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A Novel Mesomorphic Homologous Series of Ethylene Derivatives α-4-(4′-n-Alkoxy benzoyloxy) Benzoyl β-3″-Nitro Phenyl Ethylenes

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A novel homologous series of 11 ethylene derivatives has been synthesized and evaluated. The methoxy to pentyloxy homologues are nonmesomorphic, whereas the hexyloxy to dodecyloxy derivatives are enantiotropically smectogenic and enantiotropically nematogenic in character. The tetradecyloxy and hexadecyloxy homologues exhibit only nematogenic character without showing of any smectogenic character. An odd–even effect is not observed in either of the transition curves from a phase diagram. The average smectic and nematic thermal stabilities are 126.7°C and 148.6°C, respectively. The liquid crystal properties of the novel series are compared with other structurally similar compounds. The texture of the nematic phase is a threaded or Schlieren type, and that of smectic phase shows the smectic A type as determined by optical polarizing microscopy. Analytical data support the molecular structures in all cases. The novel series is predominantly nematogenic and partly smectogenic with mesophase temperature ranges between 12°C and 63°C.

Keywords Mesomorphism; nematic; smectic

Introduction

Molecular rigidity and flexibility are very important factors controlling the mesomorphic behavior of a substance. The present investigation involves the synthesis and evaluation of a benzoester homologous series with three phenyl rings bridged through –COO– and –CO–CH=CH– as central linking groups within the rigid core. The terminal n-alkoxy chain and the meta substituted $–NO_2$ group serve as flexible units. Thus, molecular rigidity and flexibility are varied by introducing central linking groups and varying n-alkoxy terminal chain. The meta substituted $–NO_2$ group partly broadens the molecule, and linking groups lengthen the molecular structure. This study will discuss structural property relationships in terms of the effect of molecular breadth, length, polarity, and polarizability on the magnitude of anisotropic forces of intermolecular attractions and hence on mesomorphism.

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Experimental

Synthesis

4-Hydroxybenzoic acid, n-alkyl halides, thionyl chloride, pyridine, KOH, MeOH, 4-hydroxy acetophenone, 3-nitro benzaldehyde, and ethanol required for the synthesis were used as received. 4-Hydroxybenzoic acid was alkylated by appropriate alkylating agents. The 4-n-alkoxybenzoic acid and the corresponding 4-n-alkoxybenzoyl chloride (A) were prepared by modified method of Dave and Vora [1]. α-4-Hydroxy benzoyl β-3′-nitro phenyl ethylene (B) was prepared by an established method of Doshi and Patel [2c]. Components (A) and (B) were condensed in dry cold pyridine by an established method [2d]. The synthetic route to the series is outlined in Scheme 1.

Characterization

Selected representative homologues of novel series were characterized for their molecular structure by elemental analysis, infrared (IR), and nuclear magnetic resonance (^{1}H NMR) spectroscopy techniques. Microanalysis was performed using a PerkinElmer PE 2400 C, H, N analyzer. The IR spectra were recorded on a PerkinElmer spectrum GX, the ^{1}H NMR spectra were recorded on a Bruker instrument using $CDCl_3$ as the solvent. The mesomorphic properties were investigated using an optical polarizing microscope equipped with a heating stage (Table 1).

