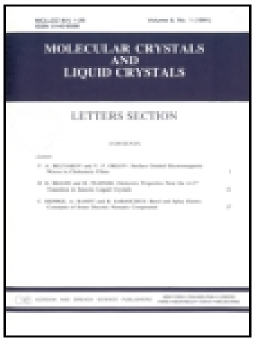

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Study of the mesomorphism of benzoates and cinnamates

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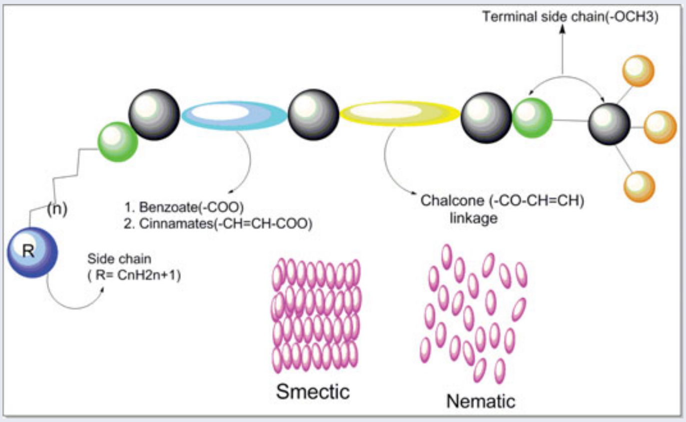
ABSTRACT

Two ester homologous series of carboxy (-COO-) and ethylene-carboxy (-CH=CH-COO-) mesogens, viz. α-4-[4′-n-alkoxybenzoyloxy] phenyl β-4″-methoxy benzoyl ethylenes (1) and α-4-[4′-n-alkoxy cinnamoyloxy phenyl β-4″-methoxy benzoyl ethylenes (2)] are discussed. Series (1) and (2) differ at their central linking group. Mesophase are observed at four and five number members in both homologue series. Enantiotropic nematogenic property is observed in both series (1) and (2), while some smectic property is exhibited in series (2). Thermal stability of nematic-isotropic in series (1) is relatively low as compared to (2), smectogenic property is totally absent in series (2). In phase diagram, solid-nematic, solid-isotropic, and nematic-isotropic curve follow zigzag path rising and falling. Transition temperatures are observed through hot stage polarizing microscope. Analytical data supports the structure of molecules. Threaded, Schlieren-type textures of homologues are observed through microscope.

KEYWORDS

Nematic; liquid crystal; isotropic; smectic

GRAPHICAL ABSTRACT



Introduction

The study of mesogenic property with their molecular structure to varying the terminal side and lateral side has been studied, but less attentiveness has been given to central bridges that link with phenyl rings. Therefore, in the present article, we have focused on the effect of central

