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Study of Liquid Crystal Behavior and Dependence on Additional Central Bridge of Ester Homologous Series

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A novel homologous series of esters was synthesized and studied with a view to understanding and establishing the effects of molecular structure on liquid crystal (LC) properties. The series consists of 11 members, and all exhibit enantiotropically the smectogenic mesophase. The nematogenic mesophase is totally absent. The textures of smectic phases are of the type A or C. The Sm-I transition curve of the phase diagram behaves in abnormal manner. The average Sm-I thermal stability is 124.53°C with mesomorphic phase length between 6.5°C and 52.3°C and is of a middle-ordered melting type. LC properties of the novel series are compared with a structurally similar other known series. Analytical and spectral data of the homologous match the molecular structure.

Keywords Enantiotropic; liquid crystals; mesomorphism; nematic; smectic

Introduction

Since from the discovery in 1888 of a novel physical state of a matter [1] between a crystalline solid and a true isotropic liquid called the liquid-crystal (LC) state, various groups of scientific and technological researchers have contributed enormously with different views, aims, and objects or purposes [2–4]. Among the scientific groups, the chemists have played an important basic role by designing and synthesizing novel LC materials useful to other research groups [5–7]. LC materials are well known for their applications in pharmaceuticals and medicinal preparations and importantly displays. The present investigation is planned with a view to understanding and establishing the relation between LC properties of substances and their molecular structure [8–10]. The proposed investigation consists of the synthesis and characterization of novel ester derivatives of 4-hydroxy-4′-chloro benzyl benzoate with *n*-alkoxy aromatic acids. Such derivatives are useful in the biological field due to their bioactivity [11–13] and other fields of applications like heat-sensitive recording material [14]. The LC behavior of the novel substances will be discussed and interpreted in terms of molecular rigidity and flexibility with reference to the corresponding molecular structures [15–18].

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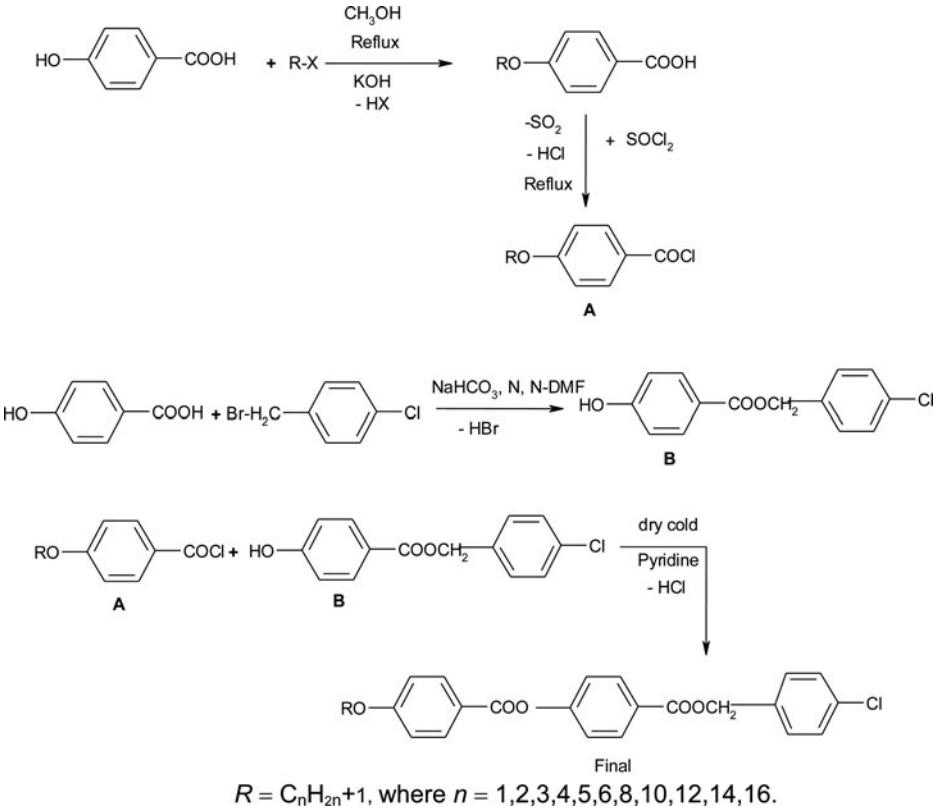
Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agents R-X by the modified method of Dave and Vora [19]. 4-Hydroxy-4′-chlorobenzyl benzoate (m.p. −120 to −130°C) was prepared from 4-chloro benzyl bromide and 4-hydroxy benzoic acid by the method the modified method of Doshi and Patel [20,21]. *n*-Alkoxy benzoic acids and 4-hydroxy-4′-chlorobenzyl benzoate were individually condensed in pyridine through their corresponding acid chlorides by a usual established method [22,23]. Final esterified products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained.

