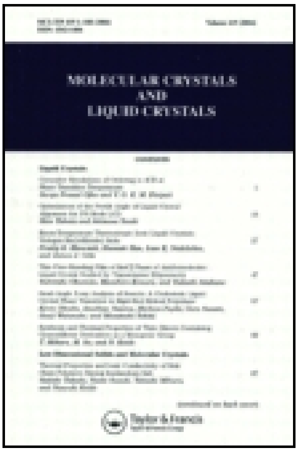

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The Synthesis and Mesomorphic Properties of a Novel Homologous Series: α-4-[4′-n-Alkoxy benzoyloxy] Benzoyl -β-2″-nitro Phenyl Ethylenes

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The synthesis and mesomorphic properties of novel homologous series are reported. All 11 members of the series, except the methoxy and ethoxy derivatives, are enantiotropically mesogenic. The propoxy to tetradecyloxy homologues exhibits smectognic amd nematogenic behavior, while the hexadecyloxy homologue shows only nematogenic behavior. An odd-even effect is observed for the smectic–nematic and the nematic–isotropic transition curve in the phase diagram. Analytical data support the structure of molecules. The textures of the nematic mesophase are threaded or Schlieren, and that of smectic mesophase are of type-A. The transition temperatures of homologues and other mesomorphic properties are determined using optical polarizing microscopy. The smectic and nematic thermal stabilities are 138.0°C and 163.8°C respectively. The novel series is predominantly nematogenic and partly smectogenic with middle-ordered melting type. The nematic and smectic phase ranges vary between 16°C and 38°C and 6°C and 22°C respectively. The mesogenic properties of the novel series are compared with other structurally similar homologous series.

Keywords Liquid crystal; mesogens; mesophase; nematic; smectic

Introduction

Materials with two phenyl rings and central linking groups (−CH=CH−CO− or −CO−CH=CH−) have been synthesized previously [1a]. However, liquid crystal mesophase formation did not feature for this type of compound. Chauhan and Doshi [1b] continued research along similar lines by increasing molecular length and aromaticity by linking three phenyl rings by two central groups, including −CH=CH−CO− or/and −CO−CH=CH− as one of the central groups. Doshi and Chauhan [1b] and Doshi and Patel [1c] independently observed mesophase formation using −COO− or −CH=CH−COO− as the central group along with a second −CH=CH−CO− central group. Doshi and Chauhan [2], Doshi and Suthar [3], and Doshi and Chaudhari [4] extended their research work using −CH=CH−CO− as one of the central groups linking three phenyl rings. The resulting molecular rigidity and flexibility [5,6] from three phenyl rings bonded through two central groups and a lateral/terminal substituent group or groups cause suitable magnitudes of anisotropic intermolecular forces of attraction to induce mesophase formation in a substance. The novel homologous series consists of three phenyl rings

