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Synthesis and Evaluation of a Novel Homologous series of Carbonylethylene-Linked Liquid Crystals

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A novel homologous series of α-4-[4′-n-Alkoxy benzoyloxy] benzoyl β-phenyl ethylenes was synthesized with a view to understand the effect of molecular structure on liquid crystal (LC) properties. The novel series consists of 11 homolog derivatives. The LC properties commence from the hexyl derivative of the series. The methyl to pentyl derivatives of the series are not liquid crystalline; however, the hexyl to hexadecyl homolog derivatives are enantiotropically nematogenic with the absence of smectogenic phases. Thus the novel series is entirely nematogenic. The melting points, transition temperatures, and mesophase morphologies were determined by optical polarizing microscopy in conjunction with a heating stage. The microscopic textures show the nematic mesophase of the threaded or Schlieren type. Analytical and spectral data support the molecular structure. The nematic to isotropic liquid transition curve behaves in a normal manner without the exhibition of an odd–even effect. Typical melting points are around 140°C and the nematic-phase stability varies from around 150°C to 180°C. The LC properties of the novel series are compared with other structurally similar series.

Keywords Enantiotropy; liquid crystal; nematic; odd-even effect; smectic

Introduction

Some substances exhibit an intermediate state of matter with a molecular ordering in between that of the conventional crystalline solid and isotropic liquid phases, and this state of matter is called a liquid crystal (LC) state or mesomorphic state, which is an anisotropic liquid. Of course, the generation of liquid crystalline phases depends on molecular structure of a substance. Molecular rigidity and flexibility combine to facilitate suitable magnitudes of intermolecular forces of attractions [1–4] required to induce an LC phase. Favorable molecular rigidity means suitable molecular aromaticity; molecular shape; size; polarity of lateral, terminal, and central groups; molecular polarizability; electronic interaction etc. that contribute to the intermolecular forces of attraction [4]. The present series involves n-alkoxy (−OR) and –H terminal end groups; three phenyl rings bonded through –COO−

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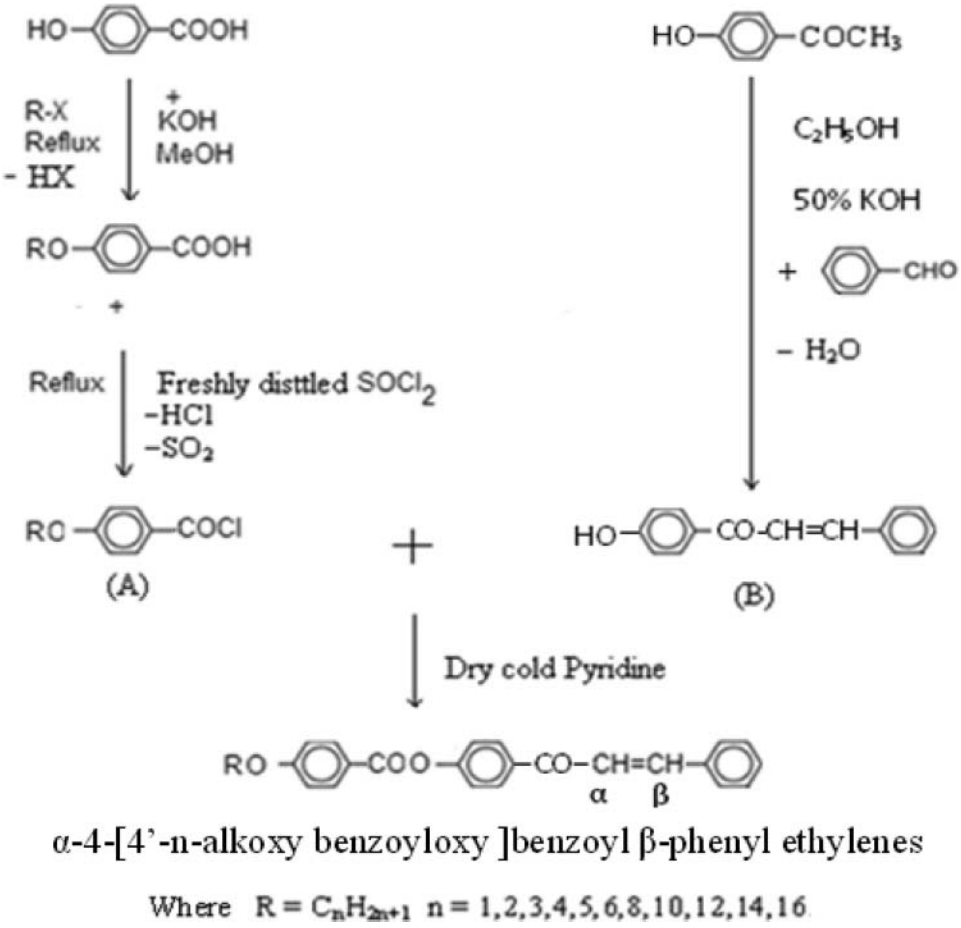
and –CO−CH=CH− central bridges with absence of any lateral group. Thus, a high length to breadth ratio of a linear lath-like molecule causing suitable magnitudes of molecular rigidity and flexibility induces LC mesophase at moderate to long terminal chain lengths.