4-Hydroxy benzoic acid, alkyl halides, methanol, KOH, 4-chloro benzyl bromide, N,N-DMF, $NaHCO_3$, HCl, pyridine, thionyl chloride, EtOH, etc. required for the synthesis were used as received, except for solvents which were dried and purified prior to synthesis. Synthetic route to the series is shown in Scheme 1.



Scheme 1. Synthetic route to the series.

Characterization

Some selected members of the novel homologous were characterized by elemental analysis, infrared spectra, ^{1}HNMR spectra, and mass spectra. Textures and transition temperatures

of the homologous were determined by an optical polarizing microscope, equipped with a heating stage. Elemental analysis was performed on Perkin-Elemer PE 2400 C,H,N analyzer. IR spectra were recorded on Perkin-Elmer spectrum GX. ^{1}HNMR spectra were determined on Bruker spectrometer using $CDCl_3$ solvent. Textures of smectic mesophase of some homologous were recognized either directly from the microscopic observations or by a miscibility method.

Analytical Data

Spectral data:

^{1}HNMR in ppm for the Hexyloxy Derivative: 0.97 (CH_3 of C_6H_{13}), 2.66 ($-CH_2-$ of $-OC_6H_{13}$), 3.93 ($-OCH_2$ of $-OC_6H_{13}$), 5.25 ($-O-CH_2$- phenyl ring), 6.81–6.90 (p-substituted phenyl ring), 7.84–7.94 (p-substituted benzene), 7.31–7.49 (p-substituted benzene).

^{1}HNMR in ppm for the Dodecyloxy Derivative: 0.969 (CH_3 of $C_{12}H_{25}$), 2.261($-CH_2$- of $-OC_{12}H_{25}$), 3.75 ($-O-CH_2$ of $-OC_{12}H_{25}$), 4.98 ($-OCH_2$- of phenyl ring), 6.53–6.64 (p-substituted phenyl ring), 7.55–7.61 (p-substituted benzene), 7.06–7.19 (p-substituted benzene).

NMR data confirm the structure.

IR in cm^{-1} for Decyloxy Derivative: 717 polymethylene of $C_{10}H_{21}$, 771 para Chloro benzene, 845 para-substituted phenyl ring, 1167 ether linkage of ($C_{10}H_{21}-O-C_6H_4$), 1105,1257,1672 ($-COO-$ester group), 2560–2664 (presence of $-COOH$ groups), 3257 ($H-$ bonding of OH).

IR in cm^{-1} for Pentyloxy Derivative: 772 para Chloro benzene, 843 para-substituted benzene, 1166 ether linkage of ($C_5H_{11}-O-C_6H_4$) polymethylene of $C_{14}H_{29}$, 821 para-substituted phenyl ring, 1018 ether linkage of ($-C_5H_{11}O-C_6H_4$),1114, 1255, 1672($-COO$-ester group), 2669, 2558 (presence of $-COOH$ groups), 3258 ($H-$ bonding of OH).

IR data confirm the structure.

Mass Spectra

Mass Spectra for Butyloxy Derivative. Molecular weight: Calculated: 438.5. Molecular formula: $C_{25}H_{23}ClO_5$

Experimental: 439.

Texture of Smectic Phase by Miscibility Method

Butyloxy (C_4) derivative $\longrightarrow$ Smectic - A
Hexyloxy (C_6) derivative $\longrightarrow$ Smectic - A
Hexadecyloxy (C_{16}) derivative $\longrightarrow$ Smectic- C

Results and Discussion

The novel ester homologous series consisting of 11 members is entirely enantiotropically smectogenic without exhibition of any nematogenic character. Transition temperatures (Table 2) were plotted versus the number of carbon atoms present in the *n*-alkoxy terminal end group. Like or related points were linked to draw solid-smectic and a smectic-isotropic transition curves for the construction of a phase diagram (Fig. 1), showing the phase behavior

