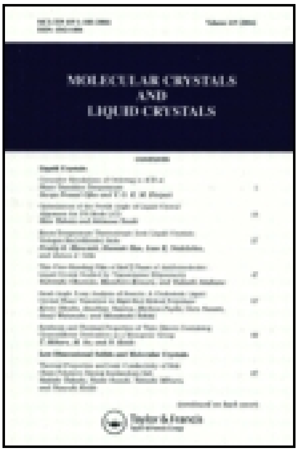

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Synthesis and Study of Liquid Crystal Properties of Novel Homologous Series: α-4-[-4′-n-Alkoxy benzoyloxy] Phenyl β-4″-Nitro benzoyl Ethylenes

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The synthesis and mesomorphic properties of a novel homologous series entitled α-4-[-4′-n-Alkoxy benzoyloxy] phenyl β-4″-nitro benzoyl ethylenes are reported. All the 11 members of the series except the methoxy and ethoxy derivatives are mesogenic. The propyloxy to pentyloxy and the hexadecyloxy homologues are only enantiotropically nematogenic and the rest of the mesogenic homologues are enantiotropically smectogenic in addition to nematogenic in character. A phase diagram shows the phase behavior through transition curves is of a normal type. An odd–even effect is observed for the nematic-isotropic transition curve. Analytical and spectral data support the molecular structure of the materials. Transition temperatures and other liquid crystal (LC) properties including average thermal stabilities for smectic and nematic were determined by optical polarizing microscopy. Average thermal stability for smectic and nematic are 125.6°C and 154.6°C, respectively. Smectogenic and nematogenic phase ranges vary between 19°C to 35°C and 14°C to 50°C, respectively. The LC properties of the novel series are compared with two other structurally similar homologous series. The textures of the nematic phase are threaded or schlieren type and those of the smectic phase is of the type A or C.

Keywords Liquid crystals; mesogen; mesomorphic; nematic; smectic

Introduction

Doshi et al. [1,2] synthesized ethylene derivatives and succeeded in generating liquid crystal (LC) properties in the homologous series due to favorable molecular rigidity and flexibility [3–5] and suitable magnitudes of anisotropic intermolecular forces of attractions. The molecular design of this novel homologous series involves a rigid core of three phenyl rings bridged through –COO– and –CH=CH–CO– linking groups. Terminal units of an *n*-alkoxy(–OR) chain and a nitro(–NO_2) group provide the flexibility in a rod-like molecular structure. The behavior of homologues on mesogenic (LC) properties is evaluated, rationalized, and discussed in terms of molecular rigidity and flexibility to correlate the effect of molecular structure on LC properties.

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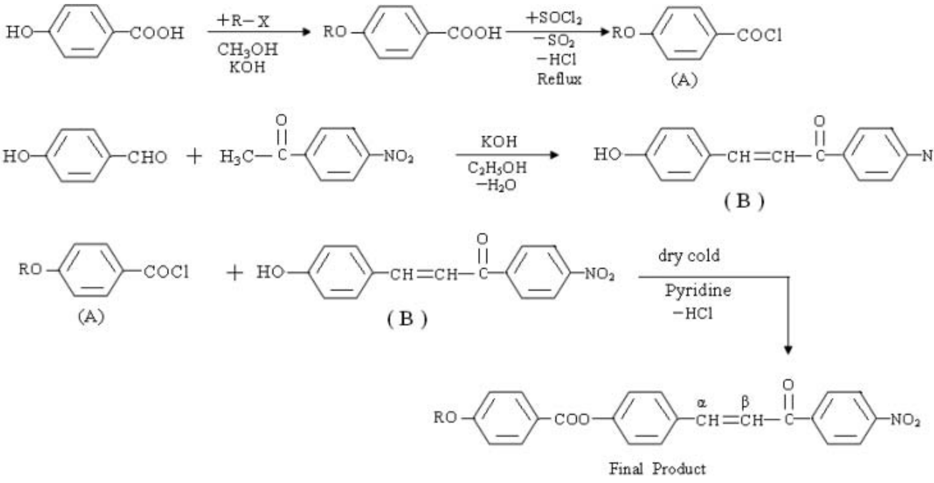
Experimental