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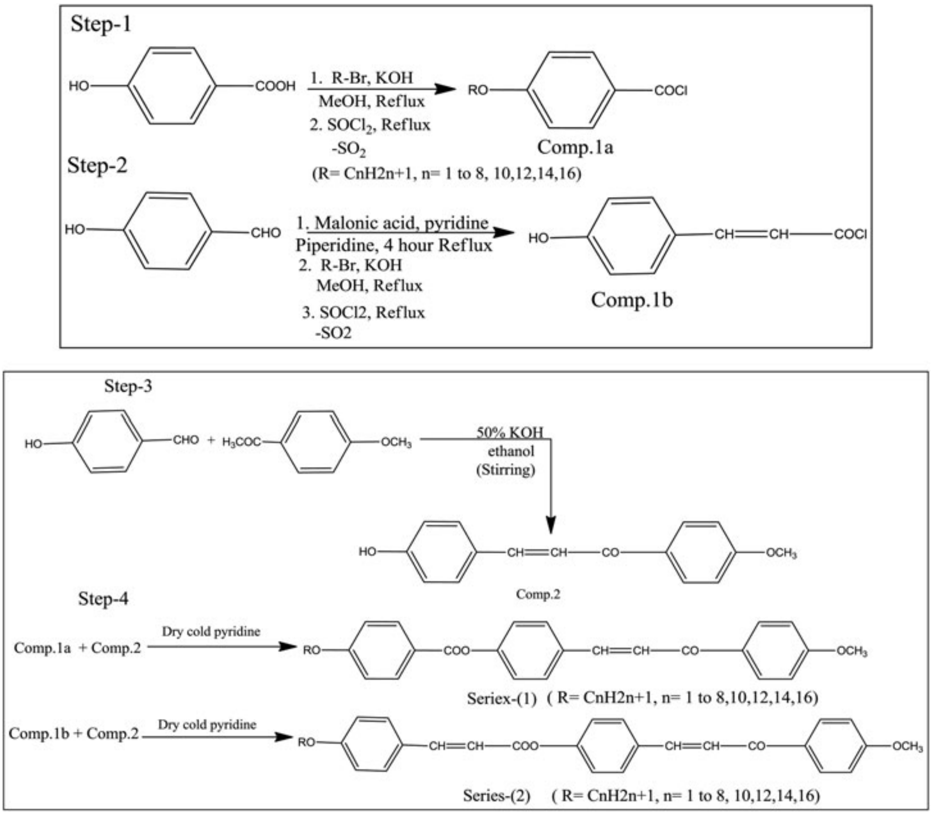
bridge on mesomorphic behavior of molecules varying with different central linkage group. Chalcone is a non-mesomorphic and biologically active compound, but when it linked with 4-n-alkoxy of benzoic acid and 4-n-alkoxy of cinnamic acid, it possesses liquid crystalline (LC) property [1–3].

A number of LC compounds with varying molecular rigidity and flexibility have been reported. Usually, structures consist of two or more rings (aromatic and heterocyclic) through central linkage bridges comprising the rigidity and terminal side chain varying flexible part of the molecule [6–10].

Experimental

4-N-alkoxy benzoyl chloride acid (1a) and 4-n-alkoxy cinnamoyl chloride (1b) acid were synthesized by the modified Dave and Vora method [4]. 3-(4-Hydroxyphenyl)-1-(4-methoxyphenyl) prop-2-en-1-one (2) was prepared by the known method [5]. The final product of series (1) and (2) were synthesized by the condensation of (1a) and (1b) with (2) in dry cold pyridine. Final products of the series were decomposed, filtered, washed, dried, and crystallized from alcohol until transition temperatures were obtained [11,12]. The synthetic route of series (1) and series (2) are given in Scheme 1.



Scheme 1. Synthetic route of preparation of series (1) and (2).

Characterization

Transition temperatures of the homologues of series (1) and (2) are determined by hot stage polarizing microscope. Infrared (IR) and nuclear magnetic resonance (NMR) spectra of evocative homologues of the series under comparison confirms the structure of the molecules. Analytical data support the structures. IR spectra were recorded on Perkin-Elmer spectrum GX, and ^{1}H NMR spectra were recorded on a Bruker spectrometer using $CDCl_3$ as solvent.

Spectral data confirm the structure of homologue in both series (1) and (2).

NMR in δ ppm (series (1))

Octyloxy derivative: 0.983 (–CH_3 of –OC_8H_{17}), 1.422 (–(CH_2)n– of –OC_8H_{17}), 3.675 (-OCH_2 of –OC_8H_{17}), 6.565 and 6.582 (-CH=CH–CO-), 7.404, 7.093, and 7.636 (phenyl ring).

Dodecyloxy derivative: 0.945 (—CH_3 of $OC_{12}H_{23}$), 1.465 (–(CH_2)n– of –$OC_{12}H_{23}$ group), 3.689 (-OCH_2 of –$OC_{12}H_{23}$), 6.575 and 6.669 (-CH=CH–CO-), 6.691, 7.610, and 7.632 (phenyl ring).

IR in cm^{-1} (series (2))

Hexyloxy derivative: 720 (–(CH_2)n– of –OC_6H_{13}), 815 (phenyl ring), 1175 (C–O of –OC_6H_{13}), 1215, 1260, and 1640 (-COO-), 930 (-CH=CH–).