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

		% Elements calculated (experimental%)		
Sr. no.	Molecular formula	C	H	Cl
1	$C_{22}H_{17}ClO_5$	66.49 (66.58)	4.05 (4.28)	8.88 (8.96)
2	$C_{23}H_{19}ClO_5$	61.28 (67.31)	4.50 (4.63)	8.33 (8.36)
3	$C_{24}H_{21}ClO_5$	67.50 (67.87)	4.89 (4.95)	7.88 (8.08)

of the novel series. The solid-smectic transition curve follows a zigzag path of rising and falling values as the series is ascended in an overall descending manner. Thus, it behaves in normal established manner. Smectic-isotropic transition curve initially shows a falling tendency with the exhibition of an odd-even effect up to the butyloxy (C_4) homologue then it rises up to the hexyloxy homologue (C_6) and then drastically falls to the octyloxy (C_8) homologue and then adopts a rising tendency to the C_{16} homologue Thus, it behaves exceptionally in an unusual manner. The odd-even effect for the Sm-I transition curve disappears from and beyond the hexyloxy (C_6) homologue Mesomorphic behavior and the degree of mesomorphism vary from homologue to homologue in the present novel series. The average thermal stability for smectic is 124.53°C and the smectogenic mesophase length varies between 6.5°C and 52.3°C. Thus novel series is entirely smectogenic without exhibition of any nematic property and of a middle-ordered melting type.

Exhibition of only smectic property throughout the series is attributed to the misalignment of molecules at an angle ninety degree with the plane of a floating surface under the influence of heat. Therefore, a narrow rod like molecule with the dipole acting across the long axis favors lamellar packing of molecules in their crystal lattices. The chloro substituent with a weaker dipole, disfavors or excludes the nematic phase, but strongly

Table 2. Transition temperatures of series in °C

	n-alkyl group (-C_nH_{2n+1})	Transition temperature in °C		
Compound no.	(*n*)	*Sm*	*N*	Isotropic
1	1	107.2	—	133.3
2	2	112.8	—	138.6
3	3	109.0	—	130.9
4	4	86.7	—	122.5
5	5	89.7	—	131.8
6	6	93.0	—	133.0
7	8	73.8	—	80.3
8	10	91.7	—	112.2
9	12	85.4	—	111.9
10	14	114.6	—	138.8
11	16	84.3	—	136.6

