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Synthesis and Liquid Crystal Properties of a Novel Homologous Series 4-(4′-n-Alkoxy benzoyloxy) Benzyl Benzoates

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A novel homologous series consisting of 11 homologues is reported. Liquid crystal properties commence from the hexyloxy homologue and continue up to the tetradecyloxy homologue as enantiotropic nematic mesomorphism only. The rest of the homologues (including hexadecyloxy homologue) are not liquid crystalline. None of the homologues show smectogenic mesophase formation. The texture of the nematic mesophase is of a threaded or Schlieren type. The transition temperatures of the homologues were determined by optical polarizing microscopy equipped with a heating stage. Transition curves of a phase diagram behave in normal manner except for the tetradecyloxy homologue which adopts an unexpected trend of propagation. An odd–even effect is absent for nematic-isotropic transition curve. Analytical and spectral data support the molecular structure of the homologues. The average thermal stability of the series is 78.8°C. Mesomorphic/nematogenic phase length varies from 2.0°C to 13.0°C. The liquid crystal behavior of the present series is compared with structurally similar other known series. Thus, the present series is enantiotropically nematogenic only without exhibition of any smectogenic character with a low melting type, whose mesomorphic phase length is relatively short.

Keywords Enantiotropy; liquid crystal; mesomorphic; smectic; nematic

Introduction

The potential ability of a molecular structure to induce liquid crystal mesophase formation, depends, upon its internal energy, that is, energy stored by a molecular structure due to its mass and other characteristics related to molecular rigidity and flexibility [1–3]. The suitable magnitudes of the combined effects of anisotropic forces of intermolecular end to end attractions and inter-layered attractions [4] as a consequence of favorable molecular rigidity and flexibility, is the root cause of inducing liquid crystal behavior in a substance. Such forces enable a two-dimensional array of molecular ordering or a less ordered orientational organization, causing smectic, and nematic mesophase formation respectively. The present investigation is planned with a view to understanding and establishing the effect of molecular structure on liquid crystal behavior by constructing a molecule containing three

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phenyl rings and two central bridges viz. –COO– and –COO–CH_2– linking phenyl rings as a rigid core and an n-alkoxy (–OR) group as a flexible part of the molecule.

Experimental

Synthesis

4-n-Alkoxy benzoic acids were prepared by alkylating dimeric 4-hydroxy benzoic acid using the suitable alkylating agents through the modified method of Dave and Vora [5]. 4-Hydroxy benzyl benzoate was used as received and recrystallized and dried before use. The m.p. (110°C) of 4-Hydroxy benzyl benzoate agrees with reported data. Final products were prepared by condensing 4-n-alkoxy benzoic acids through their corresponding acid chlorides with 4-hydroxy benzyl benzoate in dry, ice cooled, pyridine [6,7]. Each final product was individually decomposed, filtered washed, dried, and purified by alcohol until the constant transition temperatures were obtained. The synthetic route to the series is shown in scheme 1. The chemicals required for synthesis, 4-hydroxy benzoic acid, alkyl halides, 4-hydroxy benzyl benzoate, thionyl chloride, MeOH, EtOH, KOH, and pyridine were used as received, except solvents, which were dried and purified prior to use.

Characterization

Selected members of the present series were characterized by elemental analysis, Infra red spectroscopy, ^{1}HNMR spectroscopy, and mass spectrometry. These representative members were characterized by elemental analysis using a Perkin-Elmer PE 2400 CHN analyzer, infra red spectroscopy were recorded on Perkin-Elmer spectrum GX spectrometer and ^{1}HNMR spectroscopy which were recorded on Bruker spectrometer using DMSO as the solvent. The liquid crystal behavior, type of texture and transition temperatures of the novel homologues were recorded and observed through optical polarizing microscopy in conjunction with a heating stage. The type of nematic mesophase textures was determined by a miscibility method. Thermodynamic quantities enthalpy change (δH) and entropy change (δS) are qualitatively discussed.