Analytical Data

Elemental Analysis

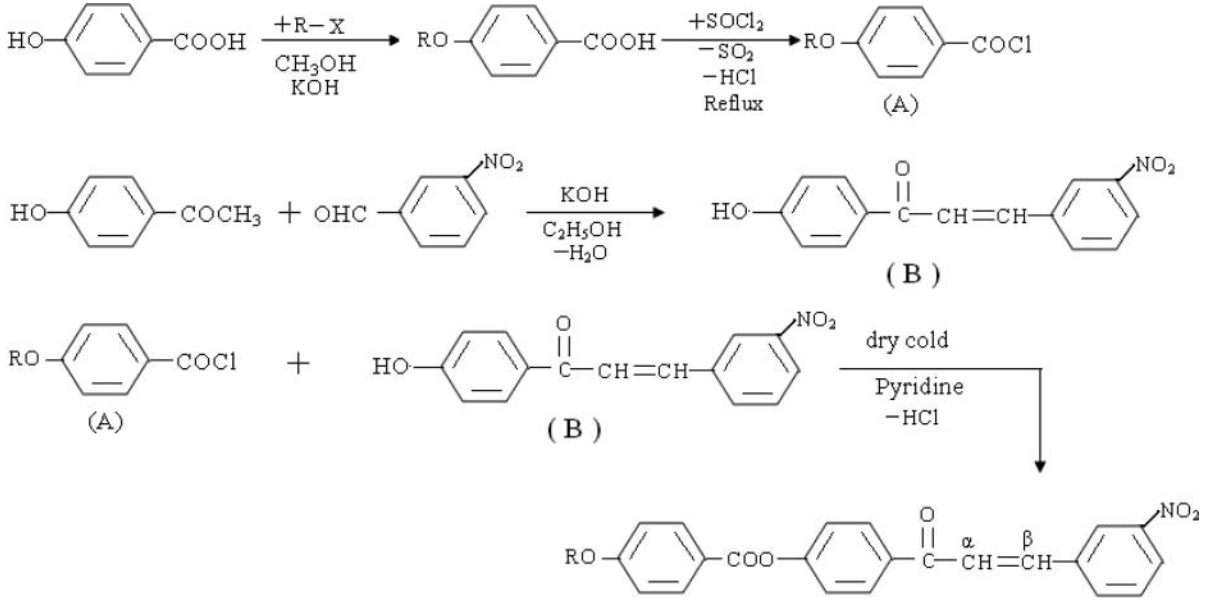
Spectral Data.

NMR in ppm for Octyloxy Derivative. 0.880 (t, CH_3 of OC_8H_{17} chain), 1.307–1.77 (m) ($(CH_2)_n$ polymethylene group of OC_8H_{17} chain), 4.00 (t, OCH_2 of OC_8H_{17} chain), 6.92 (–CH=CH–) 7.29 (–CH=CH–CO–), 6.75–8.10 (phenyl ring). The NMR supports the structure.

NMR in ppm for Dodecyloxy Derivative. 0.871 (t, CH_3 of $OC_{12}H_{25}$ chain), 1.25–1.76 (m) ($(CH_2)_n$ polymethylene group of $OC_{12}H_{25}$), 4.02 (t, OCH_2 of $OC_{12}H_{25}$), 7.2 (–CH=CH–CO–), 6.9–8.10 (phenyl ring). 7.00 (–CH=CH–). The NMR supports the structure.

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

		Elements % found (% calculated)		
Sr. no	Molecular formula	C	H	N
1	$C_{25}H_{21}NO_6$	69.68 (69.60)	4.80 (4.87)	3.31 (3.25)
2	$C_{27}H_{25}NO_6$	71.50 (71.59)	5.55 (5.45)	3.00 (3.05)
3	$C_{36}H_{43}NO_6$	72.90 (73.85)	7.23 (7.35)	2.45 (2.39)
4	$C_{38}H_{47}NO_6$	74.32 (74.39)	7.61 (7.67)	2.35 (2.28)



α-4-(4′-n-Alkoxy benzoyloxy) benzoyl β-3″-Nitro phenyl ethylenes
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.

IR in cm^{-1} for Hexyloxy Derivative. 720 ($(CH_2)_n$ polymethylene group of OC_6H_{13} chain), 680,760 (m-substituted phenyl ring), 840 (p-substituted phenyl ring), 1160, 1250,165 (ester group), 1380, 1525 (–NO_2 group), 950 (–CH=CH– group). The IR supports the structure.

IR in cm^{-1} for Decyloxy Derivative. 720 ((CH_2)n polymethylene group of $OC_{12}H_{25}$ group), 640, 760 (m-substituted phenyl ring), 830 (p-substituted phenyl ring), 1150,1250, 1600, 1660 (ester group), 1440, 1500 (-NO_2 group), 950 (–CH=CH– group). The IR supports the structure. Texture: by miscibility. Method: Hexyloxy homologue shows a threaded type texture and Tetradecyloxy homologue shows a schlieren type texture.