Synthesis

4-Hydroxybenzoic acid was alkylated by suitable alkylating agents to prepare the 4-*n*-alkoxy benzoic acids, which on further treatment with thionyl chloride gave the corresponding acid chlorides (A) by the modified method of Dave and Vora [6a]. α-4-Hydroxy phenyl β-4′-nitro benzoyl ethylene [6b] (B) was prepared by reacting 4-hydroxybenzaldehyde and 4-nitroacetophenone in 50% ethanol–KOH solution by a conventional method. Components (A) and (B) were condensed in dry cold pyridine by an established method [7,8]. Final products were individually filtered, dried, and recrystallized until constant transition temperatures were obtained. The synthetic route to the series is outlined in Scheme 1. where $R = C_nH_{2n+1}$; $n = 1,2,3,4,5,6,8,10,12,14,16$.



where $R = C_nH_{2n+1}$; $n = 1,2,3,4,5,6,8,10,12,14,16$.

Scheme 1. Synthetic route to the series.

Characterization

Some selected members of the series were characterized by elemental analysis, Infra red (IR) spectroscopy, and ^{1}HNMR spectra (Table 1). Microanalysis was performed by using a Perkin-Elmer PE 2400 CHN analyser at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab Uni. Chandigarh 160014. The IR spectra were recorded on a Perkin-Elmer

Table 1. Elemental analysis for methyloxy, butoxy, decyloxy, and tetradecyloxy derivatives

		Elements% found (% calculated)		
Sr. no	Molecular formula	C	H	N
1	$C_{23}H_{17}NO_6$	68.55 (68.49)	4.39 (4.22)	3.62 (3.47)
2	$C_{26}H_{23}NO_6$	71.07 (70.11)	5.25 (5.17)	3.19 (3.15)
3	$C_{32}H_{35}NO_6$	72.65 (72.59)	6.86 (6.62)	2.98 (2.65)
4	$C_{36}H_{43}NO_6$	73.80 (73.85)	7.29 (7.35)	2.54 (2.39)

spectrum GX spectrometer IR spectra at vaibhav Lab., Ahmedabad, and the ^{1}HNMR spectra were recorded on Bruker instrument by using $CDCl_3$ as the solvent. The transition temperatures and other LC properties were determined by optical polarizing microscopy. The textures of the nematic and smectic mesophases were determined by a miscibility method.

Analytical Data

Spectral Data. **NMR in ppm for dodecyloxy derivative:**

0.873 ($-CH_3$ of $OC_{12}H_{25}$), 1.258 ($(-CH_2-)_n$ of $OC_{12}H_{25}$), 4.008 ($-OCH_2$ of $OC_{12}H_{25}$), 6.89 and 6.91 ($-CH{=}CH-CO-$), 7.90, 7.92, and 8.10 (aromatic ring). The data support the structure.

NMR in ppm for decyloxy derivative:

0.872 ($-CH_3$ of $OC_{10}H_{21}$), 1.265 ($(-CH_2-)_n$ of $OC_{10}H_{21}$), 4.00 ($-OCH_2$ of $OC_{10}H_{21}$), 6.90 and 6.92 ($-CH{=}CH-CO-$), 7.88, 7.91, and 8.07 (aromatic ring). The data support the structure.

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

690 ($-(CH_2)_n-$ of OC_6H_{13}), 840 (aromatic ring), 1160 ($>C{=}O$), 1250, 1600, and 1690 ($-COO-$), 1430 ($-NO_2$), 940 ($-CH{=}CH-$). The data support the structure.

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

620 ($-(CH_2)_n-$ of OC_3H_7), 845 (aromatic ring), 1165 ($>C{=}O$), 1225, 1600, and 1680 ($-COO-$), 1415 ($-NO_2$), 965 cm^{-1} ($-CH{=}CH-$). The data support the structure.

