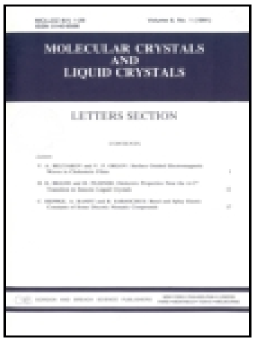

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Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: B. H. Patel, V. R. Patel & A. V. Doshi (2015) Mesomorphism Dependence on Molecular Flexibility by –OCH_3 and –H Terminal Units, Molecular Crystals and Liquid Crystals, 609:1, 10-18, DOI: 10.1080/15421406.2014.953743

To link to this article: http://dx.doi.org/10.1080/15421406.2014.953743

Mol. Cryst. Liq. Cryst., Vol. 609: pp. 10–18, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.953743

Mesomorphism Dependence on Molecular Flexibility by –OCH_3 and –H Terminal Units

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A novel ester homologous series: 4-(4’-n-Alkoxy benzoyloxy)-4”-methoxy benzyl cinnamates have been synthesized and studied with a view to understanding and establishing the dependence of liquid crystal behavior on molecular structure. The novel series of eleven homologues is entirely nematogenic without exhibition of any smectogenic character from the very first member of the series. Transition and melting temperatures were determined by an optical polarizing microscopy equipped with a heating stage. Transition curves of a phase diagram show the mesomorphism, which behaves in normal manner. An odd-even effect is exhibited by the nematic–isotropic transition curve. The textures of the nematic mesophase are threaded or schlieren in type. Analytical and spectral data confirm the molecular structures of the novel homologues. Thermal stability for the nematic phase is 211.5°C and the degree of mesomorphism varies from 17°C to 72°C and it is a high melting type series. Mesomorphic properties of the series are compared with structurally similar series.

Keywords Liquid crystals; mesomorphism; mesomorphs; nematic; smectic

Introduction

The study of liquid crystalline state [1, 2] is very important because of applications in the fields of electronic display devices, medical instruments, agriculture, pharmaceuticals preparations, dyes, plastics, and textiles [3–6] arising from a dual role of flow as a liquid and of molecular ordering that orients under the influence of electric and/or magnetic field [7, 8]. Therefore, such a unique state of matter between crystalline state and isotropic liquid state is studied with keen interest by the chemists, physicists, biologists, pharmacists, agriculturists, and technologists with different aims. A chemist has to study and synthesize novel liquid crystalline (LC) materials, to characterize their structures and textures, its mesomorphic phase length and to establish the relation between molecular structure and LC properties of a material of either thermotropic or lyotropic type [9–11]. Other researchers exploit the LC state of novel substances with different aims and objectives [12, 13]. The present study is aimed to synthesize novel thermotropic LC substances derived from derivatives of benzyl alcohol to study their LC properties by polarizing microscopy, to characterize their structure and textures and finally to correlate and to establish the relation between LC behavior and the molecular structure on the basis of molecular rigidity and flexibility [14–17].

