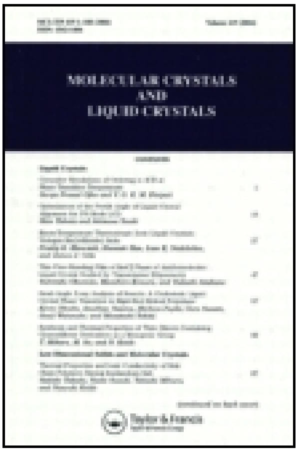

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Study of the Relation Between Molecular Structure and Mesomorphic Behavior with Reference to a Novel Homologous Series: α-3-[4′-n-Alkoxy benzoyloxy] phenyl-β-3″-Nitro benzoyl ethylenes

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Study of the Relation Between Molecular Structure and Mesomorphic Behavior with Reference to a Novel Homologous Series: α-3-[4′-n-Alkoxy benzoyloxy] phenyl-β-3″-Nitro benzoyl ethylenes

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The synthesis and mesomorphic properties of a novel homologous series is reported. With the exception of the methyl and ethyl homologues, all 11 members of the series exhibit mesomorphism enantiotropically. The propyl to pentyl homologues, and the tetradecyl and hexadecyl homologues are enantiotropic nematic without the exhibition of smectic mesomorphism; while the hexyl to dodecyl homologues exhibit smectic mesomorphism in addition to the nematic phase. The texture of the nematic-mesophase by optical polarizing microscopy is of the threaded or Schlieren type, and that of smectogenic homologues is of the focalconic fan type. A phase diagram of the series shows a typical trend. Analytical and spectral data confirm the molecular structure of the compounds. Transition temperatures and mesomorphic properties are determined by optical polarizing microscopy. Smectic and nematic thermal stabilities are 125°C and 167°C, respectively. The series is predominantly nematogenic and partly smectogenic with middle-order melting type, and the smectic and nematic-mesophase ranges vary from 8°C to 22°C and 9°C to 56°C, respectively. The mesomorphic properties of the novel series are compared with other structurally similar homologous series.

Keywords Enantiotropy; liquid crystals; mesomorphism; nematic; smectic

Introduction

The effect of molecular structure on molecular rigidity and flexibility [1,2] using different central groups has been widely studied. Lohar et al. [3a] studied the effect of molecular structure using a –CH=CH–CO– central group linking two phenyl rings, but despite a rod-like shape mesomorphism was not exhibited. Doshi et al. [3b,c] continued in this regard by linking three phenyl rings through two central groups [3a,b], but also introduced a lateral substituent and modified the terminal units. This variation of molecular structure altered the rigidity and flexibility sufficiently to induce mesomorphism [1,2]. The present series was designed to broaden the molecular width by using two angular linking groups (–CH=CH–CO– and –COO–), and an off-axis terminal nitro group. Thus, the effect of

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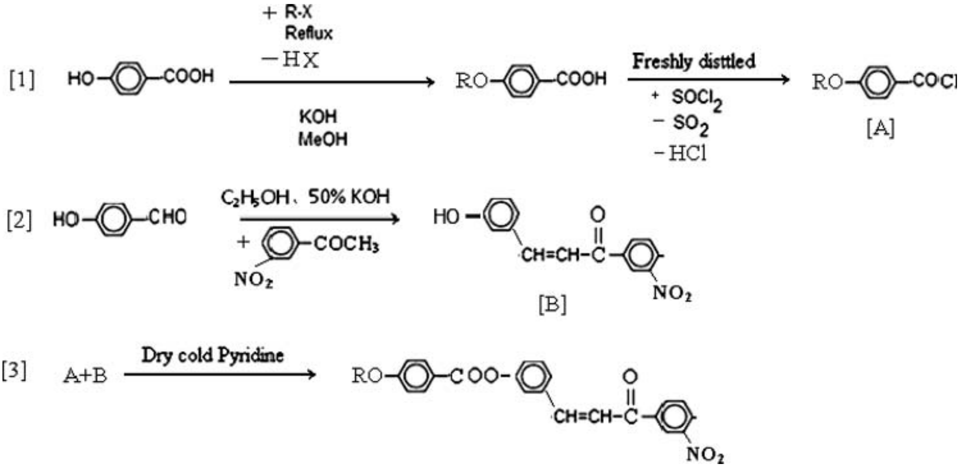
increasing molecular width and generating a nonlinear molecular structure can be correlated in terms of mesomorphic properties.