Decyloxy derivative: 760 (–(CH_2) n– of –$OC_{10}H_{21}$), 830 (phenyl ring), 1150 (C–O of –$OC_{10}H_{21}$), 1250, 1610, and 1680 (-COO-), 945 (-CH=CH-).

NMR in δ ppm (series (2))

Octyloxy derivative: 0.887 (–CH_3 of -OC_8H_{17}), 1.288 (–(CH_2)n of -OC_8H_{17}), 4.019 (-OCH_2-CH_2 of C_8H_{17}); 3.889 -OCH_3, 4.86 (-CH=CH-), 6.943 and 8.036 p-sub. phenyl ring.

IR in cm^{-1}(series (2))

Hexyloxy derivative: 1700, 1260 (-COO-) group, 820 (p-sub. phenyl ring), 1120 (-CO- of alkoxy).

Dodecyloxy derivative: 1200, 1250, 1670 (-COO-) group, 1150 (-CO- group), 820 (p-sub. phenyl ring), 720(-(CH_2)n of $C_{12}H_{25}$.

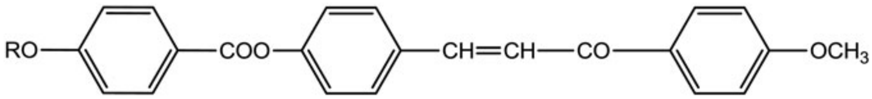
Result and discussion

4-N-alkoxy benzoic acids and 4-n-alkoxy cinnamic acids are dimeric in nature, wherein two molecules are linked through hydrogen bonding during esterification; dimerization disappears due to breaking of hydrogen bonding. The first five homologues (methyl to pentyl) in both series are non-mesogenic due to high crystallity of left short flexible part side chain, which arises from relatively stronger intermolecular fascination generated as a consequence of unsuitable magnitude of molecular rigidity and flexibility, which neither allow statistically parallel orientational order of molecules nor it tolerates layered arrangement (two-dimensional) of molecules in fluctuating condition, and seven number homologue in series (2) could not showed mesophase both linked to benzoates and cinnamates central linkage in series (1) and (2).

Homologues of series (1) are giving smectic and nematic mesophase, while homologues of series (2) exhibit nematogenic character without lacking any smectic mesophase. Phase diagrams for transition temperature versus the number of carbon atoms in n-alkoxy terminal in both series (1) and (2) are plotted and mention in Figure 1 and Figure 2 respectively.

In Fig. 1, the solid-isotropic curve rises and falls as the series ascends with an overall falling nature. The smectic–nematic transition curve initial rises, passes through maxima, and then