Sm: Smectic *N:* Nematic

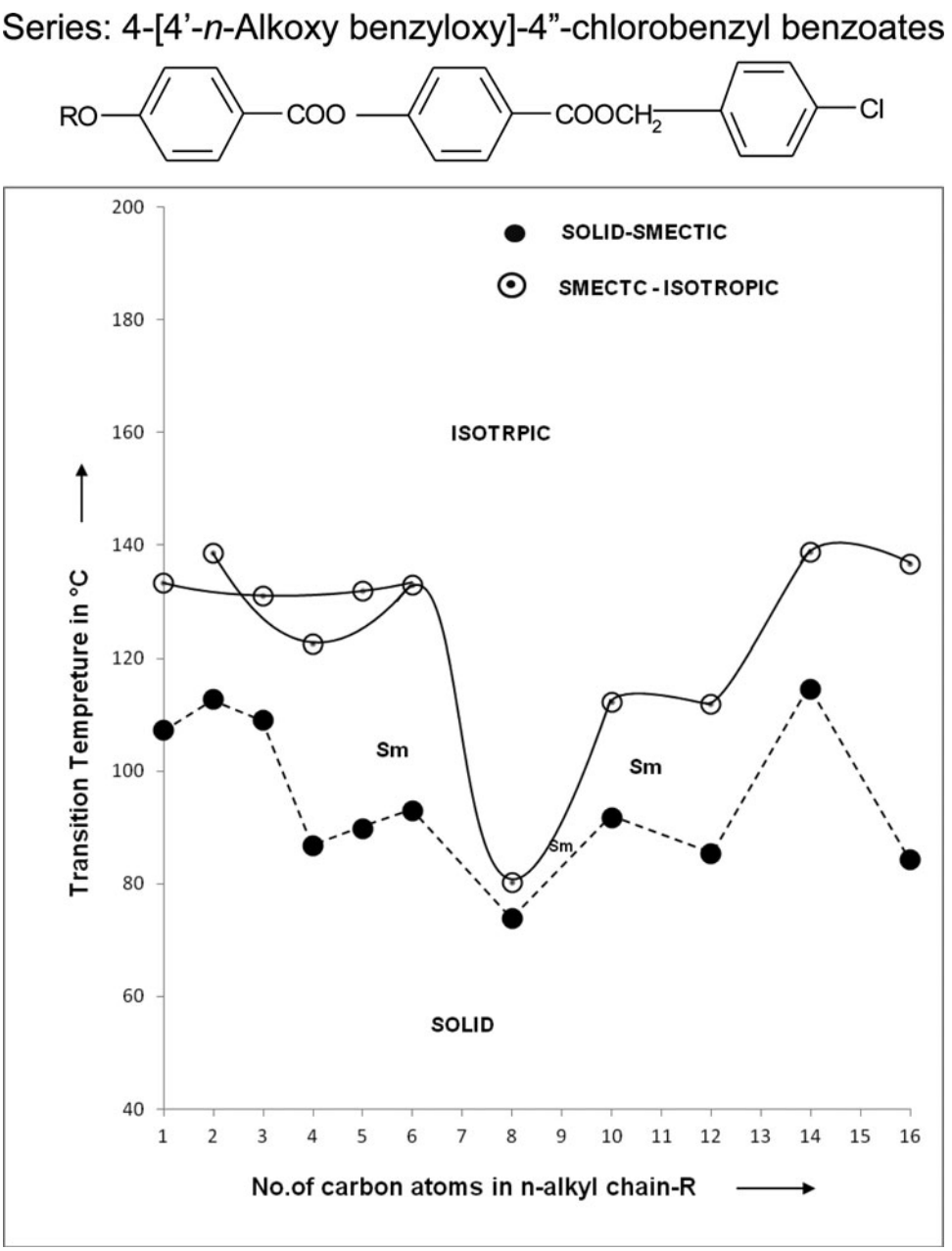


Figure 1. Phase behavior of series.

favors a layered crystal lattice. Consequently, the lateral intermolecular attractions of suitable magnitude of anisotropic forces retain the layered molecular arrangement to exhibit the smectogenic mesophase only. The odd-even effect observed for the smectic-isotropic transition curve is attributed to the sequentially added methylene unit at the *n*-alkoxy chain bonded to the phenyl ring. The disappearance of the odd-even effect for higher homologous from and beyond the hexyloxy (C_6) homologue is due to the coiling or bending or

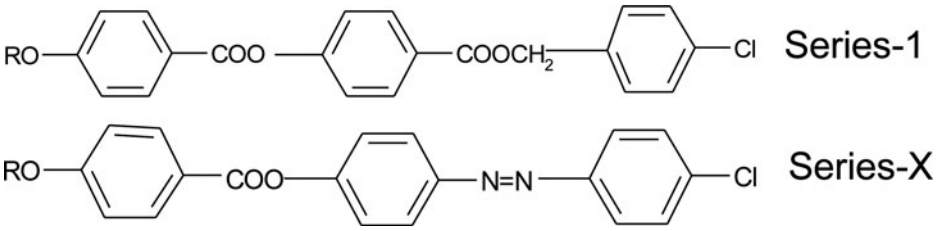


Figure 2. Structurally similar series.

flexing or coupling of *n*-alkyl chain with the major axes of the core structure. Thus, uncertainty in the status of longer *n*-alkyl chain affects considerably the suitable magnitudes of molecular flexibility and molecular rigidity operating. However, the molecules of the novel homologous series consist of three phenyl rings and two central ester bridges as well as two flexible end groups (-OR and −Cl) are narrow rod like with dipoles acting across the long molecular axis, which induces suitable magnitudes of anisotropic forces of lateral to terminal intermolecular attractions to favor strongly smectogenic property right from the very first member to the last member (C_{16}). Thus, the combined effects of molecular rigidity and flexibility from homologue to homologue in the present series exerts variations in the suitable magnitudes of the ratio of lateral to terminal attractions to favor layered and sliding layered lattices with varying degree of smectogenic behavior without the exhibition of nematic property. Thus, the novel series is entirely smectogenic whose mesophase ranges from a minimum of 6.5°C at the octyloxy (C_8) homologue to a maximum of 52°C at the hexadecyloxy (C_{16}) homologue The LC behaviors of present novel series-1 are compared with the structurally similar other known series-X [24] as shown in Fig. 2.