Experimental

Synthesis

The 4-Hydroxybenzoic acid was alkylated with a suitable alkyl halide (R–X). The resulting alkoxy benzoic acids were converted to corresponding acid chlorides (A) using thionyl chloride by the modified method of Dave and Vora [4]. The 3-Hydroxybenzaldehyde was reacted with 3-nitroacetophenone to form α-3-hydroxy phenyl β-3′-nitrobenzoyl ethylene (B) by an established method [5]. Components (A) and (B) were condensed in dry cold pyridine to form the final products [4,5,6]. All final products of the series were filtered, washed, dried, and purified until constant transition temperatures were obtained. The synthetic route to the series is outlined 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 representative selected members of the series were characterized by elemental analysis (Table 1), infrared (IR), and ^{1}HNMR spectroscopy. Microanalysis was performed on a

Table 1. Elemental analysis for butyloxy, pentyloxy, decyloxy, and dodecyloxy derivatives

	Element found (%calculated)		
Molecular formula	C	H	N
$C_{26}H_{23}NO_6$	70.35 (70.11)	5.95 (5.17)	3.19 (3.25)
$C_{27}H_{25}NO_6$	70.64 (70.60)	5.53 (5.45)	3.08 (3.15)
$C_{32}H_{35}NO_6$	72.87 (72.60)	6.88 (6.61)	2.91 (3.05)
$C_{34}H_{39}NO_6$	73.81 (73.58)	7.28 (7.05)	2.58 (2.39)

Perkin–Elmer PE 2400 CHN analyzer. IR spectra were recorded on a Perkin–Elmer spectrum GX instrument, and ^{1}HNMR spectra were recorded on a Bruker spectrometer using $CDCl_3$ as solvent. The textures of the smectic and the nematic phase were determined by a miscibility method using an optical polarizing microscopy.

Analytical Data

NMR in PPM for octyloxy derivative: 0.89 ($-CH_3$ of OC_8H_{17}), 1.29 ($((-CH_2-)_n$ of OC_8H_{17}), 4.00 ($-OCH_2$ of OC_8H_{17}), 7.88–8.10 (aromatic ring) 6.89 and 6.92 ($-CH{=}CH-CO-$). The data support the molecular structure.

NMR in PPM for tetradecyloxy derivative: 0.87 ($-CH_3$ of $OC_{14}H_{29}$), 1.44 ($((-CH_2-)_n$ of $OC_{14}H_{29}$), 4.00 ($-OCH_2$of $OC_{14}H_{29}$), 7.90–8.11 (aromatic ring), 6.89 and 6.92 ($-CO-CH{=}CH-$). The data support the molecular structure.

IR in cm^{-1} for propyloxy derivative: 740, 880 (aromatic ring), 1160 (C–O), 1420 ($-NO_2$ group), 1250, 1600, 1680 (–COO-group), 970 ($-CH{=}CH-$), and 640 (polymethelyne of C_3H_7). The data support the molecular structure.

IR in cm^{-1} for hexyloxy derivative: 840 (aromatic ring), 1170 (C–O), 940 ($-CH{=}CH-$), 1250, 1600, 1680 (–COO group), 1430 ($-NO_2$ group), 750 (polymethelyne of C_6H_{13}). The data support the molecular structure.