Series-1



α–4–[4'-n-alkoxy Benzoyloxy] Phenyl-β–4"-Methoxy benzoyl ethylenes

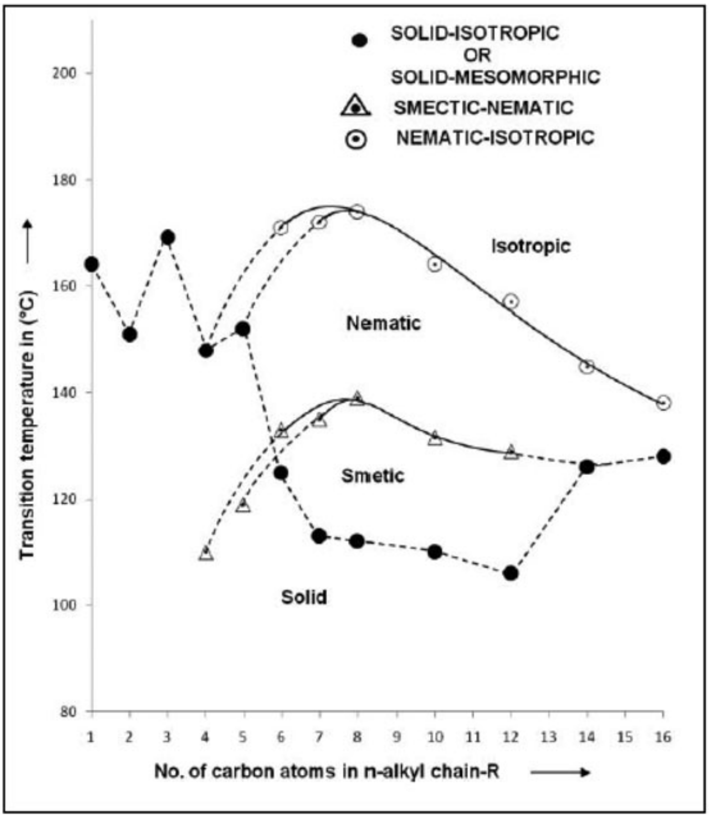


Figure 1. Phase diagram of series (1).

falls in usual manner up to the decyloxy homologue, but it rises by 1° in dodecyl derivative. The curve is extrapolated to pentyl, butyl, and tetradecyl derivatives to forecast their latent transition temperatures (LTT) for the smectic phase, which are exhibited monotropically as 111, 118, and 126°C respectively. The curve shows very narrow range of odd-even effect. Nematic–isotropic transition curve behaves in usual manner with an odd-even effect. In Fig. 2, the curve of solid-nematic or isotropic transition curve adopt a zigzag path of rising and falling with alternation of transition temperature (Table 1) as series is ascended and behaves in a normal expected manner [13–15].

The cis-p-n-alkoxy cinnamic acids are non-mesomorphic as they do not form linear dimers. Trans-p-n-alkoxy cinnamic acid exhibits more thermally stable phase as compared to p-n-alkoxy benzoic acid due to its high polarizability and dimeric nature with -CH=CH- units [16,17,18].

Here we compare two series containing the same long narrow molecule and differ at central bridges group associated with permanent dipole moment and its polarizability that exhibits high degree of mesomorphism. The polarizability of an atom increases with increasing atomic

Series-2:

α-4-[4'-n-alkoxy cinnamoyloxy phenyl β-4"-methoxy benzoyl ethylenes

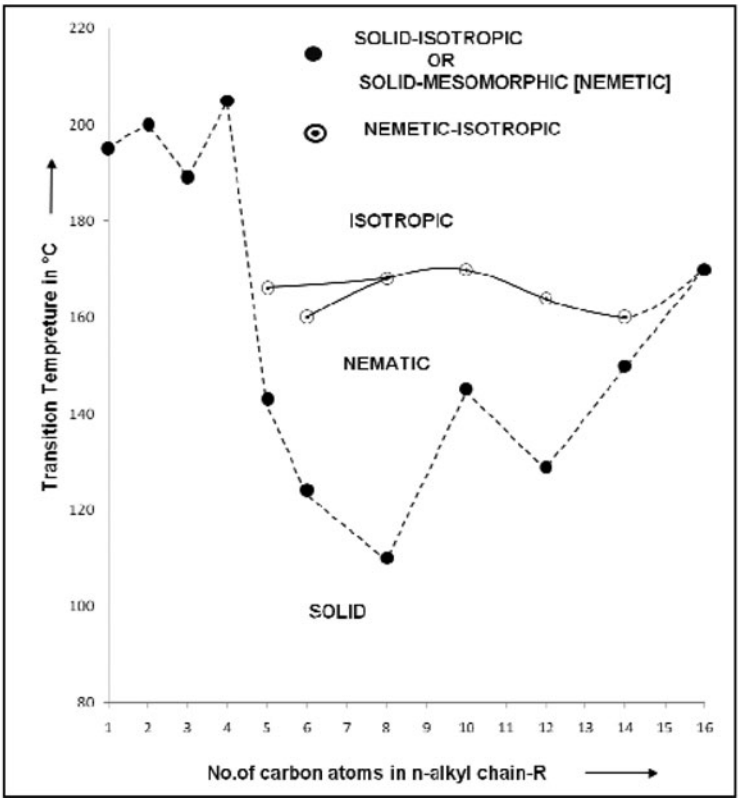


Figure 2. Phase diagram of series (2).

Table 1. Transition temperatures of homologous series (1) and (2).

