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Synthesis and Mesogenic Behavior of Novel Liquid Crystals With a –CH=CH–CO– Central Bridge

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A novel homologous series α-3-[-4′-n-alkoxy benzoyloxy] phenyl-β-4′′-methoxy benzoyl ethylene, which consists of 11 members, has been synthesized and the mesomorphic behavior studied in relation to the molecular structure. The pentyl to hexadecyl homologues are mesomorphic and the remaining homologues are non-mesomorphic. The pentyl, tetradecyl, and hexadecyl derivatives are only enantiotropic nematic, while the hexyl, octyl, decyl, and dodecyl homologue derivatives exhibit smectic mesomorphism in addition to the enantiotropic nematic phase. The transition and melting temperatures were determined by an optical polarizing microscope with a heating stage. Analytical and spectral data confirm the molecular structures. The texture of the nematic phase is of the threaded or Schlieren type and that of the smectic mesophase is a typical smectic A phase. The transition curves of the phase diagram behave in normal manner without showing an odd–even effect. The smectic and nematic thermal stabilities are 129.5°C and 150.7°C, respectively. The novel series is partly smectogenic and predominantly nematogenic with a middle-ordered melting type whose mesomorphic phase length varies from 7°C to 46°C. The mesomorphic properties are compared with other structurally similar homologous series.

Keywords Liquid crystals; mesogen; mesomorphic; nematic; smectic

Introduction

Liquid crystalline materials are useful in electronic devices (LCDs), medical thermographic instruments, pharmaceutical preparations, and the textile industry. The exhibition of the liquid crystalline state by a substance depends upon its molecular rigidity and flexibility [1–3], which in turn directly depends upon its molecular geometrical shape, size, aromaticity, polarity, and polarizability of the terminal, lateral, and central groups, which induce suitable magnitudes of anisotropic intermolecular forces of attractions [4] as a consequence of the molecular rigidity and flexibility [1–3]. Thus, the present investigation is aimed at understanding and establishing the relationship between the liquid crystal (LC) state formation and molecular structure by synthesizing novel substances with a left *n*-alkoxy(–OR) and

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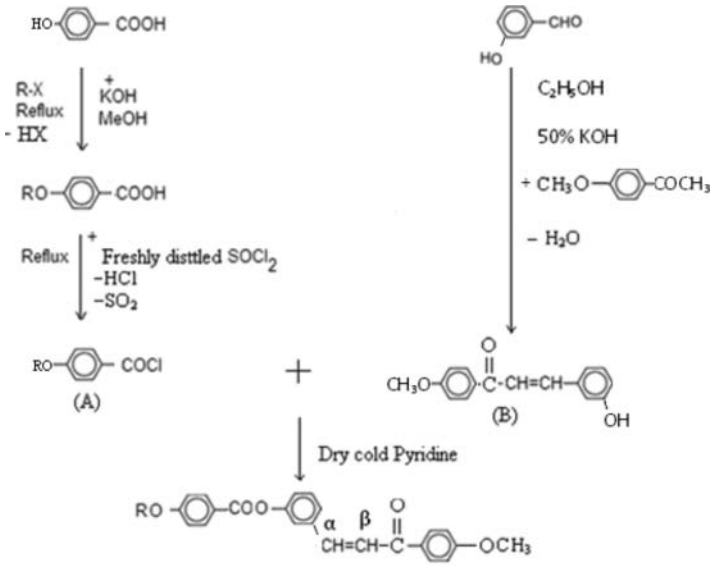
a right $-OCH_3$ terminal end groups without any lateral substitution with three phenyl rings bridged through –COO– and –CH=CH–CO– central groups in a non-linear shaped molecule. Hence, the effect of the non-linear shaped molecule inducing different magnitudes of polarizability in comparison with a linear molecule is studied. Thus, the liquid crystalline properties will be discussed and evaluated in comparison with known series.