Texture by miscibility method

Result and Discussion

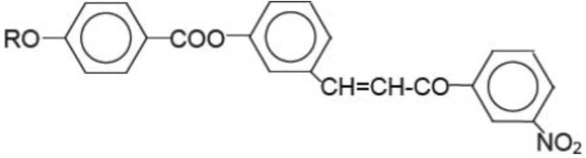
Eleven members of the novel series under discussion were investigated for melting point, transition temperatures, and mesophase morphology using optical polarizing microscopy. The propyl to pentyl homologues, and the tetradecyl and hexadecyl derivatives of the series are enantiotropically nematogenic. The hexyl to dodecyl derivatives are enantiotropic nematic with exhibition of smectogenic character. The transition temperatures are shown in [Table 2]. A plot of the transition temperatures versus the number of carbon atoms in the terminal alkoxy chain gives rise to a phase diagram (Fig. 1) which consists of solid-isotropic or solid-mesomorphic, smectic–nematic or smectic-isotropic, and nematic-isotropic transition curves. The solid-isotropic or solid-mesomorphic transition curve follows a zigzag path of rising and falling temperatures with an overall descending tendency. The smectic–nematic transition curve initially rises, passes through maxima at the decyl derivative and then falls at the dodecyl homologue, and then behaves in the usual expected manner. The curve was extrapolated [7,5] to the tetradecyl derivative to predict its latent transition temperature for the smectic phase, which gave a value of 86°C. However, the actual transition is not realizable practically due to the high-crystallizing tendency. The smectic-nematic transition curve behaves in normal manner without any odd–even effect. The nematic-isotropic transition curve descended as the series is ascended upto the tetradecyl homologue, but it shows an ascending tendency of 10°C at the hexadecyl derivative. An odd–even effect is observed for the nematic-isotropic transition curve. The series is predominantly nematogenic and partly smectogenic with middle ordered melting type and methyl and ethyl derivatives are not mesomorphic. The mesomorphic-isotropic transition temperatures for the series vary between 185°C and 152°C.

The methyl and ethyl derivatives of the novel series are not mesomorphic due to their high-crystallizing tendency, which arises from the shorter and hence stiffer alkoxy terminal chains. The molecules of mesomorphic the homologues are able to resist thermal vibrations exposed upon them and disaligned on the plane of a surface at an angle $< 90°$. As

Table 2. Transition temperatures of series in °C

		Transition temperatures in °C		
Sr. no.	n-alkyl group –C_nH_{2n+1}	Sm	*N*	Isotropic
1	1	–	–	213.0
2	2	–	–	205.0
3	3	–	170.0	185.0
4	4	–	166.0	175.0
5	5	–	142.0	177.0
6	6	109.0	118.0	174.0
7	8	116.0	124.0	170.0
8	10	108.0	130.0	163.0
9	12	96.0	118.0	152.0
10	14	–	132.0	151.0
11	16	–	142.0	160.0

Sm, Smectic; N, Nematic.



α-3-[4′-n-Alkoxy benzoyloxy] phenyl-β-3″-Nitro benzoyl ethylenes

a result the molecules are floating either with parallel orientational or a sliding interlayered arrangement to cause nematic- or smectic-mesophase formation. The propyl to hexadecyl derivatives exhibit the nematic-mesophase as do the hexyl to dodecyl derivatives, however, these also exhibit the semctic phase. Such mesomorphism is a result of suitable magnitudes of anisotropic intermolecular forces of attraction as a consequence of favorable molecular rigidity and flexibility [1,2] between two temperatures to cause a statistically parallel orientation of the molecules resulting in a nematic phase. The hexyl to dodecyl derivatives possess lamellar packing in their crystal lattices, which under the influence of heat, resist thermal vibrations exposed upon them to maintain a two dimensional array of molecules with sliding layered molecular arrangement to cause smectogenic-mesophase formation. An odd–even effect for the smectic-isotropic curve and variations in mesomorphic properties from homologue to homologue in the same series is observed due to the sequentially added methylene unit in the alkoxy terminal chain. Both curves for odd and even homologues merge into each other at the heptyl homologue. The odd–even effect diminishes for higher homologues, because longer chain may coil, bend, flex, or couple to lie in a line of major axis of the core [8]. Thus, the higher homologues may show a deviating behavior from normal behavior because of the molecular rigidity and flexibility [1,2]. The mesomorphic properties of the novel homologous series-1, are compared with structurally similar homologous series-X [9] and series-Y [10] in Fig. 2.