Homologous series-1 and a series-X chosen for comparison are identical with respect to their aromaticity, i.e., three phenyl rings, a left *n*-alkoxy (−OR) and a right terminal end group (−Cl) for the same homologue from series to series, a central bridge of −COO− linking first and middle phenyl ring. However, they differ with respect to the second central bridge of $-COOCH_2-$ and −N=N− linking the middle and third phenyl rings. Therefore, series-1 and series-X under comparison differ with respect to molecular rigidity and the intermolecular forces involved, for the same homologue from series to series and from homologue to homologue in the same series. Therefore, the LC properties and the degree of mesomorphism vary for the same homologue from series to series and from homologue to homologue in the same series. Table 3 represents the average thermal stabilities, commencement of smectic and/or nematic phase, degree of mesomorphism, etc. for the series under comparison.

From the Table 3, it is clear that

- Series-1 is entirely smectogenic, while series-X is smectogenic in addition to nematogenic.
- Smectic thermal stability of series-1 is relatively lower than the series-X under comparison.
- Smectic mesophase commences from very first member of series-1, but it commences late from the sixth (C_6) member of a series-X.
- Nematic mesophase is absent for a series-1 but nematic mesophase is present from very first to last member of a series-X.

Table 3. Average thermal stability in °C

Series→	1	X
Smectic-nematic		
Or	124.53	148.8
Smectic-isotropic	(C_1—C_{16})	(C_6—C_{16})
Commencement of	C_1	C_6
Smectic phase		
Nematic-isotropic		217.6
Commencement of	—	(C_1—C_{10})
Nematic phase		C_1
	Sm 6.5–52.0	*Sm* 18–66
Mesophase length	*Nm*	*Nm* 25–121
Range	Total 6.5–52.0	Total 16–121

- Smectogenic mesophase length ranges from 6.5 to 52°C for series-1, whereas it ranges from 18 to 66°C for series-X, i.e., 52-6.5 = 45.5°C and 66-18 = 48°C.

Thus, series-1 is entirely smectogenic and series-X is predominantly nematogenic and partly smectogenic.

In all other respects, there is close similarity, except the second central bridge which is azo —N=N— for series-X and —COO—CH_2- in case of series-1. The oxygen atom of the second central bridge bonded through —CH_2- unit of series-1 will undergo bumping into the adjacent hydrogens of the aromatic ring which will cause considerable strains on the molecules of series-1. Consequently, a twist around C—O bond will occur forcing the phenyl ring out of the plane of the molecule. Thus, the coplanarity of the molecule is reduced to some extent making them broader. The central bridge —N=N— certainly endows the molecules with coplanarity in the trans position of series-X. On account of such differences, the smectic-isotropic thermal stabilities of series-1 are lower than the corresponding smectic thermal stability of series-X. Moreover, when a system consisting of three phenyl rings are linked through one of the central group involving multiple bond (—N=N— series-X), the LC transition temperatures are relatively higher because —N=N— central group as compared to —COO—CH_2- extend the molecular rigidity and linearity associated with para substituted phenyl rings. However, an additional central group like —$COOCH_2$- in which conjugation is less extended in the mesogenic system which results into less thermally stable LC than that central group (—N=N—) of a kind, which permit conjugative interactions. Thus, lowering of smectic thermal stability, transition temperatures, mesophase length, range, and early commencement of smectic phase and absence of nematic phase of present series-1, as compared to series-X are can be attributed to changing molecular rigidity and flexibility.

Conclusions

- The smectic and/or nematic group efficiency order derived on the basis of (i) thermal stability and (ii) the early commencement of mesophase with respect to additional or second central bridge are as under.

I) Smectic: $-N=N- > -COO-CH_2-$
Nematic: $-N=N- > -COO-CH_2-$
II) Smectic: $-COO-CH_2 > -N=N-$
Nematic: $-N=N- > -COO-CH_2-$
III) Smectic mesophase length range
$-COO-CH_2- \approx -N=N-$
(45.5°C) (48.0°C)
Nematic mesophase length range
$-N=N- >>>>> -COO-CH_2-$

- LC substances derived from the para-chloro-substituted benzyl alcohol are smectogenic.
- LC property of substance is sensitive and susceptible to the suitable magnitudes of molecular rigidity and flexibility.
- Present novel series is entirely smectogenic without exhibition of nematogenic property and it is of middle ordered melting type.
- Central group of a molecule contributes to molecular rigidity, LC property, and degree of mesomorphism.
- LC property and its magnitudes or intensity depends on its molecular structures.
- LC property of substance is a function of molecular structure.

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