Experimental

Synthesis

4-Hydroxybenzoic acid is alkylated by suitable akly halides to prepare 4-*n*-alkoxybenzoic acids. The dimerized *n*-alkoxybenzoic acids were converted to corresponding 4-*n*-alkoxybenzoyl chlorides (A) using freshly distilled thionyl chloride by a modified method of Dave and Vora [5]. α-3-Hydroxy phenyl-β-4′-methoxy benzoyl ethylene (B) was prepared by reacting 3-hydroxybenzaldehyde with 4-methoxyacetophenone by the usual established method [6,7]. Components (A) and (B) were condensed in dry cold pyridine by an established method [8]. The final products of each homologue were decomposed filtered, washed, dried, and purified by crystallization until constant transition temperatures were obtained by an optical polarizing microscope with a heating stage. Synthetic route to the series is shown in Scheme 1.



Scheme 1. The synthetic route to the novel series.

Characterization

A selected number of representative homologues were characterized by elemental analysis, Infrared (IR) and ^{1}HNMR spectroscopy. Microanalysis was performed on a Perkin-Elmer PE 2400 CHN analyzer (Vaibhav Lab. Ahmedabad, Gujarat) as shown in Table 1. IR spectra were recorded on Perkin-Elmer spectrum GX instrument (Punjab University, Chandigarh).

Table 1. Elemental analysis for propyloxy, pentyloxy, decyloxy, and hexadecyloxy derivatives

Sr. no	Molecular formula	Elements % found (% Calculated)	
		C	H
1	$C_{26}H_{24}O_5$	75.03 (75.00)	5.81 (5.77)
2	$C_{28}H_{28}O_5$	75.71 (75.68)	6.33 (6.30)
3	$C_{33}H_{38}O_5$	77.02 (77.05)	7.36 (7.39)
4	$C_{39}H_{50}O_5$	78.29 (78.26)	8.38 (8.36)

^{1}HNMR spectra were recorded using $CDCl_3$ as the solvent. LC properties were determined by an optical polarizing microscopy equipped with a heating stage. The textures of the nematic and the smectic phase were determined by a miscibility method. Thermodynamic quantities enthalpy (ΔH) and entropy (ΔS) are discussed qualitatively instead of using differential scanning calorimetry.

Analytical Data

Analytical data includes spectral data for dodecyloxy, tetradecyloxy, hexyloxy, and octyloxy derivatives.

Spectral Data.

NMR in ppm for Dodecyloxy Derivative. 0.870 (–CH_3 of –$OC_{12}H_{25}$ group), 1.4388 (–CH_2– of –$OC_{12}H_{25}$), 4.0038 (–OCH_2– of –$OC_{12}H_{25}$), 6.9024 and 6.9216 (–CH=CH–CO– group), 7.8818 and 7.90 (*p*-substituted phenyl ring). NMR supports the structure.

NMR in ppm for Tetradecyloxy Derivative. 0.885 (–CH_3 of –$OC_{14}H_{29}$ group), 1.4270 (–CH_2)– of –$OC_{14}H_{29}$ group, 3.49 (–OCH_2– of –$OC_{14}H_{29}$ group), 6.9015, 6.9232, and 6.9397 (–CH=CH–CO– group), 7.8850 and 7.9069 (*p*-substituted phenyl ring). NMR supports the structure.

IR in cm^{-1} for Hexyloxy Derivative. 660 –$(CH_2)n$– group of –OC_6H_{13}, 850 *p*-substituted phenyl ring, 1170 C–O of –OC_6H_{13} group, 1250 and 1600 –COO ester group, 935 –CH=CH– group. IR supports the structure.

IR in cm^{-1} for Octyloxy Derivative. 780 –$(CH_2)n$– group of –OC_8H_{17}, 820 *p*-substituted phenyl ring, 1160 C–O of –OC_8H_{17} group, 1250 and 1680 –COO ester group, 935 –CH=CH– group. IR supports the structure.

Texture

The texture for tetradecyl, octyl, and hextyl are listed as follows.

