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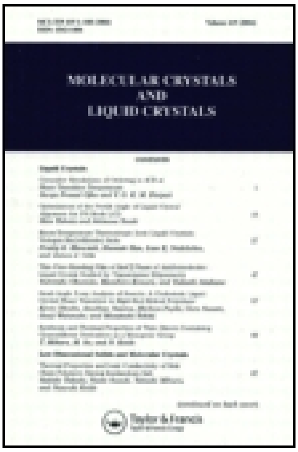

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A Study of Liquid Crystalline Properties and Their Relation to the Molecular Structure of Novel Ethylene Derivatives

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A Study of Liquid Crystalline Properties and Their Relation to the Molecular Structure of Novel Ethylene Derivatives

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A novel homologous series α-4-[4′-n-Alkoxy benzoyloxy] benzoyl β-4″-methoxy phenyl ethylenes of 12 homologue substances is presented and comprises of 5 compounds (heptyl to tetradecyl) that exhibit both a smectic and a nematic phases. The pentyl, hexyl, and hexadecyl homologues only exhibit the nematic without exhibition of any smectogenic property. The methyl to butyl homologues are not liquid crystalline. All novel liquid crystal (LC) substances of novel series are enantiotropically mesomorphic. The textures of nematogenic homologues are threaded or Schlieren and that of the smectogenic homologues are typical of the smectic A or C. Analytical and spectral data support the molecular structures. Solid-mesomorphic or isotropic, Sm-N, and N-isotropic transition curves of a phase diagram behave in a normal manner. An odd–even effect is exhibited by the Sm-N and N-isotropic transition curves. Thermal stabilities for the smectic and nematic mesophases are 118.0°C and 157.0°C, respectively. The Sm-N mesophase length is between 13°C and 21°C, whereas the N-I mesophase length varies between 20°C and 46°C. The liquid crystal properties of the novel series are compared with known structurally similar homologous series.

Keywords liquid crystals; smectic; mesogen; mesomorphic; nematic

Introduction

A unique physical state of a matter called the liquid crystalline state, mesomorphic state, or anisotropic state is neither fully liquid nor crystalline. Thus, not all, but some of the substances exhibit this intermediate state between crystalline solid and isotropic liquid on heating. The liquid crystal (LC) state is exploited in many industrial applications. Exhibition of an LC state by any substance requires suitable magnitudes of anisotropic intermolecular forces of attractions [1] as a consequence of favorable molecular rigidity and flexibility [2–4], which arises from the appropriate construction of a molecular structure made up

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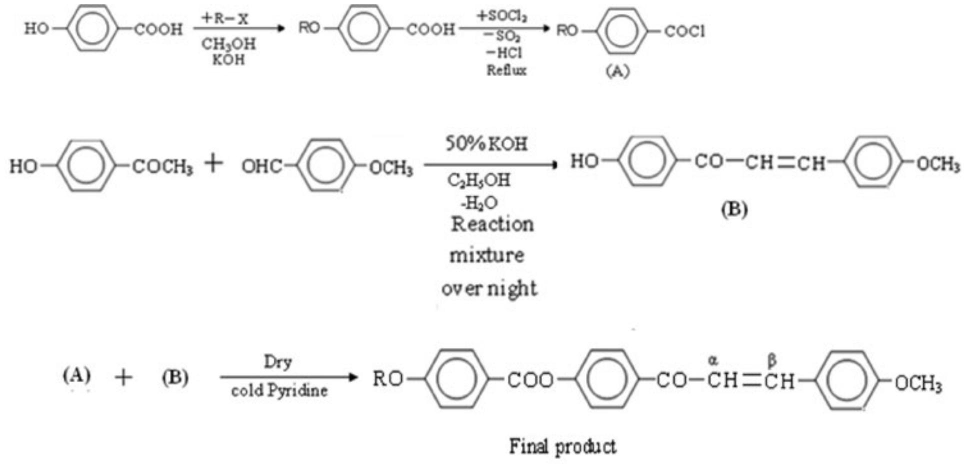


α-4-[4′-*n*-Alkoxy benzoyloxy] benzoyl β-4″-methoxy phenyl ethylenes
Where R = C_nH_{2n+1} n = 1,2,3,4,5,6,7,8,10,12,14,16.