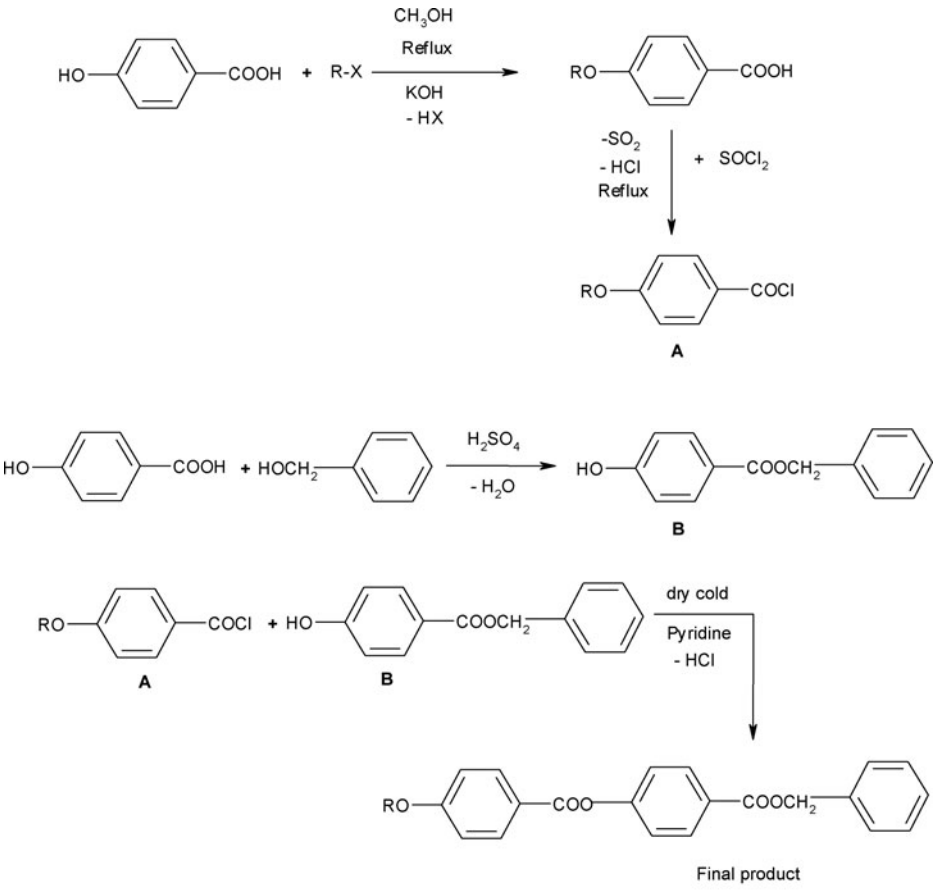
Analytical Data

Spectral Data. ^{1}HNMR in ppm for the octyloxy derivative: 3.4 (–OCH_2 of –OC_8H_{17} group), 4.0 (–COO–CH_2–C_6H_5 group), 6.98 and 7.1 (p-substituted benzene), 7.8 and 8.07 (another p-substituted benzene), and 7.3–7.5 (multiplex mono-substituted benzene).

^{1}HNMR in ppm for the decyloxy derivative: 3.2 (–OCH_2 of –$OC_{10}H_{21}$ group), 3.9 (–COO–CH_2–C_6H_5 group), 6.7 and 7.03 (p-substituted benzene), 7.7 and 8.0 (another p-substituted benzene), and 7.2–7.5 (multiplex mono-substituted benzene).

IR in cm^{-1} for the dodecyloxy derivative: 694 and 759 mono-substituted benzene, 842 p-substituted phenyl ring, 1215 ether linkage of (–O– group), 1730, 1256, and 1163 (–COO– ester group), and 723 (polymethylene of $C_{12}H_{25}$ group).