The homologous series-1 and series-X are structurally similar with respect to three phenyl rings and the terminal groups, but they differ in their geometrical shape because series-1 has the bent core in the center of the molecules. Series-1 and series-Y are isomeric

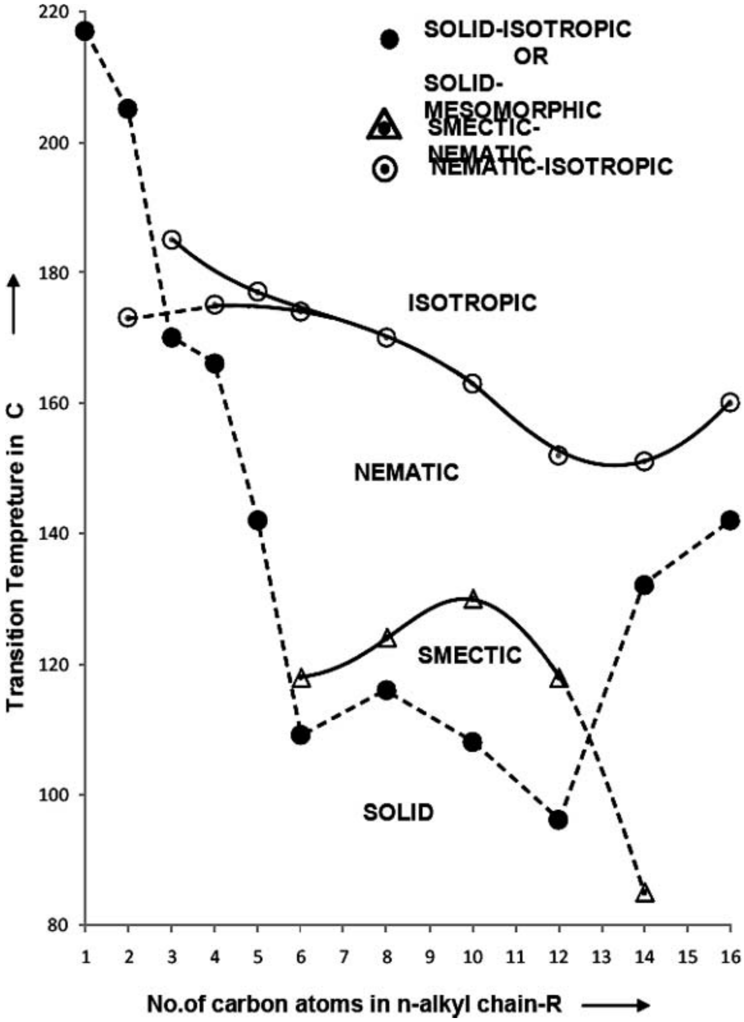


Figure 1. Phase behavior of series.

and identical in the linking groups and terminal groups, but they differ in their molecular geometrical shape and linearity because of the bent-core nature of series-1. Therefore, the difference in mesomorphic properties and degree of mesomorphism are correlated with the differing structural features of series-1, series-X, and series-Y under comparison. Thermal stabilities and the commencement of mesophase formation are outlined in Table 3.

The smectic and nematic thermal stabilities of series-1 and series-Y differ due to their molecular shape difference and magnitudes of molecular width. The intermolecular closeness varies, though the molecular length is almost equivalent. Therefore, length to breadth ratio and the ratio of the molecular polarity to polarizability varies accordingly. The difference in intermolecular closeness of series-1 and series-Y causes a difference in the magnitudes of molecular polarizability and intermolecular distance. The net effect due to polarizability exceeds the effect due to intermolecular width. Hence, the net magnitudes of

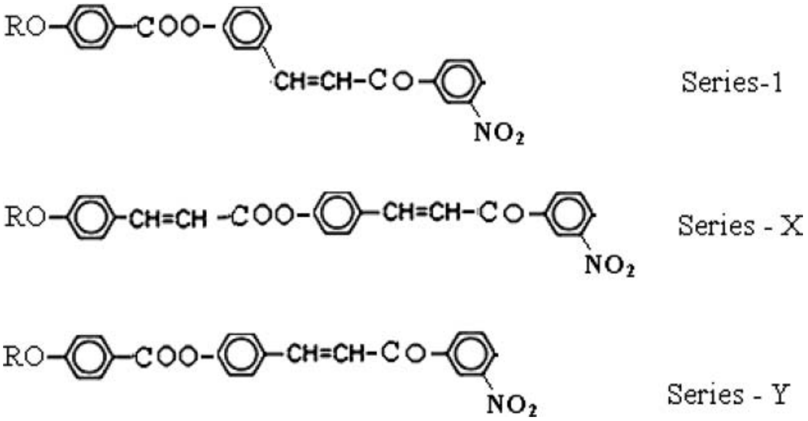


Figure 2. Structurally similar/isomeric series.