Sr. No.	n-alkyl group	Transition temperature (°C)					
		Smectic Series		Nematic Series		Isotropic Series	
		(1)	(2)	(1)	(2)	(1)	(2)
1.	C1	—	—	—	—	164.0	195.0
2.	C2	—	—	—	—	151.0	200.0
3.	C3	—	—	—	—	169.0	189.0
4.	C4	—	—	—	—	148.0	205.0
5.	C5	—	—	—	143.0	152.0	166.0
6.	C6	125.0	—	133.0	124.0	171.0	160.0
7.	C7	113.0	—	135.0	—	172.0	—
8.	C8	112.0	—	139.0	110.0	174.0	168.0
10.	C10	110.0	—	131.5	145.0	164.0	170.0
12.	C12	106.0	—	129.0	129.0	157.0	164.0
14.	C14	—	—	126.0	150.0	145.0	160.0
16.	C16	—	—	128.0	—	138.0	170.0

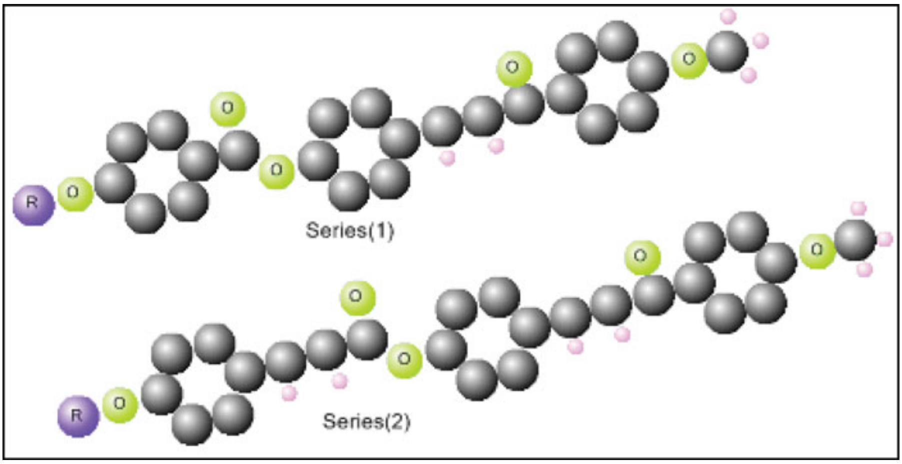


Figure 3. 3D atomic model of series (1) (2).

radius and the bond presented in-between two atoms. If bond order increases, its polarizability also increases. The 3D-model diagram (Fig. 3) shows the arrangement of group in space

Chalcone forms the central core (-CH=CH-CO-) and biologically active compounds. Chalcone are α, β-unsaturated ketone containing ethylene group. It has been studied that -CO-CH=CH- linkage is less conductive to mesomorphism compared to -COO-(ester) and -CH=CH-COO (vinyl ester). The increasing molecular breadth forces at left of molecules decrease interactions. This changes the property with linking to carbonyl and ethylene groups in chalcone derivative. In our previous work, we reported the ester-chalcone base homologous series; in this paper, we have focused on the effect of central linkage group ester (-COO-) and vinyl ester (-CH=CH-COO-) in the present series under comparison.

The geometrical shape of molecules is linear rod-like without any lateral substitution in both series (1) and (2) as shown in Fig. 4. The linearity of both the series are compared with respect to linking group –COO– in series(1) and –CH=CH–COO– in series (2). In Figure 5, it represent the graphical arrangement of molecular layered packing in smectic phase in both homologues series.

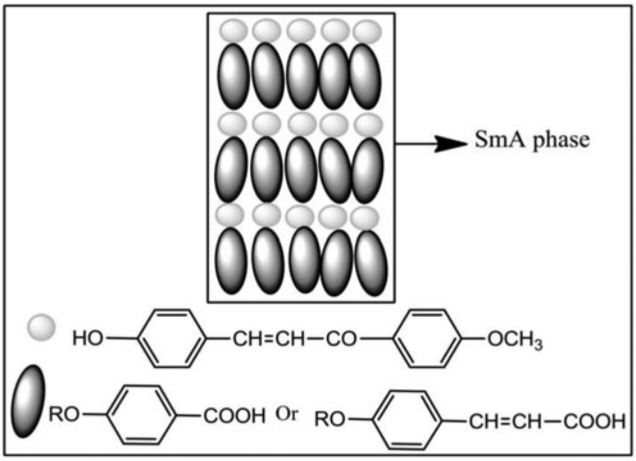


Figure 4. Proposed molecular packing of SmA phase of some homologues in series (1) and (2).