Scheme 1. Synthetic route to the novel series.

of phenyl rings, a central group or groups lateral and terminal end groups substituted on phenyl rings. A novel molecular structure consists of three phenyl rings bridged through –COO– and –CO–CH=CH– central groups and *n*-alkoxy (–OR) and $–OCH_3$ terminal end groups without any laterally substituted functional group. Thus, the influence of the $–OCH_3$ terminal end group on liquid crystal properties of the substance can be established, discussed, and understood.

Experimental

Synthesis

4-Hydroxybenzoic was alkylated by suitable alkylating agents (R–X) to form *n*-alkoxy benzoic acids, which on reacting with thionyl chloride yielded the corresponding 4-*n*-alkoxy benzoyl chlorides (A) by the modified method of Dave and Vora [5]. α-4-Hydroxy benzoyl-β-4′-methoxy phenyl ethylene (B) was prepared by the usual established method [6] from 4-hydroxyacetophenone and anisaldehyde. Components (A) and (B) were condensed in dry cold pyridine. 4-Hydroxybenzoic acid, 4-hydroxyacetophenone, anisaldehyde, pyridine, MeOH, KOH, alkyl halides required for synthesis were used as received, except for solvents that were dried and purified prior to use. The synthetic route to the series is shown in Scheme 1.

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 as shown in Table 1. IR spectra were recorded on Perkin–Elmer spectrum GX. ^{1}HNMR spectra were recorded using $CDCl_3$ as solvent. Liquid crystal properties were determined by an optical polarizing microscope equipped with heating stage. Textures of the nematic and smectic phase were determined by a miscibility method.

Analytical Data

Table 1. Elemental analysis for methoxy, propoxy, heptyloxy, and tetradecyloxy derivatives

		Elements% found (% Calculated)	
Sr. no	Molecular formula	C	H
1	$C_{24}H_{20}O_5$	74.28 (74.23)	5.23 (5.15)
2	$C_{26}H_{24}O_5$	75.14 (75.00)	5.97 (5.77)
3	$C_{30}H_{32}O_5$	76.48 (76.27)	7.01 (6.78)
4	$C_{37}H_{46}O_5$	78.12 (77.89)	8.18 (8.07)

Spectral Data

NMR in ppm for Decyloxy Derivative. 0.88 (–CH_3 of –$OC_{10}H_{21}$ group), 1.42 (–$(CH_2)n$– of –$OC_{10}H_{21}$), 3.99 (–OCH_2–CH_2– of –$OC_{10}H_{21}$), 6.70, 6.77, and 6.93 (–CO–CH=CH– group), 7.84, 7.88, and 7.90 (*p*-substituted phenyl ring). The NMR spectrum supports the molecular structure.

NMR in ppm for Dodecyloxy Derivative. 0.89 (–CH_3 of –$OC_{12}H_{25}$ group), 1.26, 1.41 ((–CH_2)*n*– –$OC_{12}H_{25}$ group), 3.99 (–OCH_2–CH_2– of –$OC_{12}H_{25}$ group), 6.82, 6.84, and 6.91 (–CO–CH=CH–group), 7.84, 7.90, and 7.92 (*p*-substituted phenyl ring). The NMR spectrum supports the molecular structure.

IR in cm^{-1} for Pentyloxy Derivative. 750 (–$(CH_2)n$– group of –OC_5H_{11}), 845 (*p*-substituted phenyl ring), 1160 (C–O of –OC_5H_{11} group), 1250, 1280, and 1640 (–COO ester group), 920 (–CH=CH– group), The IR spectrum supports the molecular structure.