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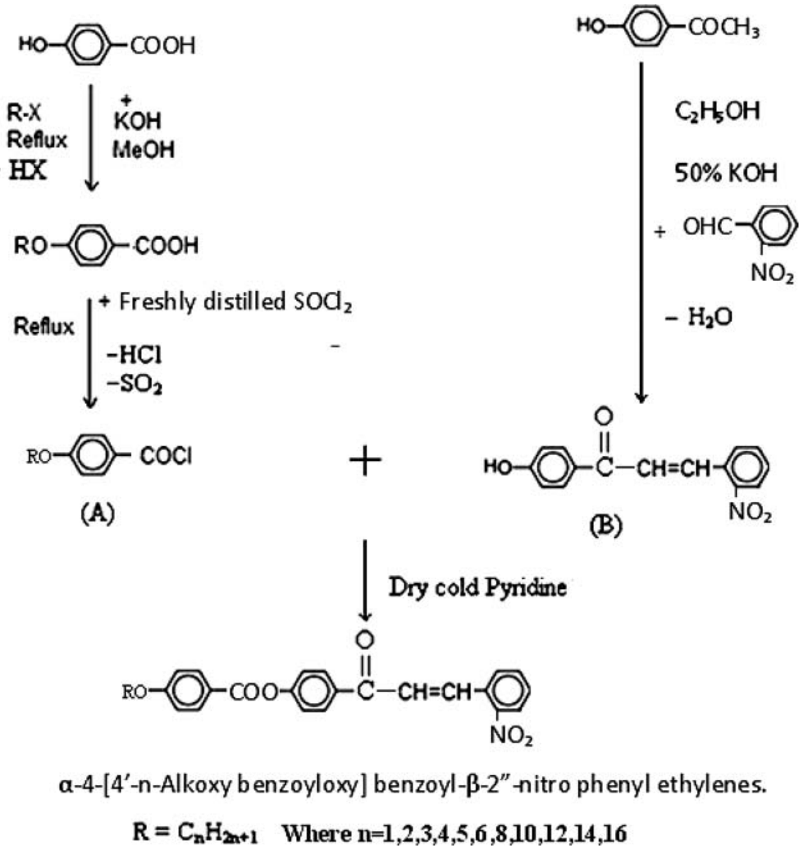
bridged through two central groups (—COO— and —CO—CH=CH—) as the rigid core and n-alkoxy (–OR) and nitro (—NO_2) as flexible units of a molecule. Thereby, the molecular structural effect on liquid crystallinity in relation to thermal stability, commencement of mesophase, mesophase range, and the types of mesophase are evaluated and discussed in terms of molecular polarity and polarizability, length to breadth ratio, and molecular shape.

Experimental

Synthesis

4-Hydroxybenzoic acid was alkylated by suitable alkylating agents (R-X) to form 4-n-alkoxybenzoic acids, which are converted into the corresponding acid chlorides (A) using freshly distilled thionyl chloride by the method of Dave and Vora [7]. 4-Hydroxyacetophenone was treated with 2-nitrobenzaldehyde by the known method [1,7] to form α-4-hydroxy benzoyl-β-2′-nitro phenyl ethylene (B). Components (A) and (B) were condensed in ice-cooled pyridine [2,8] to form final products. The synthetic route to the series is shown in Scheme 1.



Scheme 1. Synthetic route to the series.

Table 1. Elemental analysis for butoxy, hexyloxy, and dodecyloxy derivatives

		Elements found (% calculated)		
Sr. No.	Molecular formula	C	H	N
1	$C_{26}H_{23}O_6N$	70.31 (70.07)	5.47 (5.14)	3.35 (3.13)
2	$C_{28}H_{27}O_6N$	71.64 (71.02)	5.11 (5.74)	2.66 (2.98)
3	$C_{34}H_{39}O_6N$	73.65 (73.26)	7.10 (6.98)	2.82 (2.49)

Characterization

Representative members of the novel series were characterized by elemental analysis (Table 1), infra-red (IR), and Hydrogen-1 Nuclear Magnetic Resonance (^{1}HNMR) spectroscopy. Microanalysis was performed on Perkin-Elmer PE2400 CHN analyser. IR spectra were recorded on Perkin-Elmer GX spectrometer, and ^{1}HNMR spectra were recorded on Bruker instrument using $CDCl_3$ as a solvent. The textures of the nematic and smectic mesophases were determined by a miscibility method using optical polarizing microscopy.

Analytical Data

Spectral Data

NMR in ppm for decyloxy derivative

0.99 ($-CH_3$ of $-OC_{10}H_{21}$), 1.17 ($-(CH_2)n-$ of $-OC_{10}H_{21}$), 3.75 ($-OCH_2$ of $-OC_{10}H_{21}$), 6.73 & 6.63 ($-CO-CH{=}CH-$), 7.53, 7.65, and 8.01 (phenyl ring). The data support the structure.

NMR in ppm for tetradecyloxy derivative

0.94 ($-CH_3$ of $-OC_{14}H_{29}$), 1.43 ($-(CH_2)n-$ of $-OC_{14}H_{29}$), 3.23 ($-OCH_2$ of $-OC_{14}H_{29}$), 3.91 ($-CH{=}CH-$), 6.97 ($-CO-CH{=}CH-$), 7.51,7.77, and 8.20 (phenyl ring). The data support the structure.