IR in cm^{-1} for the tetradecyloxy derivative: 694 and 760 mono-substituted benzene, 843 p-substituted phenyl ring, 1215 ether linkage of (–O– group), 1729, 1256, and 1163 (–COO– ester group), and 723 (polymethylene of $C_{14}H_{29}$ group).



Scheme 1. Synthetic route to the series.

Mass Spectra. Mass spectra for the pentyloxy derivative:

Molecular formula $C_{26}H_{26}O_5$ Calculated Molecular weight 418. Practical mass observed by Mass spectroscopy 418.

Texture of Nematic phase by miscibility method

Hexyloxy derivative ——————→ Threaded nematic
Octyloxy derivative ——————→ Schlieren nematic

Results and Discussion

The dimerization of 4-hydroxy benzoic acid or n-alkoxy benzoic acids disappears on esterification. 4-Hydroxy benzyl benzoate is a nonliquid crystal component, however, liquid crystal properties are induced from the hexyloxy homologue to the tetradecyloxy homologue as an enantiotropic nematic phase, without the exhibition of any smectogenic

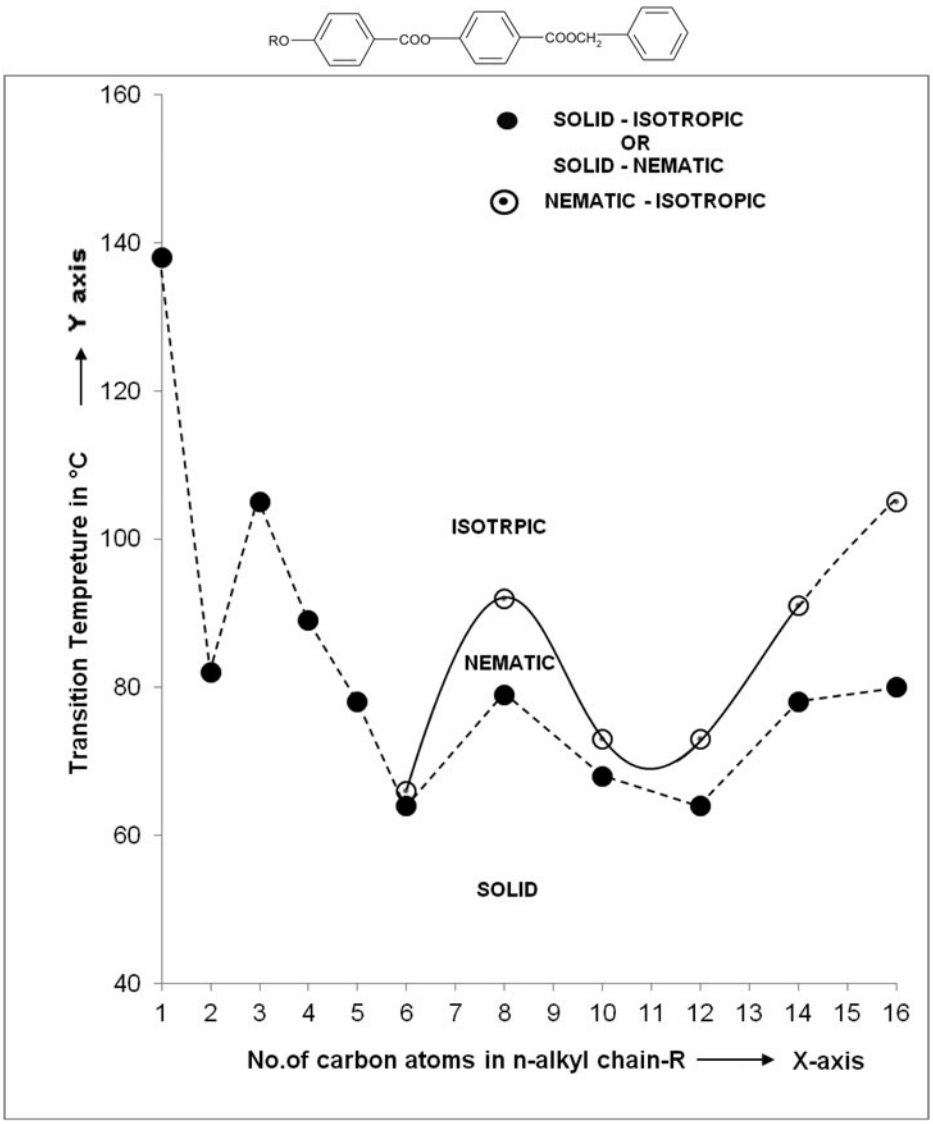


Figure 1. Phase behavior of series.

mesophase. The methoxy to pentyloxy and hexadecyloxy homologues are nonliquid crystal. A phase diagram, showing phase behavior (Fig. 1) of the novel series is drawn for the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group versus the transition temperatures, as determined by optical polarizing microscopy equipped with a heating stage. The solid-nematic or isotropic and nematic-isotropic transition curves are drawn smoothly by joining like or related points. The solid-isotropic or nematic transition curve adopts a zigzag trend of rising and falling values in a normal manner. The nematic-isotropic transition curve initially rises from the hexyloxy to the octyloxy homologue and then descends as the series is ascended up to the dodecyloxy homologue, without exhibition of an odd-even effect. Then, it abnormally ascends instead of showing descending tendency

for the tetradecyloxy homologue only. Thus, the nematic-isotropic transition curve behaves in a usual established manner for all nematogenic homologues except the tetradecyloxy homologue. The average nematic thermal stability of the series is relatively low at 78.8°C and its nematogenic mesophase length varies between 2.0°C and 13°C. Liquid crystal behavior of the novel series varies from homologue to homologue for changing molecular flexibility [1–3] by the n-alkyl chain of the left n-alkoxy terminal end group. Thus, the presently investigated novel homologous series is nematogenic and of a low-melting type, whose, mesomorphic phase length is relatively short. The nematic-isotropic transition curve is extrapolated [8,9] for the hexadecyloxy homologue in order to predict its ability for a probable nematic-isotropic transition temperature, the hypothetical