IR in cm^{-1} for Octyloxy Derivative. 765 (–$(CH_2)n$– group of –OC_8H_{17}), 840 (*p*-substituted phenyl ring), 1165 (C–O of –OC_8H_{17} group), 1250, 1605, and 1680 (–COO ester group), 850 (–CH=CH– group). The IR spectrum supports the molecular structure.

Texture Determination

Hexyl homologue—Threaded nematic
Hexadecyl homologue—Schlieren nematic
Octyloxy homologue—Smectic-A

Results and Discussion

n-Alkoxybenzoic acids are dimeric and their dimerization disappears on esterification through the breaking of hydrogen bonding between two molecules of *n*-alkoxybenzoic acids. Enantiotropic smectic and/or only nematic mesophase formation occurs from the pentyl to hexadecyl homologues of the novel homologous series α-4-[4′-*n*-alkoxy benzoyloxy] benzoyl β-4″-methoxy phenyl ethylenes. The methyl to butyl homologue derivatives are nonmesomorphic as shown in Table 2. A phase diagram (Fig. 1) shows the phase

Table 2. Transition temperatures of series in °C

Compound no.	n-alkyl group $-C_nH_{2n+1(n)}$	Transition temperatures in °C		
		Sm	N	Isotropic
1	1	—	—	200.0
2	2	—	—	210.0
3	3	—	—	196.0
4	4	—	—	183.0
5	5	—	142.0	170.0
6	6	—	132.0	175.0
7	7	106.0	112.0	168.0
8	8	96.0	116.0	162.0
9	10	91.0	112.0	145.0
10	12	105.0	122.0	142.0
11	14	105.0	118.0	145.0
12	16	—	116.0	149.0

Note: Sm = Smectic; N = Nematic.

behavior through a graph of the number of carbon atoms present in the left n-alkoxy terminal end group versus the transition temperatures as determined from an optical polarizing microscope equipped with a heating stage. The phase diagram (Fig. 1) consists of three transition curves: (1) First is the solid-mesomorphic or isotropic transition curve, which adopts a zigzag path of rising and falling values with an overall descending tendency as the series is ascended and behaves in the normal established manner. (2) Second is the smectic–nematic transition curve, which initially rises, passes through maxima at the dodecyloxy homologue and then descends at the tetradecyloxy homologue with the exhibition of an odd–even effect, and behaves in the usual manner. The curve is extrapolated [7] to the hexadecyloxy derivative of the series, which merges into the solid-nematic transition temperature of hexadecyloxy homologue suggesting that from and beyond the hexadecyloxy homologue, the smectogenic mesophase formation ceases to appear and hence lamellar packing of the molecules is absent. (3) Third is the nematic–isotropic transition curve, which follows a descending tendency as the series is ascended with a negligible rise of few degrees at the tetradecyloxy and hexadecyloxy homologues and exhibits an odd–even effect. Thus, all three transition curves behave in a normal established manner. The textures of the nematic phase are threaded or Schlieren and for the smectic phase of the type A or C. Variations in mesomorphic properties from homologue to homologue in the present series are observed. The smectic mesophase length varies from 13°C to 21°C and the nematic mesophase length ranges from 20°C to 46°C as shown in Table 2. The smectic–nematic and nematic–isotropic thermal stabilities are 118°C and 157°C, respectively. The smectic and nematic mesophases commence from heptyloxy and pentyloxy homologues, respectively. Thus, the present homologous series is predominantly nematogenic and partly smectogenic with a middle ordered melting type and a short range of liquid crystallinity. The mesomorphic properties of the novel homologous series are compared with known structurally similar homologous series. The spectral and analytical data confirm the molecular structure of the homologues concerned.