IR in cm^{-1} for propoxy derivative

700 ($-(CH_2)n-$ of $-OC_3H_7$), 840, 880 (phenyl ring), 1160 ($-CO-$ of $-OC_3H_7$), 1250, 1600, and 1700 ($-COO-$), 1430 ($-NO_2$), 970 ($-CH{=}CH-$). The data support the structure.

IR in cm^{-1} for ethoxy derivative

690 ($-(CH_2)n-$ of $-OC_2H_5$), 825 (phenyl ring), 1160 ($-CO-$ of $-OC_2H_5$), 1250, 1600, and 1680 ($-COO-$), 1395, 1430 ($-NO_2$), 930 ($-CH{=}CH-$). The data support the structure.

Texture by Miscibility Method

- Dodecyl–Nematic–Threaded
- Octyl–Smectic–Smectic-A Type
- Hexadecyl–Nematic–Schlieren

Table 2. Transition temperatures (in °C) of series

Compound No.	N-alkyl group $-C_nH_{2n+1\ (n)}$	Transition temperatures in °C Sm	N	Isotropic
1.	1	–	–	190.0
2.	2	–	–	213.0
3.	3	156.0	162.0	182.0
4.	4	122.0	140.0	165.0
5.	5	112.0	122.0	160.0
6.	6	112.0	124.0	161.0
7.	8	120.0	132.0	164.0
8.	10	124.0	142.0	164.0
9.	12	120.0	142.0	160.0
10.	14	128.0	140.0	162.0
11.	16	–	140.0	156.0

Note: Sm: smectic; N: nematic.

Results and Discussion

Of the 11 members of the novel homologous series, α-4-[4′-n-alkoxy benzoyloxy] benzoyl β-2″-nitro phenyl ethylenes, the methoxy and ethoxy derivatives are non-mesomorphic, while the propoxy to hexadecyloxy derivatives are enantiotropic liquid crystals. The hexadecyloxy derivative exhibits only the nematic mesophase without the exhibition of any smectogenic character. The remaining mesogenic homologues exhibit smectic and nematic mesomorphism. The transition temperatures of the homologues, as recorded in Table 2, are plotted versus the number of carbon atoms present in the n-alkoxy terminal chain of the members of the series to obtain a phase diagram. Like points are joined to draw the transition curve to understand the phase behavior of the series as shown in Fig. 1. The solid-isotopic or solid-mesomorphic transition curve follows a zigzag path of rising and falling values with an overall falling nature and behaves in a normal manner. The smectic–nematic transition curve initially adopts descending tendency and then rises, passes through a maximum, and finally falls gradually up to the tetradecyloxy derivative. The curve is extrapolated to the non-smectogenic hexadecyloxy derivative to predict a latent transition temperature (LTT) [9] for the smectic phase, which coincides with the solid-nematic transition point (140°C). The nematic–isotropic transition curve follows a descending tendency as the series is ascended and behaves in normal expected manner. An odd-even effect is observed for the smectic–nematic and nematic–isotropic transition curves with a narrow temperature range. Both curves for the odd and even members merge into each other at the seventh member of the series. The odd-even effect diminishes for higher homologues from seventh homologue because the longer n-alkyl chain may coil, bend, or flex or couple to lie in the line of major axis of the core [10]. The nematogenic phase range varies from a minimum of 16°C at the hexadecyloxy derivative to a maximum of 38°C at the pentyloxy derivative. Similarly, the smectogenic mesophase range varies from a minimum of 6°C at the propoxy derivative to a maximum of 22°C at the dodecyloxy derivative. The non-mesomorphic behavior of methoxy and ethoxy derivatives of the series is attributed to the high crystallizing tendency of homologues that arises from their relatively stronger intermolecular attractions due to