value comes out to be 105 °C, which is above the real or actual melting point. The disappearance of dimerization of the alkoxy acids is attributed to the breaking of hydrogen bonding between two molecules. The process of esterification yielded homologues that formed through acid chlorides with 4-hydroxy benzyl benzoate, and resulted in final products, 4-(4′-n-alkxoy benzoyloxy) benzyl benzoates with relatively lower transition temperatures. Nonmesomorphic behavior of methoxy to pentyloxy homologues is due to the relatively shorter n-alkyl chain length of left n-alkoxy group, which induces unfavorable magnitudes of molecular rigidity and/or flexibility that hinders the suitable magnitudes of anisotropic forces of intermolecular attractions. The hexadecyloxy homologue with longer a n-alkyl chain is susceptible to a high crystallizing tendency and so is not mesogenic. The molecules of homologues from hexyloxy to tetradecyloxy possess suitable magnitudes of anisotropic forces of intermolecular attractions and so disalign at an angle less than ninety degree resisting exposed thermal vibrations for definite range of temperature and show a statistically parallel orientational order of molecules in floating condition with sufficient end to end attractions, favoring exhibition of nematogenic behavior. The absence of smectogenic behavior of a novel series is attributed to absence of lamellar packing of molecules in their crystal lattices, which is hindered by insufficient magnitudes of intermolecular attractions caused by their molecular structures. Absence of an odd–even effect in the nematic-isotropic transition curve is attributed to (i) the absence of mesophase formation by the odd members of a series viz. methoxy, propyloxy, pentyloxy, (ii) the exhibition of a nematogenic property by even numbered higher homologues from hexyloxy to tetradecyloxy, whose longer n-alkyl chain of left n-alkoxy terminal end group may undergo coiling, bending, flexing, or coupling with major axis of the core structure to diminish the odd–even effect [4,7]. The observed variations in nematogenic property in terms of the alternation of transition temperatures from homologue to homologue is due to the sequential addition of methylene units in the n-alkyl chain terminal end group. Low-melting behavior, shorter mesophase length and low thermal stability of homologues indicates relatively inadequate magnitudes of intermolecular adhering forces to facilitate neither high degree of mesomorphism, nor lamellar packing of molecules in the crystal lattices, to show smectogenic behavior. The liquid crystalline behaviors of presently investigated novel homologous series-1 are compared with other structurally similar known homologous series X [10] and Y [11] as shown below in Fig. 2.