The nonmesomorphic behavior of the methyl to butyl homologues is attributed to the high crystallizing tendency, which arises from the shorter, less flexible n-alkoxy terminal end

Homologous Series:α-4-[4′-*n*-Alkoxybenzoyloxy] benzoyl-β-4″-methoxy phenyl ethylenes

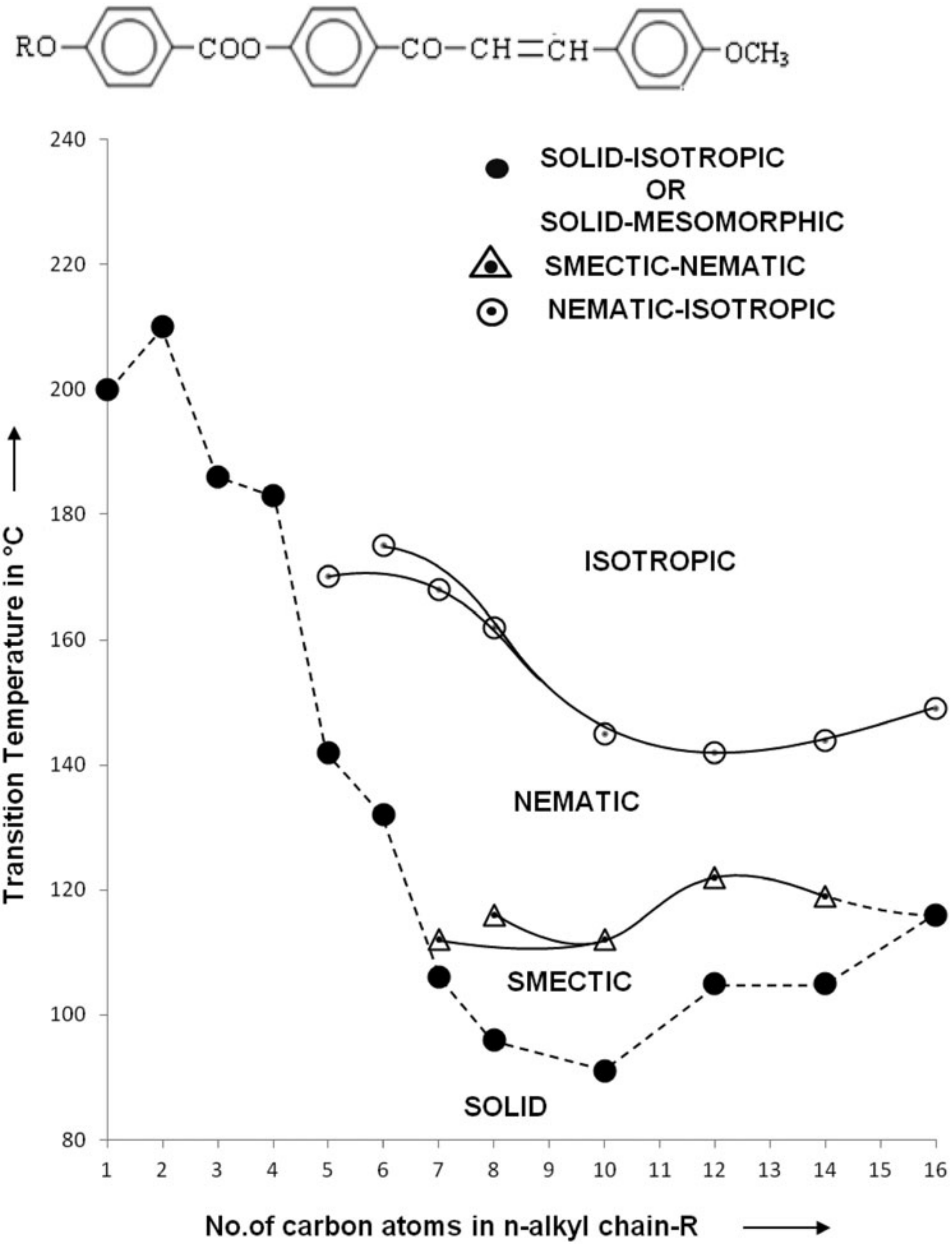


Figure 1. Phase behavior of series.