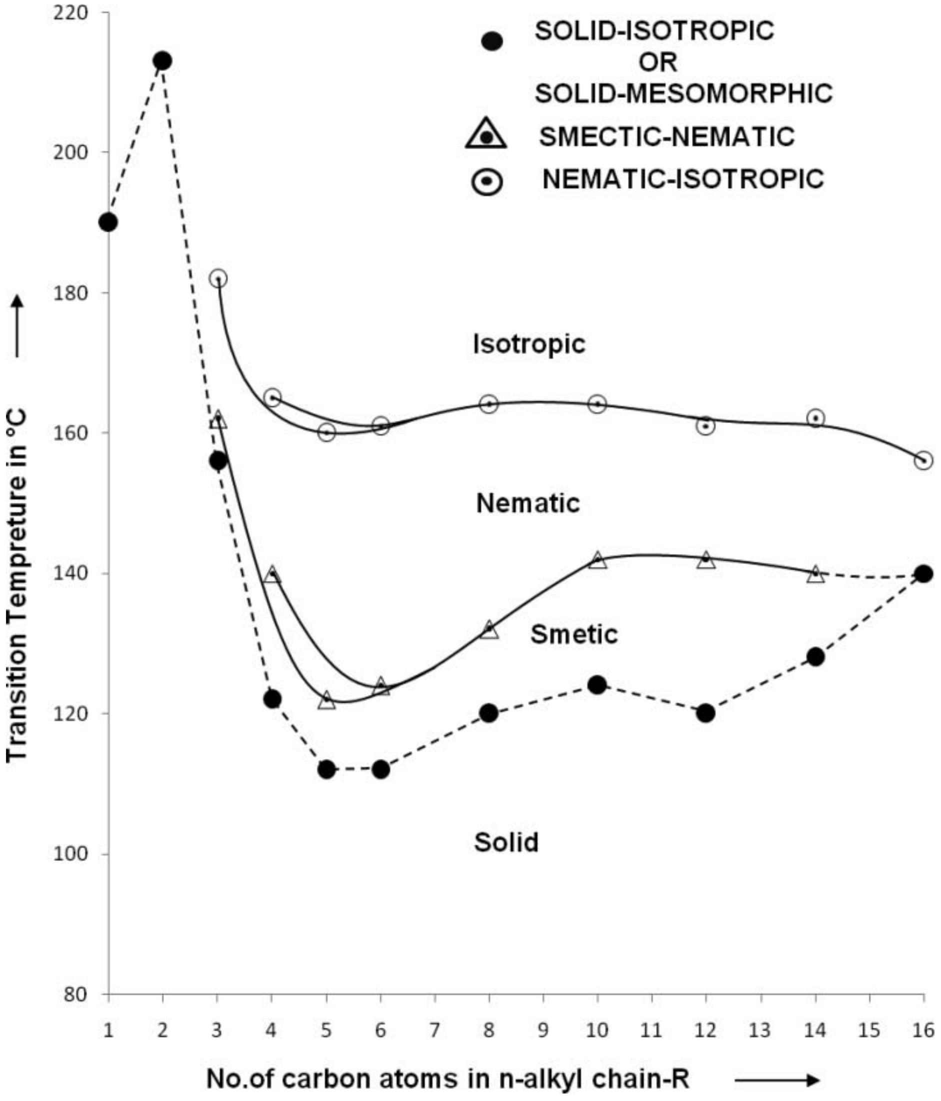


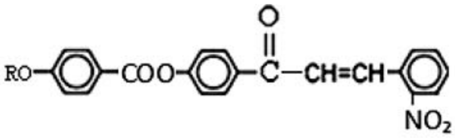
Figure 1. Phase behavior of series.

the presence of highly polar and shorter n-alkyl chains, which causes unsuitable molecular rigidity and flexibility [5,6]. Therefore, both methoxy and ethoxy derivatives sharply transform into isotropic liquid from solid state without passing through a liquid crystal phase. The exhibition of the nematic mesophase from the propoxy to hexadecyloxy derivatives is attributed to the dis-alignment of molecules on gradual heating at an angle less than 90°, withstanding the exposed thermal vibrations which results in suitable magnitudes of anisotropic intermolecular forces of end-to-end attractions and allows the molecules to float with statistically parallel orientational order in two-dimensional array within a definite temperature range reversibly. The smectogenic behavior showed by propoxy to tetradecyloxy homologues within a definite range of temperature reversibly is attributed to the presence of lamellar packing of molecules in their crystal lattices which forms a sliding