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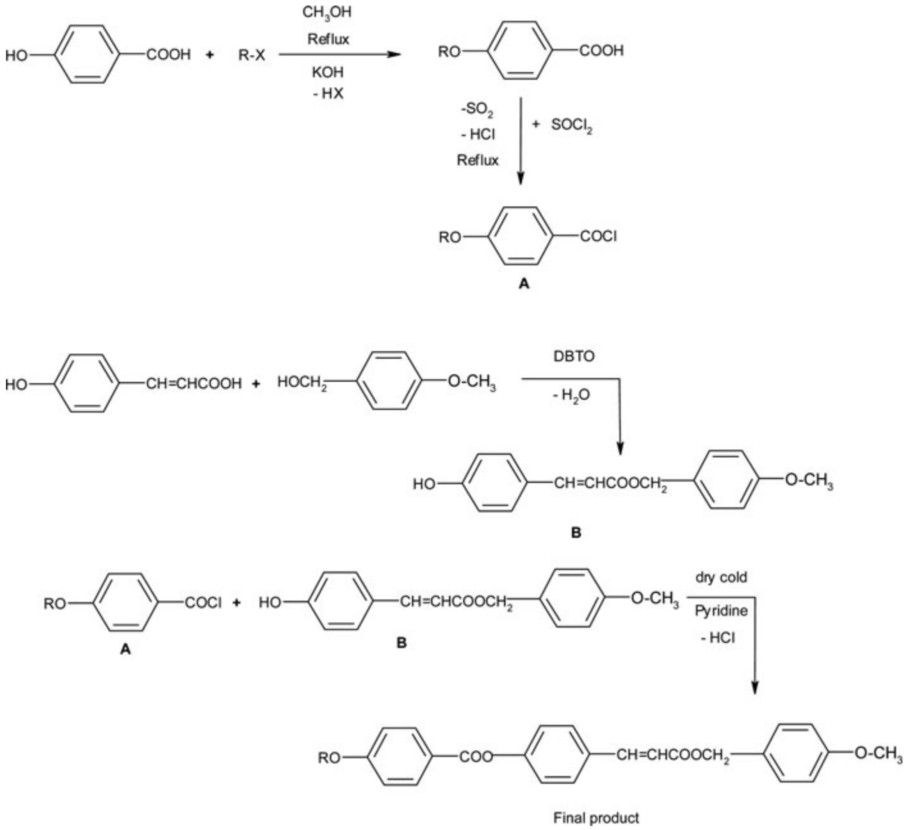
Experimental

Synthesis

4-Hydroxy benzoic acid was converted to 4-*n*-alkoxy benzoic acids using suitable alkylating (*R-X*) agents by modified method of Dave and Vora [18]. 4-Hydroxy cinnamic acid was converted to 4-hydroxy-4'-methoxy benzyl cinnamate by the modified method of European patent EP0117502B1 [19]. 4-*n*-alkoxy cinnamic acids were individually condensed with 4-hydroxy-4'-methoxy benzyl cinnamate (m.p. 204°C, yield is 35%) in pyridine through their acid chlorides in dry cold pyridine [20]. Final products were individually decomposed, filtered, washed dried, and purified in ethanol until constant transition temperatures were obtained. Transition and melting temperatures were determined by an optical hot stage polarizing microscopy.

The chemicals 4-hydroxy cinnamic acid, 4-methoxy benzyl alcohol, dibutyltin oxide, pyridine, alkyl halides, MeOH, EtOH, thionyl chloride, HCl, and KOH were used as received, except solvents, which 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. Where $R = C_nH_{2n+1}$; $n = 1,2,3,4,5,6,8,10,12,14,16$.

Characterization

Some selected members of the present novel series were characterized by elemental analysis, infra red spectra, ^{1}HNMR spectra, and mass spectra. Micro analysis was performed using a Perkin-Elmer PE 2400 CHN analyzer, ^{1}HNMR spectra were recorded on a Bruker instrument using dimethyl sulfoxide solvent. Infrared spectra were recorded on Perkin Elmer spectrum GX spectrometer. Transition temperatures and the textures of the nematic mesophases were determined by a miscibility method through an optical polarizing microscope equipped with a heating stage.

Analytical Data

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

		Elements % found (% calculated)	
Sr. no.	Molecular formula	C	H
1	$C_{25}H_{22}O_6$	71.55 (71.77)	5.18 (5.26)
2	$C_{26}H_{24}O_6$	72.17 (72.22)	5.28 (5.55)
3	$C_{27}H_{26}O_6$	74.60 (72.64)	5.71 (5.82)

Spectral Data

^{1}HNMR in ppm for the decyloxy Derivative: 0.85–1.76 (H of $C_{10}H_{21}$), 2.51 ($-O-CH_2-CH_2$ of $-OC_{10}H_{21}$), 3.73 ($-OCH_3$), 3.98 ($-O-CH_2$ of $-O-C_{10}H_{21}$), 5.04 ($-CH{=}CH-$), 6.51 (p-substituted benzene ring) 6.9–8.09 (indicates presence of more than one benzene rings).