group [1–4]. The pentyl to hexadecyl homologue derivatives are liquid crystalline because the molecules set themselves at an angle less than 90° and resist thermal vibrations exposed upon them between two temperatures with or without lamellar packing of molecules in their crystal lattices. All such molecules have an ordered two-dimensional array and exhibit either/both a smectogenic or/and a nematogenic mesophase [1]. Thus, the molecules of

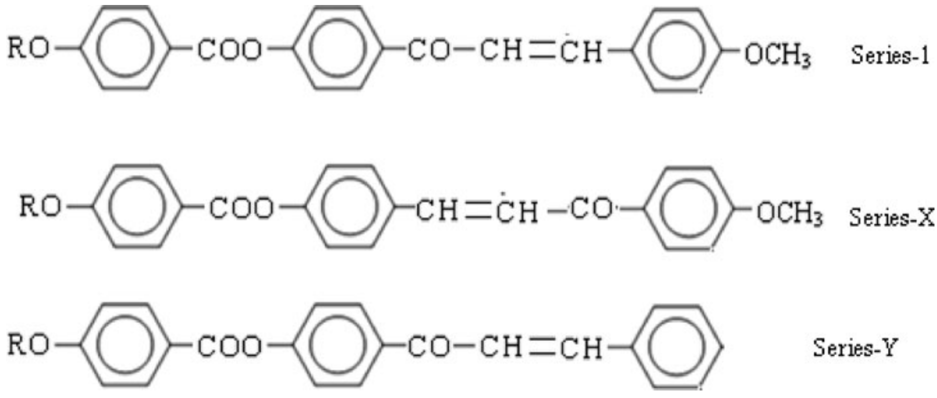


Figure 2. Structurally similar homologous series.

the heptyloxy to tetradecyloxy homologues have a layered molecular arrangement due to the lamellar molecular packing in their crystal lattices from the temperature t_1 to higher temperature t_2 enantiotropically and on further continued heating up to a higher temperature t_3, with a statistically parallel orientational molecular two-dimensional order. Thus, the smectic mesophase formation between t_1 and t_2 and the nematic mesophase formation between t_2 and t_3 occurred. The pentyl, hexyl, and hexadecyloxy homologue derivatives have an absence of lamellar packing of the molecules with only a statistically parallel orientational order between t_1 and a higher temperature t_2, enantiotropically showing only a nematogenic mesophase without smectogenic mesophase formation. The exhibition of an odd–even effect and a variation of mesomorphic properties from homologue to homologue in the novel series is attributed to the sequentially added methylene unit to the *n*-alkoxy terminal end group. The overall mesomorphism induced from pentyl to hexadecyloxy homologue derivatives is attributed to the suitable magnitudes of anisotropic intermolecular forces end to end and lateral adhesion as a result of varying favorable molecular rigidity and flexibility [2–4] against exposed thermal vibrations. The mesomorphic properties of the present homologous series (1) are compared with other structurally similar homologous series X [8] and Y [9]; as shown in the Fig. 2.

Homologous series 1 and X are isomeric and identical in all respects except for the position of the –CO– group between the middle and third phenyl rings of the molecules. The molecules of series 1 and X identically consist of three phenyl rings bridged through identical –COO– and nonidentical –CO–CH=CH– (series 1) –CH=CH–CO– (series X) central groups, with identical left and right terminal end groups. However, they differed in types of linking groups –CO–CH=CH– central bridge for series 1 and X, respectively. The –CO– group is bonded directly with the middle phenyl ring (series 1) and bonded directly to the third phenyl ring (series X). Therefore, the net molecular rigidity and flexibility [2–4], the lateral and terminal end to end anisotropic intermolecular forces of attractions differ considerably, which reflects in the differing mesomorphic behavior and the degree of mesomorphism of the homologous series under discussion. Homologous series 1 and Y are identical to each other except for the right sided terminal end groups $–OCH_3$ and –H of different polarities, respectively. Therefore their molecular length, length to breadth ratio, molecular polarities, molecular rigidity and flexibility, end to end attractions, lateral intermolecular attractions, as well as suitable magnitudes of anisotropic intermolecular forces of adhesion—which all have direct effect on mesophase formation and degree of mesomorphism—differ considerably.Table 3 shows the thermal stabilities and commencement of mesophase, etc., for the series under comparison.