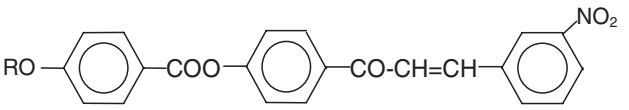
Results and Discussion

The alkoxybenzoic acids are dimeric through hydrogen bonding. However, hydrogen bonding breaks and disappears on esterification by linking it with α-4-hydroxy benzoyl β-3′-nitro phenyl ethylene (B). Dimerized n-alkoxybenzoic acids involve two phenyl rings, but, the final compound consists of –COO– and –CO–CH=CH– linking groups and three phenyl rings. Thus, the number of phenyl rings though increases overall by one as compared to the dimerized n-alkoxybenzoic acid. Overall, the melting point and transition temperatures of the resultant ester derivatives do not rise proportionately. The esterification process of n-alkoxybenzoic acids lowers the transition temperatures due to breaking of hydrogen bonding. The methoxy to pentyloxy homologues are nonliquid crystalline, and sharply melt at their melting point without showing a liquid crystal mesophase. The hexyloxy to hexadecyloxy homologues are liquid crystalline and exhibit enantiotropic smectogenic and nematogenic phases. The tetradecyloxy and hexadecyloxy derivatives exhibit an enantiotropic nematic phase without any smectic character. The transition temperatures are shown in Table 2, and the phase diagram (Fig. 1) shows the phase behavior of the homologues versus the number of carbon atoms present in n-alkoxy terminal chain. The phase diagram indicates that the solid–isotropic or solid–mesophase curve rises and falls in a zigzag manner with an overall falling tendency. The smectic–nematic transition curve initially falls from the hexyloxy to the octyloxy homologue, and then behaves in the usual manner by rising up to the dodecyloxy derivative and then smectic mesophase disappears.

Table 2. Transition temperatures in °C of series-1

Compound no.	R = C_nH_{2n+1} (n)	SmA	N	Isotropic
1	1	–	–	183.0
2	2	–	–	160.0
3	3	–	–	169.0
4	4	–	–	161.0
5	5	–	–	170.0
6	6	116.0	134.0	165.0
7	8	99.0	112.0	155.0
8	10	109.0	125.0	172.0
9	12	106.0	136.0	158.0
10	14	–	105.0	120.0
11	16	–	110.0	122.0

Note: SmA = smectic A; N = nematic.