- Tetradecyl: Threaded nematic
- Octyl: Schlieren nematic
- Hextyl: Smectic-A

Results and Discussion

Dimerzation of 4-*n*-alkoxybenzoic acids disappears on the esterification process. Component B of the ethylene homologue derivative is not liquid crystalline. However, on linking it

Table 2. Transition temperatures of series in °C

Compound no.	*n*-alkyl group: C_nH_{2n+1}	Transition temperatures in °C		
		Sm	Nm	Isotropic
1	1	—	—	210.0
2	2	—	—	166.0
3	3	—	—	165.0
4	4	—	—	172.0
5	5	—	125.0	132.0
6	6	126.0	136.0	172.0
7	8	118.0	144.0	163.0
8	10	115.0	123.0	152.0
9	12	113.0	115.0	147.0
10	14	—	110.0	146.0
11	16	—	136.0	143.0

Note. Sm = Smectic; Nm = Nematic.

with an acid chloride, i.e., with component A, the resultant product exhibits LC properties from the pentyl to the hexadecyl homologues, while the methyl to butyl homologues do not exhibit LC properties (Table 2). A plot of the transition temperature versus the number of carbon atoms present in *n*-alkyl terminal chain consists of three transition curves, solid-isotropic or mesomorphic curve, smectic–nematic curve, and nematic–isotropic curve, as shown in Fig. 1. The solid–isotropic or mesomorphic transition curve rises and falls as the series is ascended in a zigzag manner with an overall descending tendency. The smectic–nematic transition curve initially rises from the hexyl homologue and then passes from a maxima at the octyl derivative and then falls up to the dodecyl derivative of the series. This curve is extrapolated to the tetradecyl homologue and it merges into a point where the smectic phase ceases to appear and only the nematic phase appears. Thus, the smectogenic property is exhibited by the hexyl to the dodecyl homologues of the novel series. The nematic–isotropic transition curve initially rises and then descends as the series is ascended without the exhibition of an odd–even effect. Thus, all three transition curves of the phase diagram (Fig. 1) behave in the usual established manner. The mesomorphic phase length ranges from 7°C to 46°C at the pentyl to the hexadecyl homologues. The series is partly smectogenic and predominantly nematogenic with a middle-ordered melting type. The mesomorphic properties vary from homologue to homologue in the same series with different magnitudes of phase length including smectic and nematic phase lengths. An odd–even effect is absent in the smectic–nematic and nematic–isotropic transition curves. The smectic mesophase commences from the hexyl homologue (Table 2). All the mesogenic members of the series are enantiotropic mesomorphic. The breaking of hydrogen bonding due to the esterification process gives rise to esters with lower transitions than the corresponding alkoxy acids. However, the addition of a third phenyl ring bonded through a –CH=CH–CO– central group increases molecular rigidity and flexibility and raises transition temperatures. Non-mesomorphic behavior of the methyl to the butyl homologue derivatives is attributed to their high crystallizing tendency due to their relatively short alkoxy terminal chains. Hence, the corresponding homologue molecules are unable to resist exposed thermal vibrations,

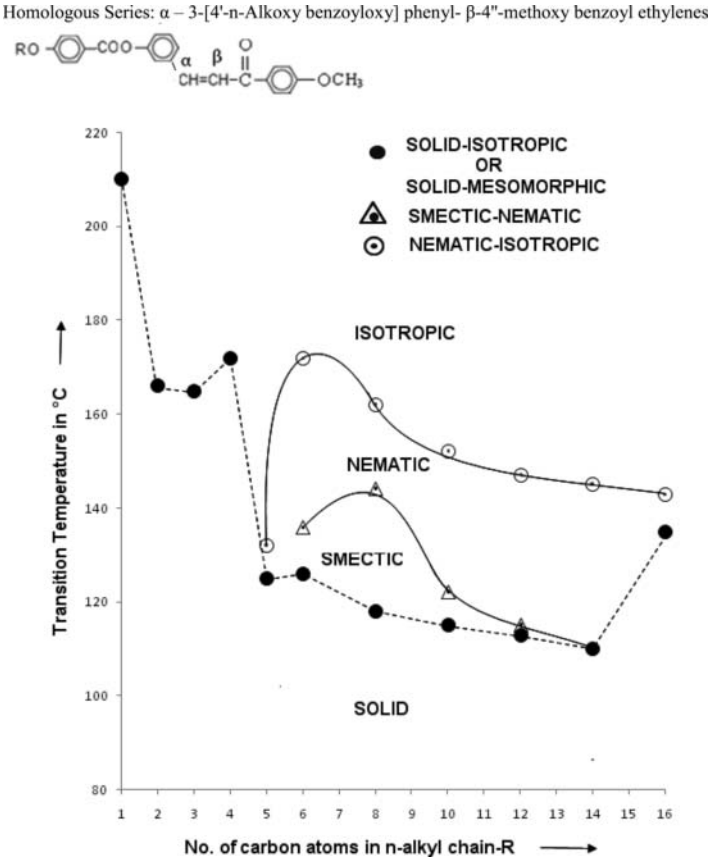


Figure 1. Phase behavior of series.