Experimental

Synthesis

4-hydroxybenzoic acid was alkylated with suitable alkylating agents (R-X) and then converted into the corresponding n-alkoxybenzoyl chloride [A] using freshly distilled thionyl chloride by a modified method of Dave and Vora [5]. α-4-Hydroxybenzoyl β-phenyl ethylene [B] was prepared by a well-established method [6]. Components A and B were condensed in dry, cold pyridine [7]. The final products were individually synthesized, filtered, washed, dried, and purified until constant transition temperatures were obtained. 4-hydroxybenzoic acid, alkyl halides, MeOH, KOH, HCl, $SOCl_2$, ethanol, pyridine, 4-hydroxyacetophenone, benzaldehyde etc. were used as received. All solvents were dried and distilled prior to use. The synthetic route to the series is shown in Scheme 1.



Scheme 1. Synthetic route to the series.

Characterization

Some of the selected homologs of the novel series were characterized for the determination of molecular structures by elemental analysis, infrared (IR) and ^{1}HNMR (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}HNMR spectra were recorded on a Bruker instrument using $CDCl_3$ as solvent. The mesogenic properties and transition temperatures of the series were investigated using an optical polarizing microscope equipped with a heating stage. Thermodynamic quantities, enthalpy (ΔH), and entropy (ΔS) are qualitatively discussed through differential scanning calorimeter (DSC) scan.

Analytical Data:

Table 1 Spectral data:

NMR in ppm for decyloxy derivative:

0.885 ($-CH_3$ of $-OC_{10}H_{21}$ group), 1.251 ($-CH_2-$ of $-OC_{10}H_{21}$), 3.998 ($-OCH_2CH_2-$ of $-OC_{10}H_{21}$), 7.488 ($-CO-CH=CH-$ group), 6.88 to 8.045 (p-substituted phenyl ring). NMR supports the structure.

NMR in ppm for tetradecyloxy derivative:

0.8822 ($-CH_3$ of $-OC_{14}H_{29}$ group), 1.2 ($-CH_2-$ of $-OC_{14}H_{29}$), 3.184 ($-OCH_2CH_2-$ of $-OC_{14}H_{29}$), 6.856 ($-CO-CH=CH-$ group), 7.3 3to 7.906 (p-substituted phenyl ring). NMR supports the structure.

IR in cm^{-1} for butoxy derivative:

700 $-CH_2-$ group of $-OC_4H_9$, 840 phenyl ring, 1160 $-CO-$ of $-OC_4H_9$ group, 1210, 1255, & 1600 $-COO-$ ester group, 975 $-CH=CH-$ group. IR supports the structure.

IR in cm^{-1} for ethoxy derivative:

760 $-CH_2-$ group of $-OC_2H_5$), 845 phenyl ring, 1160 $-CO-$ of $-OC_2H_5$ group), 1250 &1600 $-COO-$ ester group. IR supports the structure.

Results and Discussion

Dimeric 4-n-alkoxybenzoic acid on esterification gives rise to a product with relatively lower transitions. But, on linking it to a third phenyl ring through a $-CO-CH=CH-$ central bridge, the transition temperatures of a final product rise. The presently investigated series consists of the methyl to pentyl homolog derivatives, which are not liquid crystalline and the hexyl to hexadecyl homolog derivatives as enantiotropically liquid crystals (LC) with a nematogenic type of mesophase. None of the homolog derivatives exhibit smectogenic character. The nematogenic mesophase is seen as a threaded or Schileren type of texture. The transition temperatures (Table 2) were observed through an optical polarizing microscopy with heating stage. The transition temperatures were plotted versus the number of carbon atoms in n-alkyl chain [$-R-$] of left n-alkoxy terminal end group. The phase diagram