Table 3. Average thermal stability in °C

Series	Series-1	Series-X	Series-Y
Smectic–nematic or isotropic commencement of smectic phase	138.0 $(C_3–C_{14})C_3$	—	125.6 $(C_6–C_{14})C_6$
Nematic–isotropic commencement of nematic phase	163.8 $(C_3–C_{16})C_3$	171.5 $(C_5–C_{10})C_5$	154.6 $(C_3–C_{16})C_3$

layered arrangement of molecules in a floating condition, resisting the exposed thermal vibrations due to suitable magnitudes of anisotropic intermolecular forces of attractions. The absence of smectogenic character shown by the hexadecyloxy derivative indicates the absence of lamellar packing of molecules in its crystal lattices. The odd-even effect for the smectic–nematic and nematic–isotropic transition curve, as well as variation in mesomorphic properties observed from homologue to homologue in the same series, is due to the sequentially added methylene unit in the n-alkoxy terminal chain [10]. Liquid crystal properties of the novel homologous series, including average thermal stabilities of the smectic and nematic mesophases, are compared (Table 3) with structurally similar/isomeric series as shown in Fig. 2.



α-4-[4′-n-Alkoxy benzoyloxy] benzoyl-β-2″-nitro phenyl ethylenes.

All the homologous series under comparison contain three phenyl rings bridged through —COO— or —CH=CH—COO— and —CO—CH=CH— or —CH=CH—CO— central groups. The n-alkoxy (—OR) terminal end group is commonly present in all homologous series, i.e., series-1, series-X [4], and series-Y [3], and the $-NO_2$ group features in either

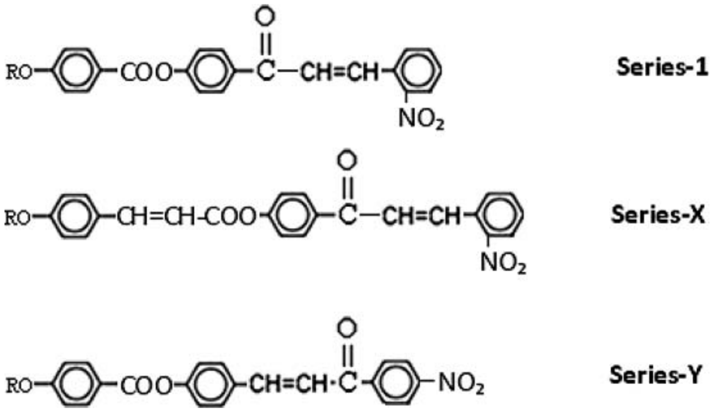


Figure 2. Structurally similar/isomeric series.

terminal or lateral position. Therefore, molecular rigidity and flexibility [5,6] vary from series to series due to varying n-alkoxy terminal end group and varying positional difference of $-NO_2$ group as well as variation arising from central groups from series to series except molecular aromaticity. However, molecular aromaticity can also vary with molecular polarity and polarizability, length to breadth ratio, and hence the suitable or unsuitable magnitudes of anisotropic forces of intermolecular attractions [8,10] which are directly related with the tendency of inducing or not inducing liquid crystal mesophase in a sample substance under examination. As mentioned above, even minor structural variations affect molecular rigidity and flexibility [5,6] and hence cause variation in mesogenic properties in terms of the degree of mesomorphism, thermal stability, commencement of mesophase formation (Table 3), transition temperatures, and mesophase range.