which results in the sudden breaking of the crystal structure and converts the substance sharply into isotropic liquid state from solid state without exhibition of a liquid crystalline mesophase. Such a situation also arises for a mesomorphic (LC) substance from and beyond the mesomorphic–isotropic transition temperature. The exhibition of mesogenic properties from the pentyl to the hexadecyl homologues is attributed to the suitable magnitudes of anisotropic intermolecular forces [4] of attraction caused by favorable molecular polarity and polarizability, aromaticity, electronic–electronic interactions, length-to-breadth ratio, and the ratio of the polarity to polarizability as a consequence of the resultant molecular rigidity and flexibility [1–3]. The exhibition of only nematogenic character by the pentyl, tetradecyl, and hexadecyl homologues, or in addition to smectogenic character by the hexyl to the dodecyl homologues, is attributed to the statistically parallel orientational order of molecules in a floating condition due to favorable intermolecular end-to-end adhesion in which molecules appear to lie at an angle less than 90° on the plane of a surface, with the thermal vibration resisting under the influence of applied heat within definite temperature range. The exhibition of smectogenic character by the hexyl to dodecyl homologues is due to the presence of lamellar packing of the molecules in their crystal lattices that on heating gradually yield a sliding layered arrangement of molecules in a floating condition resisting thermal vibrations within a definite range of temperature. Thus, the presently investigated

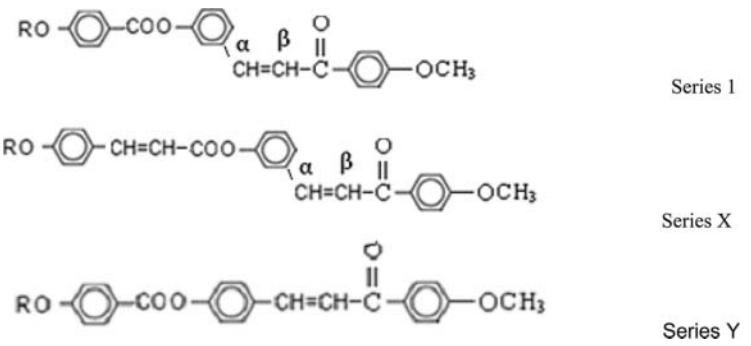


Figure 2. Structurally similar series.

homologous series is predominantly nematogenic and partly smectogenic without showing an odd–even effect. The absence of an odd–even effect in either of the curves in the phase diagram (Fig. 1) is due to the absence of mesophase formation by the methyl and propyl derivatives of the series. The disappearance of the smectogenic character in the tetradecyl and hexadecyl homologues indicates the absence of lamellar molecular packing due to the longer terminal chains, which may coil, bend, flex, or couple to lie with the major axis of the core adversely affecting the molecular rigidity and flexibility [1–3], which hinders lamellar molecular packing. The variation of mesogenic properties from homologue to homologue in the same series is due to the sequential addition of methylene unit [4] in the terminal alkoxy chain, which causes variation in molecular polarity and polarizability affecting the intermolecular lateral attractions.

The mesomorphic properties of the novel Series 1 is compared with two other structurally similar homologous Series X [8] and Y [9] in Fig. 2.