Table 1. Elemental analysis for methoxy, hexyloxy, and octyloxy derivatives

		Elements % found (% Calculated)	
Serial numbers	Molecular formula	C	H
1	$C_{23}H_{18}O_4$	77.10 (76.92)	5.03 (5.14)
2	$C_{28}H_{28}O_4$	78.50 (78.12)	6.54 (6.44)
3	$C_{30}H_{32}O_4$	78.95 (79.18)	7.02 (6.98)

Table 2. Transition temperatures of the novel series in °C

Compound numbers numbers	n-alkyl group $-C_nH_{2n+1\ (n)}$	Transition temperatures in °C		
		Sm	N	Isotropic
1	1	—	—	210.0
2	2	—	—	192.0
3	3	—	—	202.0
4	4	—	—	182.0
5	5	—	—	162.0
6	6	—	148.0	167.0
7	8	—	150.0	178.0
8	10	—	135.0	180.0
9	12	—	140.0	165.0
10	14	—	132.0	152.0
11	16	—	138.0	145.0

Sm = smectic; N = nematic.

obtained is represented in Fig. 1. Solid to isotropic or nematic transition curve adopts a zigzag path of rising and falling tendency with an overall descending manner. The nematic to isotropic transition curve initially rises and then falls as series is ascended without the exhibition of an odd–even effect. Thus, both transition curves behave in a normal manner with absence of smectogenic behavior. The nematic–isotropic transition temperatures vary between 180°C and 145°C. Mesomorphic phase temperature range varies from 7°C to 45°C.

Dimerization of 4-n-alkoxybenzoic acids disappears because the hydrogen bonding between two molecules is removed by the esterification process. The nonmesomorphic behavior of the methyl to pentyl homolog derivatives is due to their high crystallizing tendency that arises from the relatively stronger intermolecular attractions from shorter n-alkyl chain that induces more crystalline character, but unsuitable magnitudes of anisotropic intermolecular forces of attraction mean that the molecules of a sample substance are randomly oriented in all possible directions in an irregular manner under floating condition with high entropy. Hence they sharply melt without showing any mesophase (LC) formation. On extending the n-alkyl chain from and beyond the hexyl homolog to the hexadecyl homolog, the molecules of a sample under the influence of heat gradually pass through translational, rotational, and vibrational motion and resist the exposed thermal vibrations. Consequently, molecules under examination disalign at an angle less than 90 degrees with a plane of a surface at a particular temperature t_1 and continue to resist thermal vibrations up to a higher temperature t_2. Thus, molecules are floating with a statistically parallel orientational order between a t_1 and t_2 temperature range, which shows a nematogenic mesophase formation. However from and beyond t_2, the molecules are unable to resist the thermal vibrations and disalign on the plane of a surface. At this point, the molecules lose the LC state and are converted into the isotropic state. On gradual heating of a sample homolog from room temperature, the intermolecular binding forces are loosened, depending upon the molecular rigidity and flexibility [1–4] as a consequence of molecular polarity, polarizability, length to breadth ratio etc., which governs the magnitudes of anisotropic intermolecular forces of attraction. Thus, the anisotropic intermolecular forces of adhesion