Homologous series-1 and series-Y are structurally identical with respect to n-alkoxy(-OR) terminal end group, three phenyl rings, and $-COO-$ central groups, but differ in their substitutional position of $-NO_2$ and the linking of the $-CO-$ group to the phenyl ring in series-1 and series-Y. The observed difference of smectic and nematic thermal stability as well as the commencement of mesophases can be linked with the structural difference of series-1 and series-Y. The molecules of series-1 are broader and shorter than those of series-Y. Therefore, the length to breadth ratio and the ratio of molecular polarity to polarizability cause suitable magnitudes of anisotropic intermolecular forces of adhesion. Broader molecules of series-1 with relatively higher molecular width than the molecular width of series-Y exerts two opposing effects of intermolecular attractions at a time, as (i) higher molecular width decreases intermolecular closeness and reduces intermolecular adhesion on the one hand, and (ii) increases molecular polarizability and enhances intermolecular adhesion on the other hand. The resultant effect depends upon the predominating effect of the two opposing effects, i.e., (i) and (ii) [10]. Thus, effect (ii) due to molecular polarizability is a predominating effect for series-1 of the present investigation for the smectic and nematic average thermal stabilities, which are higher than series-Y. This indicates that though intermolecular closeness of the linearly shaped molecules of series-Y whose intermolecular adhesion are expected to be more than series-1, but, molecular polarizability of series-1 exceeds the magnitudes of anisotropic forces of intermolecular attractions. On comparing series-1 with series-X, both differ in their one central group, i.e., $-COO-$ and $-CH{=}CH-COO-$ respectively, but the rest of the structure is identical. However, series-X is only nematogenic, while series-1 is smectogenic in addition to nemtogenic mesophase, with average nematic—isotropic thermal stabilities of 171.5°C (series-X) and 163.8°C (series-1) respectively. Therefore, the difference in thermal stability can be explained on the basis of the effect due to carboxy $-COO-$ and vinylcarboxylate $-CH{=}CH-COO-$ central groups. Thus, in all other respects, except central bridges, which are $-COO-$ and $-CH{=}CH-COO-$, series-1 and series-X under discussion are closely similar to each other. Both these central bridges are comparable, although the vinylcarboxylate $-CH{=}CH-COO-$ has greater length, by the $-CH{=}CH-$ unit, increased conjugation by the $-CH{=}CH-$, which increases the molecular rigidity [5,6] and lateral attractions and hence the intermolecular adhesion increases, while in the case of series-Y, the $-COO-$ central bridge is shorter. Consequently, the stereochemistry of molecule does, however, preserve the linearity, but results in less thermally stable nematogenic mesophase. Thus, thermal stability for nematic of series-1 (163.8°C) is less than that of series-X (171.5°C). Moreover, the vinylcarboxylate being longer than $-COO-$ causes more non-coplanarity due to a twist caused by interference of the vinylcarboxylate group and the adjacent hydrogen atoms of aromatic rings. On account of the difference caused in the extent of non-coplanarity [4,8], the commencement of smectic phase takes place from the third member in series-1, it commences from the sixth member of series-Y, and does not commence until hexadecyloxy homologue in series-X. This suggests that the lamellar packing of molecules in crystal lattices of homologues of series-1 enabled to facilitate from propyloxy derivative to tetradecyloxy derivative, while it is facilitated from hexyloxy derivative to tetradecyloxy derivative in the case of series-Y. Variations in mesogenic properties for the same homologue from series to series is attributed to the $-NO_2$ group of fixed polarity substituted at the ortho or para position.

Conclusions

1. Molecular rigidity and flexibility can vary by the same functional group of fixed polarity if substituted at different positions (ortho, meta, para) of the same phenyl ring.
2. Magnitudes of anisotropic intermolecular forces of attraction vary with functional group of the same polarity if substituted at ortho, meta, or para position of the same phenyl ring.
3. The group efficiency order derived for the smectic and nematic mesophases on the basis of thermal stability is as follows:

   Smectic: ortho $-NO_2$ (series-1) > para $-NO_2$ (series-Y) with.
   with —CO-CH=CH— —CH=CH-CO—

   Nematic: ortho $-NO_2$ > ortho $-NO_2$ > para $-NO_2$
   with with with
   —CH=CH-COO— —COO— —COO—
   (series-X) (series-1) (series-Y)

4. Group efficiency order derived on the basis of the early commencement of the smectic and nematic phases is as follows:

   Smectic: ortho $-NO_2$ > para $-NO_2$ > ortho $-NO_2$
   with with with
   —COO— —COO- —CH=CH-COO—
   (series-1) (series-Y) (series-X)

   Nematic: ortho $-NO_2$=para $-NO_2$ > ortho $-NO_2$
   with with with
   —COO— —COO— —CH=CH-COO—
   (series-1) (series-Y) (series-X)

5. Homologous series is predominantly nematogenic and partly smectogenic.
6. Molecular rigidity and flexibility are important factors for the construction of geometrical shape of a novel molecule to induce liquid crystalline property.

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