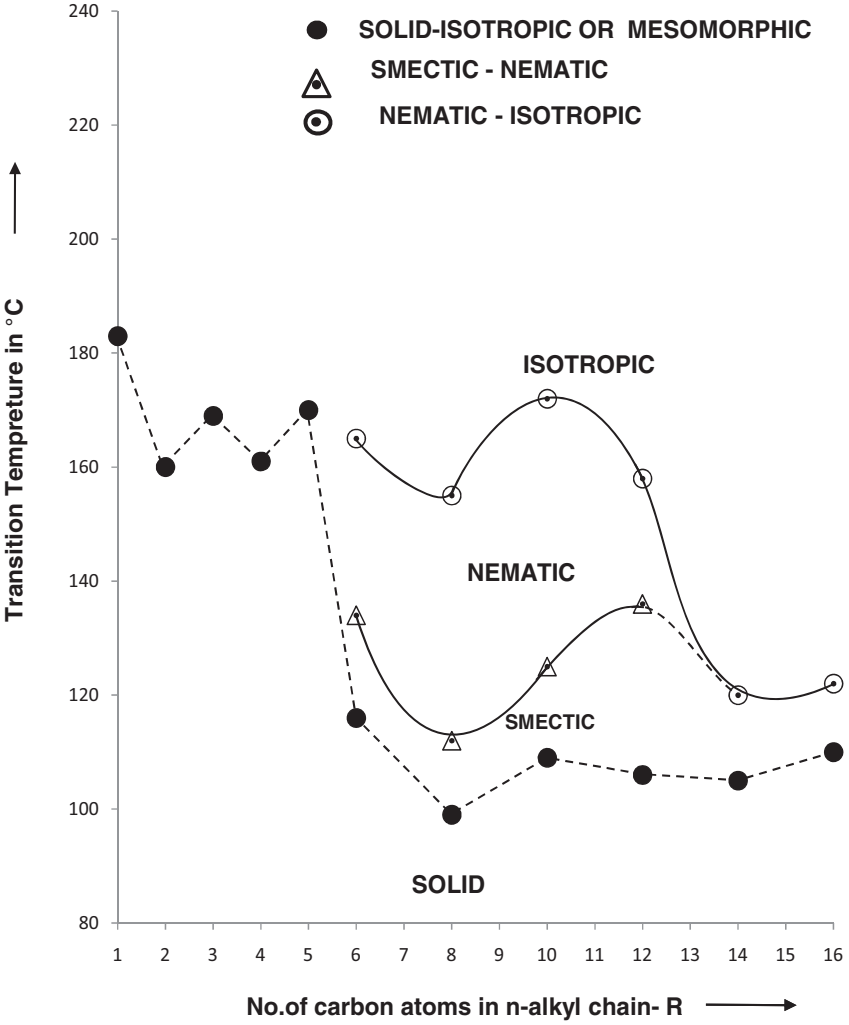


Figure 1. Phase behavior of series.

Therefore, the curve is extrapolated [2c] to the tetradecyloxy homologue following the trend of the curve. The extrapolated curve merges and coincides to the solid–nematic transition temperature 120°C. This clearly illustrates the disappearance of the smectic phase from and beyond the tetradecyloxy homologue. An odd–even effect is absent for the smectic–nematic transition curve. The nematic–isotropic transition curve also adopts a similar pattern of propagation as shown by the smectic–nematic transition as the series is ascended without showing any odd–even effect, i.e., it initially falls at the octyloxy derivative then rises and falls from the decyloxy to the hexadecyloxy homologue as the series is

Table 3. Average thermal stability in °C

Series→	1	A	B
Smectic–nematic	126.7 (C_6–C_{12})	141.0 (C_5–C_{10})	106.66 (C_{10}–C_{14})
Commencement of smectic phase	C_6	C_5	C_{10}
Nematic–isotropic	148.6 (C_6–C_{16})	156.0 (C_5–C_{16})	119.8 (C_8–C_{16})
Commencement of nematic phase	C_6	C_5	C_8

ascended. The nonmesomorphic behavior of the methoxy to the pentyloxy derivatives is attributed to their high crystallizing tendency, which arises from unsuitable magnitudes of intermolecular anisotropic forces, i.e., the molecules of first five homologues are unable to resist thermal vibrations exposed upon them from the external source of thermodynamic surroundings. Therefore, neither the statistically parallel orientational order nor the sliding layered order of the molecules occurs, which results in the absence of either the nematic or the smectic mesophase, and concerned homologues sharply transform into isotropic state from solid crystalline state. The hexyloxy to dodecyloxy derivatives of the series exhibit smectogenic character in addition to nematogenic character reversibly; while the tetradecyloxy and the hexadecyloxy derivatives exhibit only nematogenic character. The occurrence of smectogenic character is attributed to the lamellar packing of molecules in their crystal lattices, which results in a sliding layered arrangement of molecules from the hexyloxy to the dodecyloxy homologues. The absence of smectogenic behavior from the tetradecyloxy and the hexadecyloxy homologues can be due to irregular coiling, bending, and flexing of longer n-alkyl chain causing variation of molecular rigidity and flexibility maintaining only statistically parallel orientational order of the molecules without a lamellar packing of molecules. The exhibition of nematogenic character in addition to smectogenic behavior by the hexyloxy to dodecyloxy derivatives is attributed to the relatively higher magnitudes of attractions, which maintains lamellar packing of the molecules as well as stronger end-to-end attractions. Thus, favorable molecular rigidity and flexibility generates the smectic and nematic phases.

The mesomorphic properties of the novel series-1 are summarized in Table 3, and are compared with the structurally similar homologous series A [3] and B [4c] as shown in Fig. 2.