Texture: by miscibility Method:

Butyloxy homologue . . . . .Threaded nematic
Hexadecyloxy homologue . . . . Schlieren nematic
Hexyl homologue . . . . .Threaded nematic
and smectic A

Results and Discussion

The methoxy and ethoxy derivatives are not liquid crystalline. The propyloxy to pentyloxy and the hexadecyloxy homologues are enantiotropic nematic. The hexyloxy to tetradecyloxy homologues are enantiotropic nematic and additionally exhibit enantiotropic smectic mesomorphism. Transition temperatures of the homologues (Table 2) are plotted versus the number of carbon atoms in the n-alkoxy terminal chain. A phase diagram is obtained by linking like or related points to give curves representing solid-isotropic or solid-mesomorphic, smectic-nematic, and nematic-isotropic transitions (Fig. 1). The solid-isotropic or solid-mesomorphic transition curve rises and falls in zigzag manner with an overall falling tendency. The smectic-nematic transition curve falls from the hexyloxy homologue and then rises and passes through maxima at the dodecyloxy derivative, and finally falls at the tetradecyloxy homologue. The curve is extrapolated [9] for the butyloxy and the hexadecyloxy derivatives to determine their latent transition temperatures of (LTT). The LTT predicted smectic-nematic transition of the hexadecyloxy derivative is 99°C and that of the butoxy homologue is 140°C, which is actually the nematic-isotropic point. The nematic-isotropic transition curve initially rises and then falls after passing through maxima and descended as the series is ascended. Thus, it behaves in a normal expected manner. An odd–even effect is observed for the nematic-isotropic transition curve and both curves (for odd and even) merge into each other at the hexyloxy homologue. The odd–even effect and variations in mesogenic properties from homologue to homologue in the same series is due to the sequentially added methylene unit in the *n*-alkoxy terminal chain. The nematic-isotropic transition curve for odd–even homologue merges at the hexyl derivative of the series. Such an effect diminishes for higher homologues of the longer *n*-alkyl chain because longer *n*-alkyl chain may coil or flex or couple to align with the major molecular axis [10]. The nematogenic and smectogenic phase ranges vary between 14°C to 50°C and 19°C to 35°C, respectively. Total mesophase range varies between 18°C and 73°C. Thus, the novel homologous series is predominantly nematogenic and partly smectogenic with middle ordered melting type. The nonmesogenic (NLC) behavior of the methoxy and ethoxy homologues is attributed to their high crystallizing tendency arising from their high intermolecular adhesion due to their highly polar methyl and ethyl short *n*-alkyl chains. Thus, molecules sharply transform into isotropic liquid without passing through LC state.

The exhibition of smectogenic behavior from the hexyloxy to tetradecyloxy homologues of the series is attributed to the presence of lamellar packing of molecules in their crystal lattices that stabilize molecules at room temperature and provide means to resist thermal vibrations exposed upon them. The molecules are disaligned at an angle of less than 90° with the plane of a surface with a layered arrangement, which are sliding out under the influence of heat with the maintenance of a two-dimensional array in a floating condition within definite temperature range. From and beyond the smectic-nematic transition temperature of the homologues from hexyloxy to tetradecyloxy and the solid-nematic transition temperature of hexadecyloxy homologue, the molecules disalign with the plane of a surface acquiring a statistically parallel orientational order of the molecules in a floating condition with maintenance of two-dimensional array reversibly within a definite higher range of temperature than the smectic range to cause nematogenic mesophase formation. From and beyond the isotropic temperature, the molecules of a substance do not maintain any ordered molecular arrangement but randomly orient in all possible directions in an irregular manner. The magnitudes of anisotropic intermolecular forces of the end-to-end or interlayered attractions cause nematogenic and/or smectogenic mesophase formation, which depend upon the intermolecular closeness and the polarity of terminal end groups –OR and –NO_2. The molecular shape of a molecule of the present series is linear, lath like and the terminal end groups are sufficiently polar. Therefore, the length-to-breadth ratio and the molecular polarity-to-polarizability ratio satisfy the required environment to

Table 2. Transition temperatures in °C of series 1

Compound no	*n*-Alkyl R = C_nH_{2n+1}; group (n)	Smectic	Nematic	Isotropic
1	1	–	–	191.0
2	2	–	–	200.0
3	3	–	146.0	164.0
4	4	–	120.0	140.0
5	5	–	110.0	160.0
6	6	114.0	137.0	167.0
7	8	96.0	120.0	169.0
8	10	100.0	120.0	166.0
9	12	94.0	129.0	162.0
10	14	96.0	122.0	136.0
11	16	–	110.0	128.0