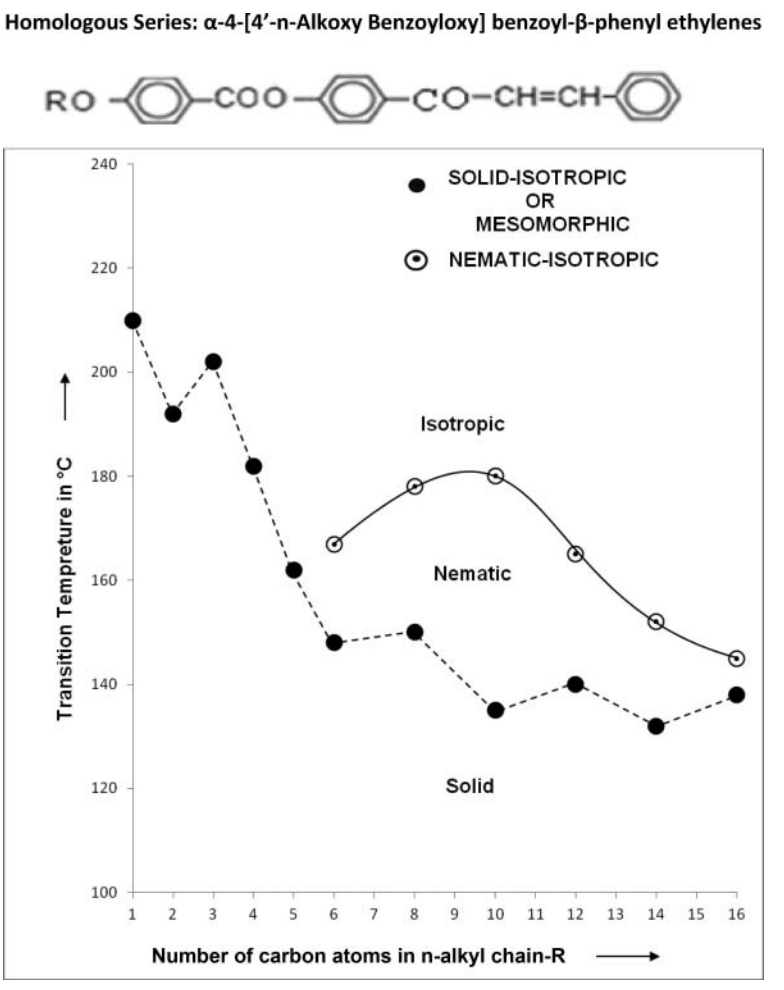


Figure 1. Phase behavior of series.

for the n-hexyl to n-hexadecyl chains of left n-alkoxy terminal end group in addition to the other molecular units favorably induce only nematogenic mesophase. However the molecules show a lack of lamellar packing and so do not allow the smectogenic mesophase even in the monotropic condition. The variation in mesomorphic properties from homolog

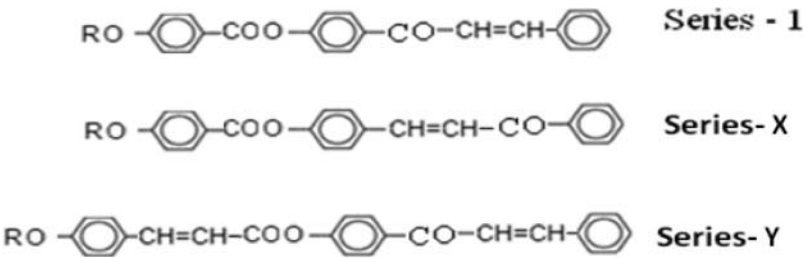


Figure 2. Structurally similar series.

to homolog [4] in the same series is attributed to the sequentially added methylene unit in n-alkyl chain of left n-alkoxy terminal end group. The absence of an odd-even effect is attributed to the absence of mesomorphic behavior for the shorter chain homologs because odd-even effects diminish with chain length. The mesomorphic properties of the presently investigated novel homologous series 1 are compared with the other structurally similar homologous series X [8] and Y [9].

Homologous series 1 and X are identical in all respects except for the position of the −CO− group of a central bridge linking middle and last (third) phenyl rings i.e. both series consist of three phenyl rings with left n-alkoxy terminal end group and right-sided unsubstituted phenyl ring. The first and middle phenyl rings bridged through −COO− common central group. However the middle and third phenyl rings are bridged through isomeric central groups −CO−CH=CH− and –CH=CH−CO− of series 1 and X, respectively. Hence, the difference of mesomorphic properties and the degree of mesomorphism is attributed to the positional difference of −CO− group between middle and third phenyl ring i.e. −CO− group directly attached to middle phenyl ring and directly attached to third phenyl ring (or away from middle phenyl ring) in case of series 1 and X, respectively. Homologous series 1 and Y are identical in all respects, but they differ in the case of one central bridge linking first (left) and middle phenyl rings i.e. −COO− and −CH=CH−COO− central bridges in case of series 1 and Y, respectively. Therefore, the observed difference in mesomorphic properties and the degree of mesomorphism are attributed [10] to the −CH=CH− unit present in the −CH=CH−COO− central group of series Y, which is absent in case of −COO− central group of series 1. Table 3 represents thermal stability and the commencement of the mesophase for series 1 and the series (X and Y) selected for the comparative study.