^{1}HNMR in ppm for the dodecyloxy Derivative: 0.80–1.67 (H of $C_{12}H_{25}$), 2.50 ($-OCH_2-CH_2$ of $-OC_{12}H_{25}$), 3.7 ($-OCH_3$), 3.95 ($-O-CH_2$ of $-O-C_{12}H_{25}$), 5.06 ($-CH{=}CH-$), 6.51 (p-substituted benzene ring), 6.9–7.7 (presence of more than one benzene rings).

IR in cm^{-1} for tetradecyloxy Derivative: 831 parasubstituted phenyl ring, 1216 ether linkage of ($-C_{14}H_{29}-O-C_6H_4$), 1171, 1238,1686 ($-COO-$ester group), 981 (trans $-CH{=}CH-$).

IR in cm^{-1} for hexadecyloxy Derivative: 830 para-substituted phenyl ring, 1217 ether linkage of ($-C_{16}H_{33}-O-C_6H_4$), 1171, 1238, 1685 ($-COO-$ester group), 981 (trans $-CH{=}CH-$).

Mass Spectra

Mass spectra for butyloxy Derivative: Molecular formula $C_{28}H_{30}O_6$ Calculated Molecular weight 460. Practical mass observed by Mass spectroscopy 460.

Texture of Nematic by Miscibility Method

Pentyloxy derivative ——————→Threaded nematic

Table 2. Transition temperatures of series in °C

		Transition temperature in °C		
Compound no.	*n*-alkyl group ($-C_nH_{2n+1}$) (*n*)	*Sm*	*N*	Isotropic
1	1	—	193.0	226.0
2	2	—	127.0	190.0
3	3	—	163.0	235.0
4	4	—	183.0	212.0
5	5	—	188.0	214.0
6	6	—	172.0	213.0
7	8	—	181.0	213.0
8	10	—	166.0	230.0
9	12	—	174.0	198.0
10	14	—	183.0	200.0
11	16	—	170.0	196.0

Sm: Smectic *N:* Nematic.

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

Results and Discussion

All the eleven members of the novel series are enantiotropcially nematogenic without the exhibition of any smectogenic character. Transition temperatures, melting temperatures, and texture of mesophase were determined by an optical polarizing microscopy, equipped with a heating stage. Transition and melting temperatures (Table 2) of homologues were plotted versus the number of carbon atoms present in *n*-alkoxy terminal end group. Like or related points were linked to form solid-nematic and nematic–isotropic transition curves to construct a phase diagram (Fig. 1) showing phase behaviors of a novel series. The solid-nematic transition curve adopts a zigzag path of rising and falling values and behaves in the usual established manner. The nematic–isotropic transition curves for odd and even homologues initially rise and then descend as series is ascended with exhibition of an odd-even effect. The transition temperatures for the odd members are relatively higher than the even members. The N-I transition curves for the odd and even homologues merge into each other at the hexyloxy homologue and then a single curve results from and beyond hexyloxy homologue. Thus, the N–I transition curve behaves in a normal manner. Mesomorphic behavior of the present series varies from homologue to homologue with alternation of transition temperatures. The novel homologous series is nematogenic without exhibition of a smectogenic mesophase. The nematogenic mesophase length varies between 17°C and 72°C giving a wide degree of mesomorphism and a high melting type. Disappearance of dimerization between two molecules of 4-*n*-alkxoy benzoic acids is due to the breaking of hydrogen bonding on esterification. 4-Hydroxy-4'-methoxy benzyl cinnamate (m.p-204°C, yield 33%) is a nonliquid crystal component, but on linking it with 4-*n*-alkoxy benzoic acids through their acid chlorides increases molecular length and the lateral attractions that result in inducing nematogenic mesomorphism throughout the entire series with elimination of

