the microscopic observations or by miscibility method.

Analytical data

Spectral data

¹*H* NMR in ppm for the octyloxy derivative: 1.19-1.23 (-CH₃ of C₈H₁₇), 3.86-3.92 (-CH₂- of -C₈H₁₇), 5.14-5.21 (-CH=CH-), 6.19-6.82 (p-substituted phenyl ring), 7.80-7.82 (p-substituted benzene).

¹*H* NMR in ppm for the dodecyloxy derivative: 0.81 (-CH₃ of $C_{12}H_{25}$), 1.17–1.22 (-CH₂- of $-C_{12}H_{25}$), 3.88–3.92 (-O-CH₂-), 5.16–5.21 (-CH=CH-), 6.20–6.24 (p-substituted phenyl ring), 6.76–6.83 (p-substituted benzene).

NMR data confirm the structure

IR in cm⁻¹ *for ethoxy derivative*: 753–770 polymethylene of C_2H_5 , 823 para-substituted phenyl ring, 1715, 1118, 1675.9 ester linkage of (COO- C_2H_5), 982 trans of (-CH=CH-) 1121 ether linkage of (C_2H_5 -O- of phenyl), 1010 aromatic -Br linkage 512, 630 (C-Br stretch).

IR in cm^{-1} for hexadecyloxy derivative: 720–771 poly-methylene of C₁₆H₃₃, 807–829 parasubstituted benzene, 982 trans (-CH=CH-), 1011 aromatic –Br linkage, 1105, 1307, 1675, 1716 (-COO-), 1220-1269 ether linkage of (C₁₆H₃₃-O-C₆H₄), 3410 (H-bonding of OH), 2850, -COOH.

IR data confirm the structure

Mass spectra Mass spectra for hexyloxy derivative Molecular weight, calculated: 537. Molecular formula: $C_{29}H_{29}BrO_5$ Experimental: 539. *Texture of smectic phase by miscibility method* Pentyloxy (C_5) derivative \longrightarrow Smectic-A

Hexyloxy (C ₆) derivative —	\longrightarrow Smectic-A
Dodecyloxy (C ₁₂) derivative——	\longrightarrow Smectic-C
Tetradecyloxy (C ₁₄) derivative ——	\longrightarrow Smectic-C

Results and discussion

Cis-4-n-alkoxy cinnamic acid and 4-hydroxy-4'-bromobenzylbenzoate (mp: 115-122°C, yield = 70%) are not LCs. However, mesomorphism is induced in the present novel ester homologous series by linking both non-mesomorphic components in dry cold pyridine. The smectogenic mesomorphism is induced from first to last (C_{16}) member of the series in an enantiotropic manner. Nematogenic character is totally absent. Transition and melting temperatures were determined by an optical polarizing microscopy equipped with a heating stage. Transition temperatures (Table 2) of the homologues were plotted against the number of carbon atoms present in n-alkyl chain bonded to phenyl ring through oxygen atom. Like points were linked to draw Cr-Sm and Sm-I transition curves indicating phase behavior of the series (Fig. 1). The Cr-Sm transition curve follows a zigzag path of rising and falling values with overall descending tendency in a typical manner. The Sm-I transition temperatures initially rise for odd and even members of the series up to the octyloxy member (C_8) of the series at a maximum and then descends up to the last C_{16} member. An odd-even effect is observed for Sm-I transition curve. Thus, Cr-Sm and Sm-I transition curves of a phase diagram behaves in a normal established manner. Curves (Sm-I) for odd and even members matches at the heptyl derivative (C_7) of a series and then, Sm-I transition curve propagate as a single transition curve until the C₁₆ homologues derivative. Textures of the smectogenic homologues are focal conic fan shape of smectic A or C. Analytical and spectral data support the molecular structures of the homologues. LC properties, such as thermal stability, molecular planarity, type of mesophase behavior, mesophase length range etc., vary from homologue to homologue in the same series as a consequence of changing molecular rigidity and flexibility depending upon the end to end and lateral intermolecular attractions of varying magnitudes. The condensation to generate the ester homologues increases molecular length, ratio of the polarity to polarizability, permanent dipole moment across the long molecular axis, dipole-dipole and electronic interactions, dispersion forces, molecular rigidity and flexibility, anisotropic forces of intermolecular end to end and lateral attractions. However, due to the suitable magnitudes of anisotropic forces of lateral and terminal attractions, the molecules of all the homologues generate mesomorphism as a result of differing molecular rigidity and flexibility. The

		Transition temperature (°C)		
Compound No.	$R = C_n H_{2n+1}(n)$	Smectic	Nematic	lsotropic
1	C1	77.0	—	84.4
2	C ₂	72.1	—	122.6
3	C ₃	66.5	—	99.7
4	C ₄	95.0	_	124.9
5	C_{5}	82.4	—	120.0
6	C ₆	64.1	—	125.0
7	C ^o	70.8	_	125.2
8	C ₁₀	62.3	_	124.5
9	C ₁₂	71.0	_	111.6
10	C14	74.3	_	101.0
11	C ₁₆	67.5	_	92.5

Table 2. Transition temperatures of series.