Table 3. Average thermal stability in °C

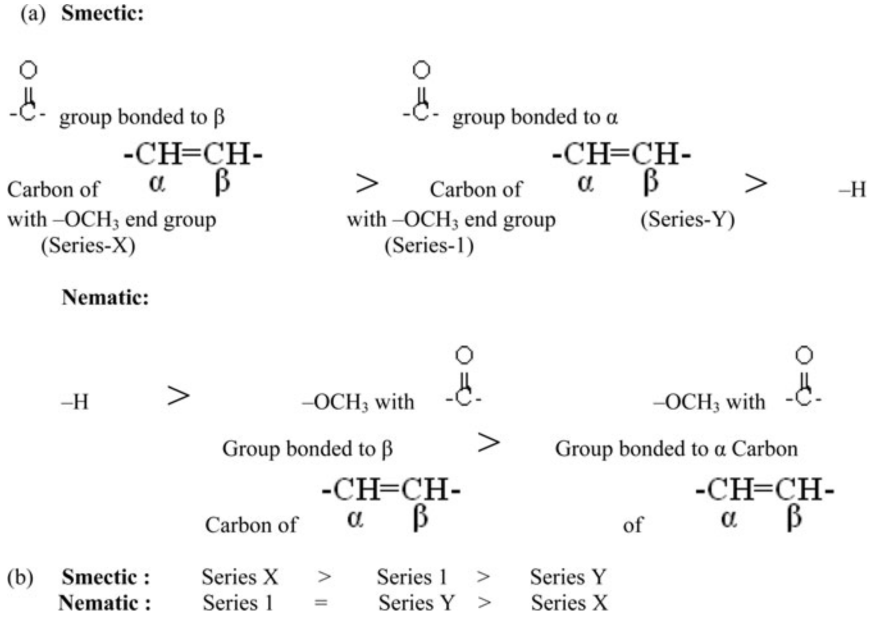
Series→	1	X	Y
Smectic–nematic or isotropic	118.0 (C_7–C_{14})	133.4 (C_6–C_{12})	—
Commencement of smectic phase	C_7	C_6	
Nematic–isotropic	157.0	159.8	164.5
Commencement of nematic phase	(C_5–C_{16}) C_5	(C_6–C_{16}) C_6	(C_5–C_{16}) C_5