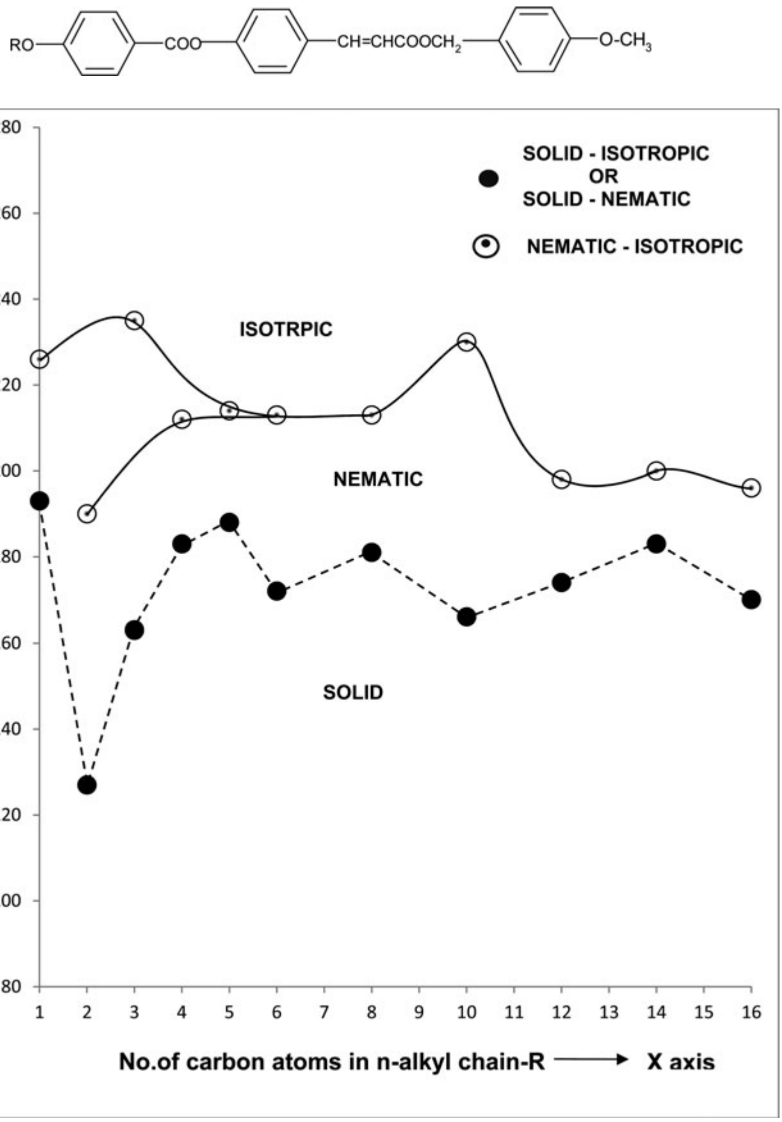


Figure 1. Phase behavior of series. Series: 4-[4'-*n*-Alkoxy benzoyloxy]-4"-methoxy benzyl cinnamates.

smectogenic character from the smectogenic homologues (C_7–C_{16}) of 4-*n*-alkoxy benzoic acids and induced nematogenic character in nonmesomorphic homologues of 4-*n*-alkoxy benzoic acids (C_1 and C_2). Elimination of smectogenic character from 4-*n*-alkoxy benzoic acids on esterification is attributed to the unsuitable magnitudes of molecular rigidity and flexibility which hinders the formation of lamellar packing of molecules in their crystal lattice. However, the magnitudes of molecular rigidity and flexibility are sufficient for all the members of a series to maintain suitable magnitudes of intermolecular end-to-end attractions which allow statistically parallel orientational order of molecules within definite range of temperatures. Thus, nematic mesophase formation is favored to appear.