Figure 2 shows structurally similar homologous series with minor variations in their geometrical shape and the central bridge linking the first and middle phenyl rings. Such minor variations cause a difference in the mesomorphic behavior in terms of the commencement of the smectic and/or nematic phase, transition temperatures, magnitudes of intermolecular anisotropic forces of adhesion, thermal stabilities, etc., as recorded in Table 3. The homologous Series 1 of the present investigation and Series X differ in their central bridge, viz., –COO– and –CH=CH–COO–, linking the first and middle phenyl

Table 3. Relative average thermal stability in °C

	Average transition temperatures in °C		
Series	Series (1)	Series (X)	Series (Y)
Smectic–nematic or isotropic	129.5 (C_6–C_{12})	138.80 (C_{10}–C_{14})	133.4 (C_6–C_{12})
Commencement of smectic phase	C_6	C_5	C_6
Nematic–isotropic	150.7 (C_5–C_{16})	165.7 (C_5–C_{14})	159.8 (C_6–C_{16})
Commencement of nematic phase	C_5	C_5	C_6

rings with the remaining molecular units and shape unchanged. The vinyl carboxylate –CH=CH–COO– group is relatively longer than the –COO– and has a conjugated double bond. The presence of the double bond strengthens the molecular rigidity of Series X, which reflects in the degree of mesomorphism and the lateral intermolecular attractions. Homologous Series 1 and Y are isomeric or identical in all respect except their molecular shape. Homologous Series 1 is broader than a Series Y, while Series Y has a lath like shape. The polarity due to the three phenyl ring central groups and terminal end group are the same, but their molecular polarity and polarizability varies with the molecular shape, which is reflected in the magnitudes and degree of mesomorphism due to intermolecular distance.

Table 3 indicates that the smectic–nematic thermal stability is lowest of Series 1 in comparison with Series X and Y chosen for comparison. Series X contains the longer vinyl carboxylate central group with the –CH=CH– additional unit, which increases the molecular length in comparison with the –COO– central bridge. Hence, the length-to-breadth ratio and the molecular polarizability of the molecules of Series X are greater than the molecules of Series 1. Thus, suitable magnitudes of anisotropic intermolecular forces of adhesion are higher in Series X than in Series 1, and this reflects the smectic–nematic thermal stability of Series 1 and X. The smectic–nematic thermal stability of Series Y is also greater than the molecules of Series 1. This is because the molecules of Series Y are lath like while the molecules of its isomeric Series 1 of present investigation are nonlinear and broader than the Series Y. Broadening of a molecule raises the intermolecular attractions by polarizability factor. But at the same time, broadening of a molecule reduces intermolecular attractions due to increase in the intermolecular distance. Thus, two opposite effects due to molecular broadening operate at a time [4] in case of Series 1. The net resultant effect of intermolecular attractions depends upon the predominating effect out of two opposing effects operating at a time. The second effect, i.e., the reduction in intermolecular attractions due to broadening of a molecule, predominates in case of Series 1, while closer packing of molecules of Series Y strengthens the suitable magnitudes of anisotropic intermolecular forces of attractions in comparison to Series 1 of present investigation. Therefore, the smectic–nematic thermal stability of Series Y is higher than for Series 1. Similarly, the nematic–isotropic thermal stabilities of Series X and Y are higher than that of Series 1 of present investigation. The commencement of the smectic mesophase takes place from fifth or sixth member of the series, which indicates that the flexible identical molecular part, viz., the –OR and $–OCH_3$ terminal groups, causes an almost equivalent extent of molecular non-coplanarity of Series 1, X, and Y. Similarly, the magnitudes of the end-to-end intermolecular attractions result in the formation of the nematogenic mesophase irrespective of the differing features of the central group or the linearity of a molecule. Thus, the variation in mesomorphic properties for the same homologue from series to series is attributed to varying features due to central group linking first and middle phenyl ring and the molecular shape or linearity.

Conclusions

(1) The group efficiency order derived for smectic and nematic on the basis of thermal stability is as under:

Smectic: –CH=CH–COO– > –COO– > –COO–
(Linear) (Nonlinear)

Nematic: –CH=CH–COO– > –COO– > –COO–
(Linear) (Nonlinear)

(2) Broadening of a molecule causes two opposing effects at a time, viz., enhances intermolecular attractions related to molecular polarizability and reduces in intermolecular attraction due to enhanced intermolecular distance. The resulting net effect depends upon predominating effect out of two opposing effects operating at a time.
(3) When terminal end groups and aromaticity of a molecule are identical, then only the molecular shape predominantly contributes to the suitable magnitudes of anisotropic forces of intermolecular adhesion.
(4) Central group, or groups, plays an important role in mesophase formation and molecular rigidity.

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