Table 3 represents average thermal stability for smectic and/or nematic mesophases.

The present homologous series-1 is nematogenic and non-smectogenic while, series X and Y selected for comparison are smectogenic in addition to nematogenic in character. Average thermal stabilities for the nematic phase increases from the novel series 1 to series X and Y chosen for comparison.

The smectic mesophase commences earliest from the second member of series Y, late from the decyloxy homologue of series X and is not exhibited by series 1.

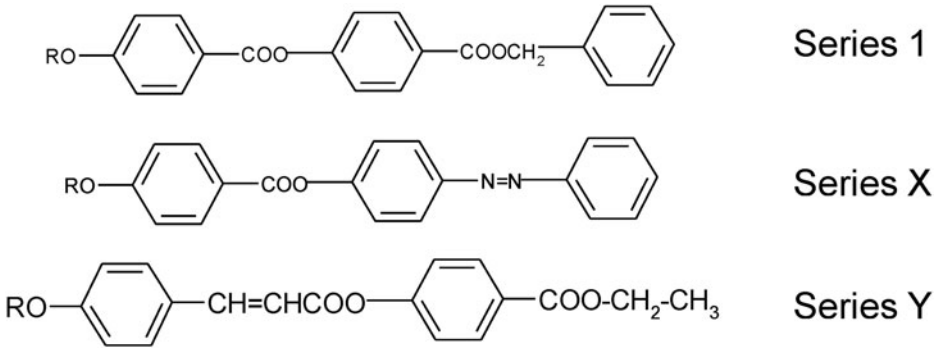


Figure 2. Structurally similar homologous series.

The nematic mesophase commences from very first member of the series X and Y chosen for comparison while, it commences late, from the hexyloxy homologue in series 1. Homologous series 1 and X are similar with respect to three phenyl rings (two phenyl rings in series Y) bridged through −COO− or −CH=CH−COO− groups and a left n-alkoxy terminal end group linked with the first phenyl ring which is also commonly present from series to series 1 to X to Y for the same homologue. However, the second central bridges of −COO−CH_2−, −N=N− and linking middle and third phenyl rings are a point of difference.

The nematic-isotropic thermal stability progressively increases from series 1 to series X and Y. Homologous series 1 and Y differ in their terminal end group of methyl or phenyl (series Y and 1) excluding the difference of second and first central bridges −COO−CH_2− and −CH=CH−COO− of series 1 and Y. Both these central bridges are comparable through the vinyl carboxylate −CH=CH−COO− has greater length and causes more noncoplanarity due to a twist obtained at the oxygen atoms of the vinyl carboxy group, which bump into the non-bonded adjacent hydrogen atoms of the aromatic phenyl ring [12]. Moreover, the phenyl ring terminal end group is more polarizable than the methyl terminal group. The phenyl ring of series 1 increases molecular length and polarizability, but the central group −COO−CH_2− relatively reduces molecular length, while in case of series Y the central group −CH=CH−COO− increases molecular length but at the same time the methyl terminal group reduces molecular length and molecular polarizability. On account of these differences, the smectic-nematic (absent) and nematic-isotropic thermal stabilities of series 1 are lower than for series Y.