Table 3. Average thermal stability in °C

Series→	Series 1	Series X
Smectic-nematic or Smectic-isotropic		144.1 (C_6–C_{16})
Commencement of smectic phase	—	C_6
Nematic-Isotropic	211.54 (C_1–C_{16})	171.4 (C_5–C_{16})
Commencement of nematic phase	C_1	C_5
Total mesophase	17°C to 72°C	33°C to 53°C
Range from t_1 to t_2	C_{14} C_{13}	C_6 C_{16}

Alternation of transition temperatures from homologue to homologue in a series and the appearance of odd-even effect in N-I transition curve is due to the sequential addition of methylene unit or units in *n*-alkyl chain bonded to phenyl ring through oxygen atom. Disappearance of odd-even effect from and beyond hexyloxy and higher homologues with longer *n*-alkyl chain is attributed to the coiling, bending, flexing, or coupling of *n*-alkyl chain with the major axis of the core structure of higher homologue molecules. Variations of mesomorphic behaviors from homologue to homologue in present series is attributed to the changing number of carbon atoms in C_nH_{2n+1} chain of left terminal end group keeping right ended –OCH_3 terminal end group unchanged. Higher values of melting and transition temperatures (Table 2) are due to the linear lath like shape and presence of highly polar –OCH_3 end group relatively longer size of molecules without lateral substitution that reduces intermolecular closeness and raises intermolecular attractions. Consequently, a high magnitude of heat energy, i.e., higher temperature is required for disruptions of molecules. Higher molecular rigidity due to presence of conjugated double bond containing central group, withstands externally exposed thermal vibrations and increases nematogenic mesophase length maximum of 72°C at the propyloxy homologue. Following Table 3 represents some mesophase behaviors of present series as under in comparative manner with structurally similar homologous series-X [21] as shown in Fig 2.

Homologous series-X chosen for comparison and presently investigated novel series-1 are structurally similar (Fig. 2) and identical with respect to three phenyl rings and two central bridges —COO— and —CH=CH—COO—CH_2- sharing their contribution mainly to the molecular rigidity in equal proportion from series to series. However, the molecular flexibility by –OR, —OCH_3, and —H are varied from series to series for same homologue and from homologue to homologue in the same series. Therefore, suitable magnitudes of anisotropic forces of intermolecular end-to-end and lateral attractions are varied from series to series for the same homologue and homologue to homologue in the same series. Thus, variations in mesomorphic behaviors and the degree of mesomorphism are attributed

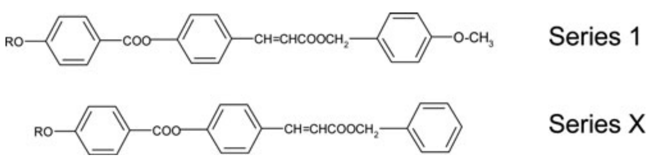


Figure 2. Structurally similar homologous series.

to the changing molecular part of the series 1 and X under comparison, affecting molecular flexibility in combination with molecular rigidity. Changing molecular flexibility by *n*-alkyl chain ($C_nH_{2n+1} = R$-), keeping $-OCH_3$ or –H unchanged, vary mesogenic properties from homologue to homologue in the same series but variation in flexibility by replacement of –H (series-X) by $-OCH_3$ (series-1) cause variations in mesogenic properties for the same homologue from series to series. Table 3 represents the difference of thermal stabilities, commencement of mesophase or mesophases, mesophase lengths, or range etc. as under.

- Homologous serie-1 is entirely nematogenic without exhibition of smectogenic property, whereas homologous series-X is predominantly nematogenic and partly smectogenic.
- Nematogenic mesophase commences from the very first member of series-1, while it commences from the fifth member of a series-X.
- Smectic mesophase commences from a sixth member of a series-X, while it does not commence till the last member of series-1.
- Mesophase length of a series-1 is relatively wider than a series-X.
- Thermal stability for the nematogenic mesophase formation of series-1 is higher than a series-X chosen for comparison.
- Smectogenic mesophase stabilizes in case of series-X with absence of mesophase formation (either smectic or nematic phase) prior to pentyloxy homologue of a series-X, while mesophase formation occurred (only nematic) from very first to last member of a present series-1 with none of the member of series as nonmesomorphic.