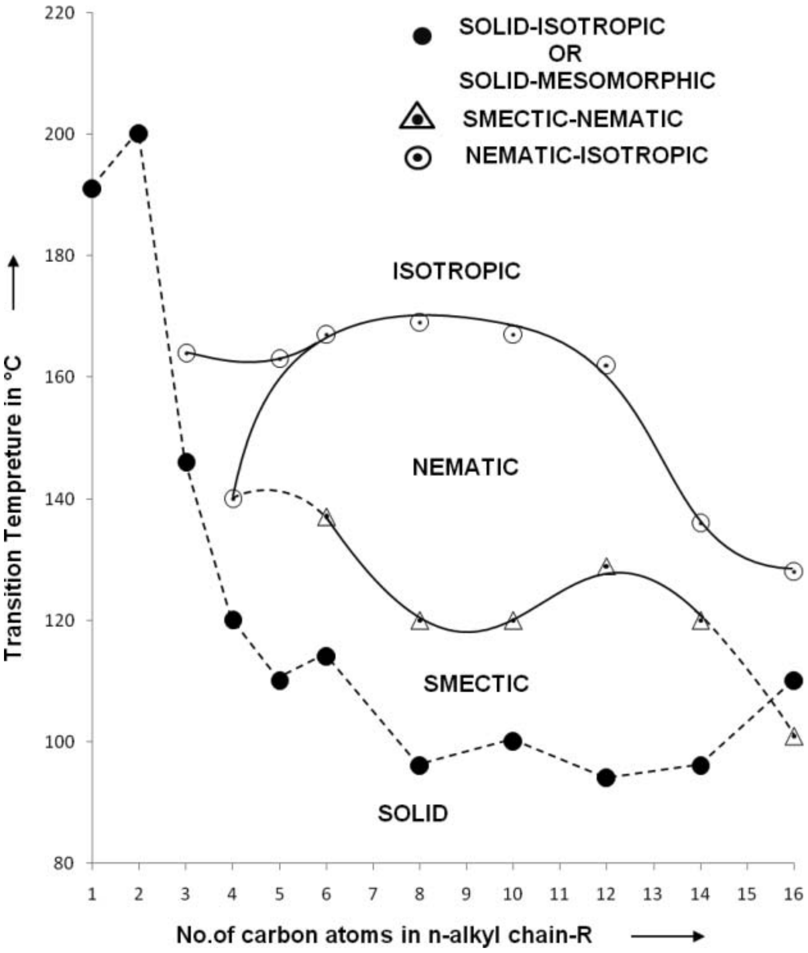


Figure 1. Phase behavior of series.

cause suitable magnitudes of anisotropic forces of intermolecular adhesion, which enables smectic and/or nematic mesophase formation within a defined range of temperature. LC properties of the present series 1 are compared with structurally similar homologous series X [2] and Y [1] (Fig. 2) and their thermal stabilities and commencement of mesophases are recorded in Table 3. Series 1, X, and Y are outlined in Fig. 2.

The homologous series 1, X, and Y are identical in all respect except their right terminal end groups (–NO_2, –OCH_3, and –H) as well as varying the *n*-alkoxy (–OR) terminal end groups. All the series under comparison consists of three phenyl rings bridged through two identical central groups (–COO– and –CH=CH–CO–). Therefore, molecular aromaticity and intermolecular closeness remains very similar. However, there are of course many differences that will cause differing mesomorphic properties, such as the different molecular lengths due to –NO_2, –OCH_3, –H terminal groups, and hence different length-to-breadth ratios, different polarities, a different ratio of the molecular polarity to polarizability, and steric factors due to the different size of the terminal groups. Hence, there is interesting comparison of the different mesomorphic properties of series 1, X, and Y as they relate

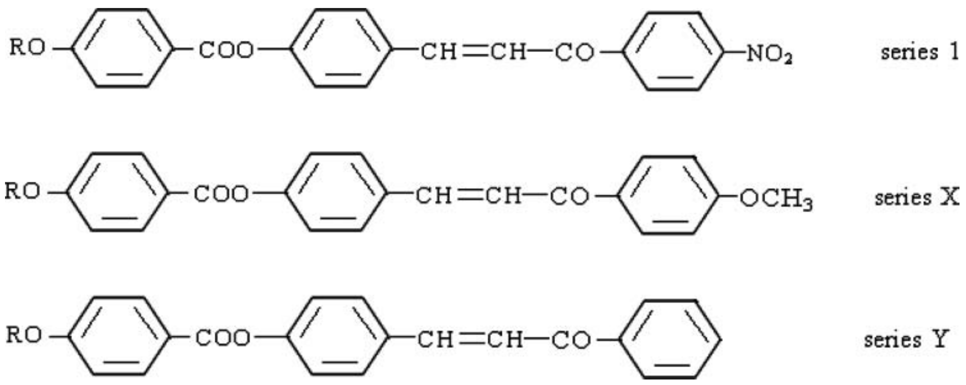


Figure 2. Structurally similar homologous series.