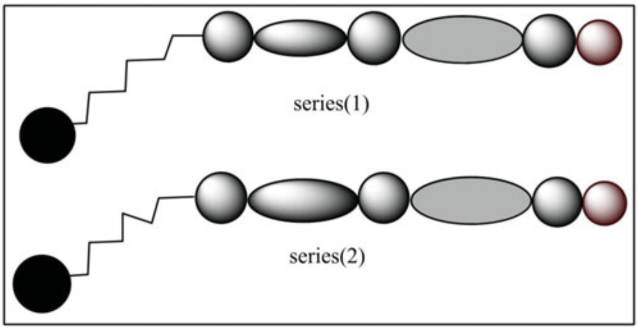


Figure 5. In figure 4, it represent the graphical arrangement of molecular layered packing in smectic phase in both homologues series.

On comparing, the transition temperature of series (1) is lower than the transition temperature of series (2) for the same homologue in both the series. This is affected by the presence of -CH=CH- units in cinnamates in series (2) and directly linked to the difference in the intermolecular forces of attractions and polarity and polarizability of molecules.

The average thermal stability of the smectic–nematic or isotropic is 133.4, and it commences with smectic phase at $C_{6.}$ In series (2), smectic phase is totally absent. The nematic-isotropic thermal stability for series (2) is more than series (1).

Chalcone is a non-mesogenic compound, but its shows in LC phase when it scaffolds with central core of benzoates and cinnamates and dependent on non-coplanarity caused by molecules. The terminal side in both the series -CH=CH-CO- is the same. Presence of double bond causes the isomerism and arrangement of atoms in space, may operate and create such an extent of non-coplanarity of molecules that smectic mesophase is observed, while in the late commencement of array, the nematic mesophase is exhibited due to orientational order of molecules in space through in-floating conditions.

The type of mesomorphic phase of series (1) and (3) (4-(3-phenylacryloyl) phenyl 4-n alkoxy benzoates) with their molecular structures is compared as follows.

Series (3) exhibits both smectic and nematic mesophase. Series (1) and (3) have the same central core -COO- and gives smectic and nematic properties, but the thermal stability of smectic phase in series (1) is lower than in series (3), while the thermal stability of nematic phase in series (3) is higher than in series (1). The carbonyl group is committed with the third phenyl ring in series (1) and linked directly with middle phenyl ring in series (3). The -CO- group linking with the middle and third phenyl rings bonded through -CH=CH- immediately at the third phenyl ring gives greater coplanarity. The -CO-CH=CH- central group maintains more molecular coplanarity than the -CO-CH=CH- central group. However, the lamellar packing of molecules in their crystal lattices can be enhanced by the -CH=CH-CO- group more than than the -CO-CH=CH- central core. Both groups are comparable with equal lengths and cause more or less non-coplanarity due to a twist obtained as the oxygen atoms of the -CO- group to non-bonded adjacent hydrogen atoms of the middle and third phenyl ring.

Smectic group efficiency
-COO- > -CH=CH-COO-
-CH=CH-CO- > -CO-CH=CH-
Nematic group efficiency
-CH=CH-COO- > -COO-
-OCH_3 with -CO- side at -CH=CH-CO- > -OCH_3 with -CO-CH=CH-

Conclusions

In summary, we examined that ester homologous series are not necessarily smectogenic but it may be entirely smectogenic or entirely nematogenic or partly smectogenic or partly nematogenic. We should compare the effect of ester linkage group in series (1) and the vinyl ester group in series (2) as linked with the chalcone linkage group. We were able to compare the mesomorphism property of series (1) and (2) with series (3), which determine the effect of linking group -CO-CH=CH- at both ends.

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