On comparing homologous series 1 and X, both series resemble each other in all respects, except the second central bridge which is −N=N− in case of series X and

Table 1. Elemental analysis for methoxy, ethoxy and propoxy derivatives

		Elements % found (% calculated)	
Sr. no.	Molecular formula	C	H
1	$C_{22}H_{18}O_5$	72.69 (72.92)	4.73 (4.97)
2	$C_{23}H_{20}O_5$	73.12 (73.40)	5.15 (5.31)
3	$C_{24}H_{22}O_5$	73.65 (73.84)	5.48 (5.64)

Table 2. Transition temperatures of series in °C

Compound no.	n-alkyl group ($-C_nH_{2n+1}$) (n)	Transition temperature in °C		
		Sm	*Nm*	Isotropic
1	1	—	—	138.0
2	2	—	—	82.0
3	3	—	—	105.0
4	4	—	—	89.0
5	5	—	—	78.0
6	6	—	64.0	66.0
7	8	—	79.0	92.0
8	10	—	68.0	73.0
9	12	—	64.0	72.0
10	14	—	78.0	91.0
11	16	—	—	80.0

Sm: Smectic *Nm:* Nematic

$-COO-CH_2-$ in case of presently investigated series 1 and series Y. Both these central bridges are comparable. The oxygen atom of the central carboxy group in the molecules of series 1 will be bumping into the non bonded sides of the adjacent hydrogens of the aromatic phenyl ring which will cause considerable strain on the molecule [12]. Consequently, the twist around C—O bond will occur, forcing the phenyl ring out of the plane of a molecule. Thus, the coplanarity of a molecule is reduced to some extent making phenyl ring thick. The linear central bridge $-N=N-$ certainly endows the molecules with coplanarity. On account of this difference, the smectic-nematic and nematic-isotropic thermal stabilities of series 1 are in general far lower than the corresponding thermal stabilities of the homologous series X. The variations in liquid crystal properties from series to series for the same homologue is attributed to the differing part or differing structural configuration of the molecules and the variations from homologue to homologue in a same series is attributed to the sequentially added methylene units.

1. Conclusions
2. The smectic and nematic group efficiency order derived on the basis of (a) thermal stability and (b) on the basis of early commencement of mesophase are as under.

Table 3. Average thermal stability in °C

Series→	Series 1	Series X	Series Y
smectic-nematic or smectic-isotropic commencement of smectic phase	—	114.0 (C_{10}–C_{16}) C_{10}	120.75 (C_7–C_{12}) C_2
nematic-isotropic commencement of smectic phase	78.8 (C_6 – C_{14}) C_6	138.54 (C_1–C_8) C_1	119.3 (C_5–C_6) C_1

a. Smectic: −CH=CH−COO− > −N=N− > −COO−CH_2−
   Nematic: −N=N− > −CH=CH—COO− > −COO−CH_2−
b. Smectic: −CH=CH—COO− > −N=N− > −COO−CH_2−
   Nematic: −CH=CH−COO− = −N=N− > −COO−CH_2−

3. Normally ester series are smectogenic, but the presence of −CH=CH− unit along with −COO− unit, induces nematic tendency more in comparison with smectogenic tendency.
4. The novel homologous series of present investigation is nematogenic without exhibition of the smectic phase with low temperature transition temperatures, thermal stability and poor degree of mesomorphism.
5. Variations in mesomorphic properties are directly related to the molecular structure of as substance.
6. Suitable magnitudes of anisotropic forces as a consequence of favorable molecular rigidity and/or flexibility operate or governs the possibility of liquid crystal formation tendency and the degree of liquid crystallinity.
7. The substitution of functional group or groups of proper polarity at lateral or terminal position or positions can yield, liquid crystal compounds of rich degree of mesomorphism.

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