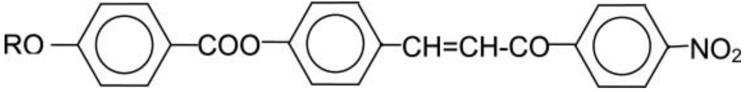
to the different molecular structure. Table 3 shows the average thermal stability and the commencement of mesophases.

The thermal stability of homologous series 1 is less than that of series X and more than that of series Y. All three homologous series under comparison exhibit smectogenic and nematogenic character within certain range of temperatures. However, the observed difference in their thermal stabilities is attributed to the difference in the polarities of the terminally substituted end groups (–NO_2, –OCH_3, and –H) and the difference in molecular length. On comparing the present series 1 with series X, whose smectic and nematic thermal stabilities are less than series X, the –OCH_3 end group is more polar and polarizable than the –NO_2 and contributes to the observed effect. Moreover, electronegativity of oxygen is more than nitrogen; therefore, the bond polarity of the –OCH_3 group is more than that of the –NO_2 group. Hence, the molecular polarity of series X is greater than that of series 1. Therefore, the magnitudes of anisotropic forces of intermolecular adhesion of series X exceed that of series 1. The intermolecular closeness of series 1 and X are almost the same, but the intermolecular adhesion differs due to different polarities of terminal end groups. The lowest values of thermal stabilities of series Y amongst the series under comparison can also be linked with the shortest molecular length and the weakest inductive effect whose C–H bond polarity is lower than C–N and C–O bond polarities, which reflects in molecular rigidity and flexibility to cause lowering of thermal stability values 106.6°C and 119.8°C for smectic and nematic, respectively. The smectogenic mesophase commences from the

Table 3. Relative thermal stability in °C

Series	1	X	Y
Smectic-nematic or isotropic	125.6 (C_6–C_{14})	133.4 (C_6 –C_{12})	106.6 (C_{10}–C_{16})
Commencement of smectic phase	C_6	C_6	C_{10}
Nematic-isotropic	154.6 (C_3–C_{16})	159.8 (C_6–C_{16})	119.8 (C_8–C_{16})
Commencement of nematic phase	C_3	C_6	C_8

Series: α – 4-[4′-*n*-Alkoxy benzoyloxy] phenyl- β-4″-nitro benzoyl ethylenes



hexyloxy homologue for series 1 and X, while it commences later from the decyloxy homologue of series Y. This indicates that lamellar packing of the molecules commences early from the sixth member of the series for the molecules of series 1 and X, while lamellar packing is hindered in case of series Y due to the weakly polar end group (–H) or the absence of a terminal end group, which affects the extent of noncoplanarity. The $-NO_2$ and $-OCH_3$ groups are more polar and polarizable, which reduce molecular coplanarity and enable earlier (i.e., from sixth homologue) lamellar packing and commencement of the smectic phase.

Conclusions

(1) Presently, investigated homologous series is: Predominantly nematogenic and partly smectogenic with middle-ordered melting type and enough phase length.

(2) The smectic and nematic group efficiency order derived on the basis of thermal stabilities are:
Smectic: $-OCH_3 > -NO_2 > -H$;
Nematic: $-OCH_3 > -NO_2 > -H$.

(3) Group efficiency order derived on the basis of early commencement of smectic and nematic mesophase are:
Smectic: $-NO_2 = -OCH_3 > -H$;
Nematic: $-NO_2 > -OCH_3 > -H$.

(4) Molecular rigidity and flexibility vary with polarity of terminal end group of fixed polarity for the same series.

(5) Molecular rigidity and flexibility from homologue to homologue of the same series vary with the sequencially added methylene unit in *n*-alkyl group of left *n*-alkoxy end group.

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