anisotropic forces of attraction of series-1 is more than for series-Y. Therefore, the smectic and nematic thermal stabilities (Table 3) of series-1 are greater than series-Y. The smectic thermal stability of series-1 is less than for series-X, but the nematic thermal stability of series-1 is greater than for series-X. The molecules of series-X due to two central groups with conjugated double bonds have higher molecular rigidity. Moreover, the –CH=CH–COO– central group increases the molecular length compared with the –COO– central group. Thus, the overall magnitudes of anisotropic forces of adhesion are enhanced for series-1. Hence, smectic thermal stability of series-1 is lower than series-X. The commencement of the smectic phase takes place for series-1, series-X, and series-Y from fifth/sixth members of the series. This indicates that the extent of noncoplanarity caused by the molecules of series-1 and series-Y are equivalent. This variation causes early commencement of smectic phase as the –COO– central group preserves molecular linearity more than the –CH=CH–COO– group. Hence, the nematic-mesophase formation of series-1 and series-Y takes place from C_3 and C_2 carbon while it commences from fifth carbon of series-X. Thus, the difference in mesomorphic properties from series to series for the same homologue is attributed to the molecular geometrical shape in the isomeric series. However, the differing central group, molecular width, and hence the molecular polarity and polarizability can also vary the degree of mesomorphism.

Table 3. Relative average thermal stability in °C

	Average transition temperatures in °C		
Series	Series (1)	Series (X)	Series (Y)
Smectic-nematic	125.0 (C_6–C_{12})	154.6 (C_5–C_8)	121.2 (C_6–C_{14})
Commencement of smectic phase	C_6	C_5	C_6
Nematic-isotropic	167.4 (C_3–C_{16})	163.8 (C_5–C_{16})	160.0 (C_2–C_{16})
Commencement of nematic phase	C_3	C_5	C_2

Conclusion

The novel presently investigated and discussed homologous series has the following points.

(1) Predominantly nematogenic and partly smectogenic with middle-ordered melting type.

(2) The group efficiency order derived on the basis of thermal stability for smectic and nematic.
With common presence of central group –CH=CH–CO– is as under

Smectic:	Series-X With –CH=CH–COO–	Series-1 With > –COO–	Series-Y With > –COO–

	Linear shape	Nonlinear shape	Linear shape
Nematic:	Series-1 With –COO–	Series-X >With –CH=CH–COO–	Series-Y >With –COO–

(3) Group efficiency order derived on the basis of early commencement of smectic- and nematic phase.

Smectic:	Series-X With –CH=CH–COO–	Series-1 >With –COO–	Series-Y =With –COO–
Nematic:	Series-1 With –COO–	Series-X >With –COO–	Series-Y >With –CH=CH–COO–

(4) The variation in mesomorphic properties from series to series for the same homologue depends upon the molecular shape, size, molecular width, and polarizability if terminal-end groups are common of fixed polarity, substituted at identical position.

(5) Magnitudes of molecular rigidity and flexibility depend upon shape, size, and molecular width when other factors affecting intermolecular adhesion forces are identical.

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[9] Paper entitled, " Synthesis of Novel Mesomorphic Homologous Series: α-4-[-4′-n-alkoxy cinnamoyloxy] Phenyll β-3″-Nitro benzoyl ethylenes." manuscript No. LCMH -156 communicated and accepted for publication in coming issue. **June-2012**.

[10] Paper entitled, " Synthesis of a novel liquid crystalline ethylene derivatives of a series: α-4-[-4′-n-Alkoxy benzoyloxy]phenyl β-3″-nitro benzoyl ethylenes." submitted to Derpharma Chemica and accepted for publication in the issue of **June-2012**.