Figure 1. Phase behavior of series.

molecules of all the homologues show a lamellar packing arrangement and hence generate a smectic phase, but the smectic to nematic transition does not appear for any of the homologues because residual end to end intermolecular attractions are weak. The exhibition of an odd-even effect is attributed to alteration of transition temperatures due to the sequentially added methylene unit at the n-alkyl chain bonded to the phenyl ring through oxygen atom. The disappearance of the odd-even effect from and beyond the heptyloxy (C_7) homologue of the series is attributed to the longer n-alkyl chain which may coil or bend or flex or couple to occupy its position with principle axes of the core structure. The early commencement of smectic phase (from C_1) is attributed to the suitable and favorable extent of molecular noncoplanarity, which causes suitability in lamellar packing of molecules. The changing trend in LC properties and the degree of mesomorphism from homologue to homologue is attributed to the changing the number of carbon atoms present in the n-alkoxy terminal end group. The LC properties of the present series are compared with structurally similar homologous series X [30] and Y [31] as shown below in Fig. 2.

A homologous series-1 of present investigation and the series-X and Y chosen for comparison are identical with respect to three phenyl rings bridged through vinyl carboxy and $-COO-CH_2$ - groups constituting molecular rigidity and the flexible -OR terminal end group for the same homologue from series to series, but all the three series under comparative study are



Figure 2. Structurally similar series.

differing with respect to flexible terminal end groups –Br, -OCH₃ and –Cl. Therefore mesomorphic properties or behaviors and the degree of mesomorphism as depended upon varying features of homologous series for the same homologue from series to series. The mesomorphic properties and related data are recorded in following Table 3 for the series 1, X and Y as under.

It is clear from Table 3 that

- Series-1 and Y are only smectogenic, and series-X is smectogenic in addition to nematogenic in character.
- Smectic and nematic thermal stabilities are highest in series X, whereas only smectogenic thermal stabilities of series 1 and Y are relatively lower than in series X.
- The smectic thermal stability of present series 1 is lowest among all three series under comparison.
- Smectogenic mesophase commences from the very first member of series 1 and Y, and it commences from C₁₀ member of series X.
- Nematic mesophase commences from the C₂ member of series X, but it does not commence till the last member of series 1 and Y.
- Mesophase length range is lowest for the present series 1 and highest for series X among all the series under comparison.

Differing features among the series 1, X, and Y are the magnitudes of flexibility for the same homologue from series to series caused by changing right-handed terminal end groups, -Br, -OCH₃, and -Cl, respectively. Terminal end groups —Br and -Cl of series 1 and Y are mono-atomic with three lone pairs of electrons, and that of series X are penta-atomic with two lone pairs of electrons that cause difference in the extent of molecular non-coplanarity,

$Series \rightarrow$	1	Х	Y
Smectic—isotropic or	102.6	182.6	128.09
Smectic-nematic	(C ₁ -C ₁₆)	(C ₁₀ - C ₁₄)	(C ₁ -C ₁₆)
Commencement of smectic phase Nematic–isotropic Commencement of nematic phase Mesophase length	C ₁	$C_{10}^{(4)}$ 242.0 $(C_2 - C_{16})$ C_2	с ₁ —
Range (Sm + N) in °C Minimum to maximum	7.4 to 62.2 C ₁ C ₁₀	18 to 100 C ₄ C ₆	8.6 to 73.2 C ₈ C ₁₄
Cα C _β			

Table 3. Average thermal stability (°C).

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which affects lamellar packing of molecules. The combined effect of molecular rigidity and flexibility varies from homologue to homologue in the same series and for the same homologue from series to series. Hence, stabilization of only smectic phase or smectic phase in addition to nematic phase is facilitated or hindered. Thus, thermal stabilities and mesophase length ranges vary from series to series as mentioned in Table 3.

Conclusions

- Novel ester homologous series is smectogenic without exhibition of nematic property, whose mesomorphic range is 7.4 to 62.2, and low thermal stability of 102.6.
- -OCH₃ group being nematogenic and halogen group being smectogenic are supported by the present investigation.
- The group efficiency order derived on the basis (i) thermal stability, (ii) commencement of mesophase, and (iii) mesophase length range for smectic and nematic are as under:
- (i) Smectic:

 $-OCH_3 > -Cl > -Br$ Nematic: $-OCH_3 > -Cl = -Br$

- (ii) Smectic
 - $-Br = -Cl > -OCH_3$

$$\frac{Nematic}{-OCH_3}$$
 > -Br = -Cl

- (iii) Smectic \pm Nematic -OCH, \rightarrow -Cl > -Br
- As size of halogen atom end groups increases, the smectic thermal stability decreases.
- Mesomorphic properties are sensitive and susceptible to molecular structure.
- Present homologues are useful in the study of binary systems for the devices operated between 40°C and 60°C. The ester derivatives may be useful in the agricultural field for the growth of flower- and fruit-giving plants.

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