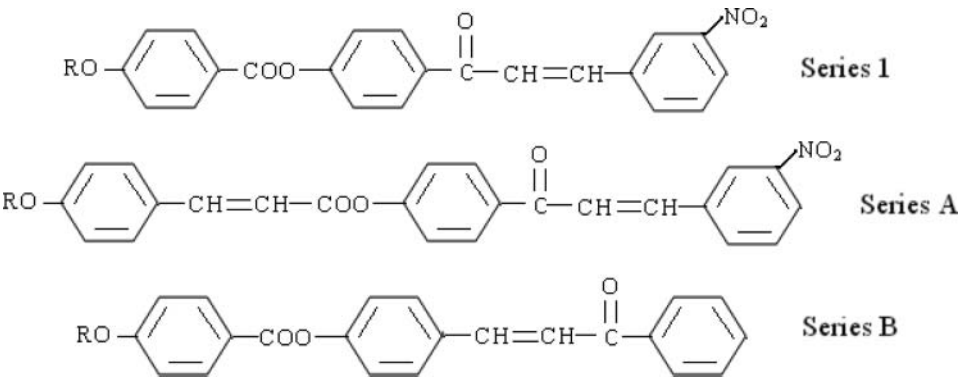


Figure 2. Structurally similar series.

Although, series 1, A and B are structurally similar, they differ from their linking groups and the nitro group. Therefore, their rigidity and/or flexibility [5–7] are different, and hence the variation in the mesomorphic properties and degree of mesomorphism accordingly. Series 1 and A are identical with respect to aromaticity due to three phenyl rings, the terminal alkoxy chain and the nitro group, but they differ with respect to a linking group. Therefore, the molecular length due to the –CH=CH– unit of series A is longer than that of series 1. Hence, the length to breadth ratios vary accordingly causing a difference of molecular rigidity and flexibility, and hence the magnitude of anisotropic forces of intermolecular attractions. Series 1 and B differ only by the absence of the nitro group in series B. Therefore, they differ in molecular breadth, and hence the difference is reflected in variations in molecular polarity and polarizability. The comparison of mesomorphic behavior is summarized in Table 3.

Table 3 indicates that smectic and nematic thermal stability for series 1 is lower than that of series A. The molecules of series 1 and A are identical in all other respects except the central bridge. Both these central bridges are comparable, though the –COO– has shorter length than the –CH=CH–COO– linking group. Therefore, greater length of the vinyl carboxylate –CH=CH–COO– causes more noncoplanarity due to a twist obtained as the oxygen atoms of vinyl carboxy group impinge on the adjacent hydrogen atoms of the aromatic rings. Moreover, increased molecular length increases length to breadth ratio, enhancing the end-to-end intermolecular anisotropic forces of attractions [8]. On account of these differences, the smectic–nematic and nematic–isotropic thermal stabilities are lower for series 1 than for the corresponding homologous series A. Lamellar packing of molecules commences from sixth and fifth member of the series 1 and A, respectively. Molecules of series 1 and B differ in isomeric central group –CO–CH=CH– and –CH=CH–CO– and the laterally substituted $–NO_2$ group in place of –H on the third phenyl ring. The shifting of the >C=O group causes an increase in thermal stabilities. Moreover, the $–NO_2$ group is more polar than –H due to its more electron withdrawing tendency than –H. Thus, the end-to-end attractions cause a rise in the nematic isotropic thermal stability. The mesomorphic phase range varies from 12°C at the hexadecyloxy derivative to a maximum of 63°C at the decyloxy derivative. The smectogenic and nematogenic phase range varies from 13°C to 30°C and 12°C to 47°C, respectively. Thus, the novel series is predominantly nematogenic and partly smectogenic.

Conclusion

(1) The novel series is predominantly nematogenic and partly smectogenic with middle range melting points.
(2) Molecular rigidity and flexibility with reference to width of molecules are the deciding factor for mesophase formation.
(3) Variation of mesomorphic properties from homologue to homologue in the same series and series to series for same homologue depends upon varying the polarity of the n-alkoxy terminal chain.
(4) Broadening of molecules increases the molecular polarizability as a result of changing molecular rigidity and flexibility. Thus, degree of mesomorphisam varies accordingly.

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