Table 3 indicates that isomeric series 1 and X differ in their Sm-N thermal stability by 15.4°C and N-I thermal stability by 2.8°C. Second, the smectic mesophase commences from the heptyl and hexyl homologues, whereas the nematic mesophase commences from the pentyl and hexyl homologues, respectively for series 1 and X. Thus, the early commencement of the smectic phase and late commencement of the nematic phase are related to the higher thermal stability (series X), and the late commencement of smectic phase and early commencement of nematic phase are related to the lower thermal stability (series 1). The early commencement of the smectic mesophase is related to the extent of molecular coplanarity [10]. Hence, the molecules of series X are more coplanar than those of series 1. The –CO– group, linking the middle and third phenyl rings bonded through –CH=CH– immediately at the third phenyl ring, gives greater coplanarity than the isomeric series taken for comparison. The –CH=CH–CO– central group maintains more molecular coplanarity than the –CO–CH=CH– central group. Consequently, the lamellar packing of the molecules in their crystal lattices can be enhanced by the –CH=CH–CO– group more than for the –CO.CH=CH– central group. Thus, both series (X and 1) under comparison are closely similar to each other. Both these central bridges (–CO.CH=CH– and –CH=CH–CO–) are comparable with equal length and causes more or less noncoplanarity due to a twist obtained as the oxygen atoms of the –CO– group bump into the nonbonded adjacent hydrogen atoms [10] of the middle or third aromatic phenyl ring. On account of this difference, the smectic and nematic thermal stabilities of series 1 are lower than the series X. Hence, the difference of linking group –CO– at the middle (series 1) or third (series X) phenyl ring in an isomeric homologous series generates a difference in mesomorphic thermal stabilities and other mesomorphic properties. The homologous series 1 and Y differ only in their right handed terminal end groups of –OCH_3 and –H, respectively; keeping rest of the molecular part identical. Thus, the length to breadth ratio, molecular polarities due to high polarity of the –OCH_3 end group (as compared to –H), polarizability, end to end and lateral attractions, intermolecular closeness, and the suitable magnitudes of anisotropic intermolecular forces of attractions as a consequence of molecular flexibility [2–4] are higher for the presently investigated homologous series-1 as compared to series Y. Thus, lower intermolecular attractions of series Y cause a lack of smectogenic character as a result of the absence of lamellar packing of molecules in their crystal lattices and exhibit only a statistically parallel orientational order of the molecules facilitating the formation of only a nematogenic mesophase from the pentyl to hexadecyl derivatives in series Y. Thus, variations in mesomorphic properties for the same homologue from series to series is attributed to the varying lateral and/or terminal end group of different polarity and from homologue to homologue in the same series is attributed to the sequentially added methylene unit. The absence of an odd–even effect for the higher homologues from and beyond the decyloxy homologue for Sm-N and N-I transition curves of the novel series is attributed to the effects of coiling, bending, or flexing of the left *n*-alkoxy terminal end groups or coupling of their longer *n*-alkyl chain with the major axis of the core. The observed odd–even effect occurs due to the progressive and sequential addition of the methylene unit at the left terminal end group [1].

Conclusions

(1) The novel series of α-4-[4′-*n*-alkoxy benzoyloxy] benzoyl β-4″-methoxy phenyl ethylenes is predominantly nematogenic and partly smectogenic with a middle ordered melting type.

(2) The group efficiency order derived for smectic and nematic on the basis of (a) thermal stability and (b) the early commencement of smectic and nematic phase are as follows:



(a) **Smectic:**

$-\overset{\overset{O}{\|}}{C}-$ group bonded to β Carbon of $\underset{\alpha\quad\beta}{-CH{=}CH-}$ with –OCH$_3$ end group (Series-X) > $-\overset{\overset{O}{\|}}{C}-$ group bonded to α Carbon of $\underset{\alpha\quad\beta}{-CH{=}CH-}$ with –OCH$_3$ end group (Series-1) > (Series-Y) –H

Nematic:

–H > –OCH$_3$ with $-\overset{\overset{O}{\|}}{C}-$ Group bonded to β Carbon of $\underset{\alpha\quad\beta}{-CH{=}CH-}$ > –OCH$_3$ with $-\overset{\overset{O}{\|}}{C}-$ Group bonded to α Carbon of $\underset{\alpha\quad\beta}{-CH{=}CH-}$

(b) **Smectic :** Series X > Series 1 > Series Y
Nematic : Series 1 = Series Y > Series X

(1)

(3) High smectic thermal stability and the early commencement of smectogenic mesophase-forming tendency are favored more in $-\overset{\overset{O}{\|}}{C}-$ group bonded to β carbon of $\underset{\alpha\quad\beta}{-CH{=}CH-}$ in isomeric series.

(4) Variations in mesomorphic properties from homologue to homologue in a same series and from series to series for same homologue is a direct result of a varying molecular rigidity and/or flexibility due to varying lateral central or/and terminal group or groups or/and varying number of aromatic phenyl ring, constituting a molecule.

(5) Suitable magnitudes of anisotropic forces of intermolecular attractions can induce mesophase formation.

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