On comparing the type of mesophase or mesophases formed by the molecules of series 1 and X, Table 3, indicates that series 1 is only nematogenic while series X exhibits smectic and nematic characters. The smectic and nematic thermal stabilities of series X are 106.66 and 119.8, respectively while that of series 1, the only nematic thermal stability is 164.5, which is much higher than series X. The mesophase formation (nematic) commences from hexyl homolog in series 1, while it occurs from the octyl homolog in case of series X. Thus, only a positional difference of the −CO− group in the isomeric homologous series 1 and X causes such drastic difference. Thus, only shifting of −CO− group in the molecular structure drastically affects the magnitudes of molecular rigidity and flexibility [1–3] and hence the suitable varying magnitudes of the anisotropic intermolecular forces of attraction

Table 3. Average thermal stabilities in °C

	Average transition temperatures in °C		
Series	Series (1)	Series (X)	Series (Y)
Smectic-nematic or smectic-isotropic	—	106.66 (C_{10}-C_{14})	—
Commencement of smectic mesophase		C_{10}	
Nematic-isotropic	164.5 (C_5–C_{16})	119.8 (C_8–C_{16})	155.4 (C_5–C_{16})
Commencement of nematic mesophase	C_5	C_8	C_5

as a consequence of their net molecular polarity, polarizability, length to breadth ratio, molecular geometry, electronic interactions, etc. [4]. Thus in spite of very close molecular similarities, the mesomorphic properties of a substance can be drastically different. Homologous series 1 and Y differ only with respect to central group −CH=CH−COO− and −COO− by −CH=CH− unit between first (left) and middle phenyl rings. Both these central bridges are comparable, though the vinyl carboxylate has a greater length and causes more noncoplanarity due to a twist obtained as the oxygen atoms of the vinyl carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic rings. The enhanced length of the vinyl −CH=CH−COO− central group, increases the conjugation through the −CH=CH− linking group, which should increase the rigidity and lateral attractions, and hence intermolecular attractions should increase by more than the −COO− central bridge. However, cis alkoxycinnamic acids from which final products of series Y are synthesized are nonmesomorphic. The hydrogen bonded n-alkoxybenzoic acids from which molecules of series 1 are formed, whose intermolecular attractions are almost equivalent to the cis isomer of cinnamic derivatives. Therefore the thermal stability of series 1 and Y is 164.5 and 155.4, respectively. Thus, the cis configured isomers of cinnamic acids yield lower magnitudes of intermolecular attractions as compared to the hydrogen bonded ring system of p-n-alkoxybenzoic acids derivatives (−COO− of series 1). Thus, the lower value of thermal stability of series Y than the series 1 under present investigation is justified. The commencement of nematogenic mesophase from pentyl homolog derivative and only nematic mesophase from the hexyl to hexadecyl derivatives with absence of smectogenic character in series 1 and Y, respectively, very well matches from the point of view of nearly equivalent magnitudes of anisotropic forces of intermolecular attractions. Absence of smectogenic property in series 1 in comparison with series X is attributed to the absence of lamellar packing of molecules of series 1 in their crystal lattices due to direct bonding of −CO− part of the group at the middle phenyl ring that inhibits to form lamellar packing of molecule. Hence, smectogenic mesophase formation does not occur until the last homolog of series 1, while presence of lamellar molecular packing in the crystal lattices of the molecules of series X allows smectogenic character from the decyl homolog due to favorable extent of noncoplanarity of the molecules in which −CO− group of −CH=CH−CO− central group linked directly to third phenyl ring of series X, instead of middle phenyl ring of series 1. Thus suitable magnitudes of intermolecular anisotropic forces of attractions are related to proper positioning of a functional group in a molecule or to a part of a functional group. Thus, a variation in mesomorphic properties from series to series is attributed to the variation in central group or groups keeping rest of the molecular part unchanged.

Conclusions

(1) The group efficiency order derived for the nematic mesophase formation is as below.

−CO−CH=CH− with −COO− central group	>	−CO−CH=CH− with −CH=CH−COO− central group	>	−CH=CH−CO− with −COO− central group

(2) Group efficiency order derived on the basis of early commencement of smectic and nematic phase is as below.

Smectic:	−CO−CH=CH− with −COO− and −CH=CH−COO− central group	<	−CH=CH−CO− with −COO− central group

Nematic:	−CO−CH=CH− With −COO− and −CH=CH−COO− central group	>	−CH=CH−CO− with −COO− central group

(3) Variations of mesomorphic properties depend upon the varying molecular rigidity and flexibility.
(4) Mesomorphic properties and the degree of mesomorphism depend upon the positional difference of a functional group or part of the functional group of a central bridge linking phenyl rings.
(5) Variation in mesomorphic properties from homolog to homolog in the same series depends upon the sequentially added methylene unit.
(6) The cis isomer of the −CH=CH−COO− central group yields a poorer degree of mesomorphism than the same homolog containing a −COO− central group at the identical position.
(7) The presence of a −CO− group in any central region directly attached to a phenyl ring does have relatively strong end-to-end intermolecular anisotropic forces of attractions.

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