Suitable magnitudes of anisotropic forces of intermolecular attractions (either only end-to-end or including lateral) and favorable closeness as a consequence of molecular rigidity and flexibility can induce either only nematic or only smectic or smectic in addition to nematic property. The observed differences of mesomorphic behaviors for the same homologue from series to series (1 to X) are attributed to the difference between two right hand sided terminal end groups in which –H (series-X) is replaced by $-OCH_3$ (series-1). The group polarity of $-OCH_3$ terminal and its contribution to molecular length are obviously more than a terminal –H. Therefore, suitable magnitudes of anisotropic forces of intermolecular end to end attractions, extent of noncoplanarity tendency to form lamellar packing of molecules in their crystal lattices for the same homologue vary from series 1 to X. Thus, the resistivity against externally exposed thermal vibrations, thermal stabilities, commencement of mesophase formation mesomorphic phase length and the type or types of mesophase vary accordingly. The presence of penta atomic $-OCH_3$ terminal end group though favors the statistically parallel orientational order of molecular floating on the surface with higher resistivity, facing exposed thermal vibrations more effectively than a terminal end group –H of series-X to stabilize and to facilitate nematic phase, but it hinders the formation of lamellar packing of molecules (of series-1) to stabilize and facilitate three-dimensional network in solid crystal or two-dimensional molecular network as sliding layered network in floating condition due to unsuitable extent of molecular noncoplanarity. Thus, molecules of entire series-1 are only nematogenic without exhibition of smectic property. However, on replacing penta atomic $-OCH_3$ (series-1) by monoatomic terminal end group –H offers, relatively unhindered and favorable intermolecular anisotropic forces of attractions of such a suitable magnitudes, that, two-dimensional molecular network as sliding layers floating on the surface are facilitated to form a smectic mesophase from the hexyloxy homologue of series-X, in addition to nematogenic mesophase. Thus, apart from more or less magnitudes of anisotropic forces of intermolecular attractions to induce liquid crystal property, a suitable magnitudes of anisotropic forces of intermolecular end to end or/and lateral attractions required to induce smectic or/and nematic phase which is an important, as a consequence of favorable molecular rigidity and/or flexibility depending on molecular structure. Hence, excessive polarity and flexibility of –OCH_3, terminal end group can enhance thermal stability for nematic, early commencement of nematic phase and relatively wider nematogenic phase length, but, fails to build up lamellar packing of molecules in their crystal lattices to induce smectic mesophase as compared to terminal end group –H of series-X. The molecules of series-X though induces smectic mesophase, in addition to nematic phase but mesophase length range is relatively shorter than series-1, because of the low resistivity against externally exposed thermal vibrations due to weakly polar end group –H as compared to –OCH_3.

Thus, variations in mesomorphic behaviors from homologue to homologue in the same series and, the series to series for the same homologue are due to the changing number of carbon atoms in *n*-alkyl chain of –OR terminal end group and varying terminals –OCH_3, -H for the same homologue from series to series, respectively.

Conclusions

- Group efficiency order derived for smectic and nematic on the basis of (i) thermal stability and (ii) the early commencement of smectic and nematic phase are as under.

  i. Smectic: $-H > -OCH_3$
  Nematic: $-OCH_3 > -H$
  ii. Smectic: $-H > -OCH_3$
  Nematic: $-OCH_3 > -H$

- Presently investigated ester homologous series using para-substituted benzyl alcohol is entirely nematogenic without exhibition of smectogenic character, whose mesophase lengths are relatively wider and high melting type.
- Suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of favorable molecular rigidity and flexibility can induce possibility of mesophase formation in a substance.
- Molecular rigidity and flexibility of a molecular structure are very sensitive and susceptible to induce liquid crystal property in a substance.
- Variations in mesomorphic behaviors from homologue to homologue in the same series depend on changing part of a molecule and solely depend upon molecular structure.
- Presently investigated novel substances may be useful as bioactive molecules.

Acknowledgments

The authors acknowledge thanks to the Green Circle Inc. Lab for research facilities services as and when needed. The authors also thank Dr. Umed Bhoya for his valuable helping hand and microscopic facility. Thanks are due to the Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh for analytical services.

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