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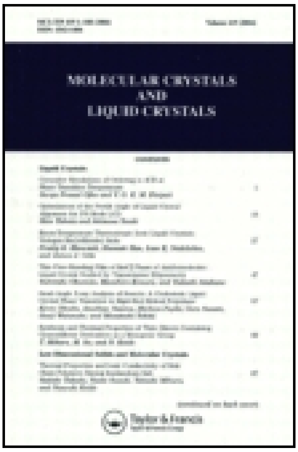

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Mesogenic Behavior of a Novel Homologous Series: α-4-[4′-n-Alkoxy benzoyloxy] benzoyl-β-4″-chloro Phenyl Ethylenes

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Mesogenic Behavior of a Novel Homologous Series: α-4-[4′-n-Alkoxy benzoyloxy] benzoyl-β-4″-chloro Phenyl Ethylenes

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A novel homologous series entitled α-4-[4′-n-Alkoxy benzoyloxy] benzoyl β-4″-chloro phenyl ethylenes consists of 12 homologues. The pentyl to tetradecyl homologues are enatiotropically nematogenic and all of the other homologues (methyl to butyl and hexadecyl) are nonmesogenic. The textures of the nematogenic mesophase are threaded or Schlieren in nature. The transition temperatures were determined by an optical polarizing microscope with a heating stage. The phase diagram of the novel series shows a normal behavior with negligible abnormality in trend of the nematic-isotropic transition curve and exhibits an odd–even effect as expected. The nematic thermal stability is 149.4°C on average. The series is nematogenic without any smectogenic character. The mesogenic properties of the novel series are compared with known series that are structurally similar.

Keywords Liquid crystal; mesogen; mesomorphic; nematic; smectic

Introduction

The exhibition of mesogenic properties by any substance is a direct result of suitable magnitudes of molecular rigidity and flexibility [1–3]. Intermolecular forces of attraction of a suitable magnitude occur as a consequence of a net favorable molecular rigidity and flexibility depending upon molecular shape, size, aromaticity, polarity, and polarizability, the position of lateral and terminal end groups, and electronic–electronic interactions etc. The present work was aimed at enhancing the understanding of and establishment of the effects and relationship between molecular structure and mesogenic behavior of a substance [4] by linking three phenyl rings to be bridged through two central groups $-COO-$ and $-CO-CH=CH-$ as well as $-OR$ and $-Cl$ as the terminal end groups, without substituting any lateral group at any phenyl ring in the lath-like linear molecule. The effect of varying the central groups other than $-COO-$ on mesogenic properties will be discussed, using structurally similar homologous series selected for comparison.

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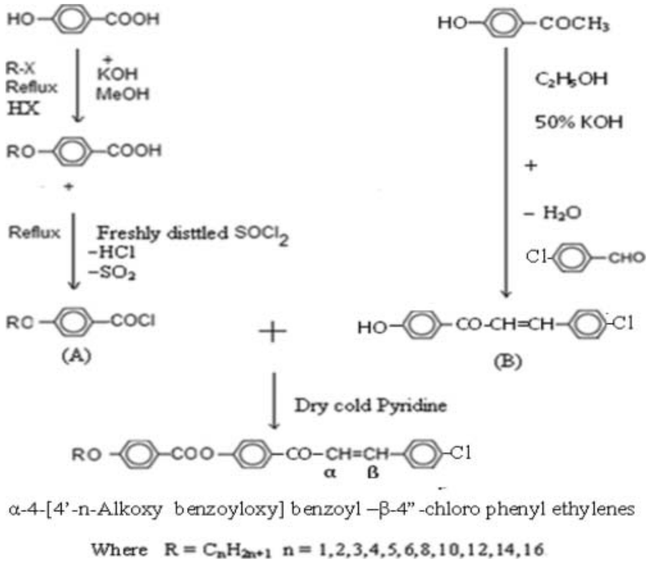
Experimental

Synthesis

4-Hydroxybenzoic acid was alkylated by suitable alkyl halides to form 4-n-alkoxybenzoic acids by a modified method of Dave and Vora [5]. Dimeric n-alkoxy benzoic acids were converted in to the corresponding n-alkoxybenzoyl chlorides [A] using freshly distilled thionyl chloride under reflux conditions. Component [B] α-4-Hydroxy benzoyl $-\beta$-4$'$-chloro phenyl ethylene was synthesized by reacting 4-chlorobenzaldehyde and 4-hydroxyacetophenone by the usual established method [6a, b(i), b(ii), c]. Components A and B were condensed in dry cold pyridine by an established method [7a, b, c, d, ...]. Final products were decomposed, filtered, washed, dried, and purified until constant transition temperatures for each individual homologue were obtained. The synthetic route to the series is mentioned below in Scheme 1. 4-Hydroxybenzoic acid, alkyl halides, thionyl chloride, methanol, KOH, HCl, 4-hydroxyacetophenone, 4-chloro enzaldehyde, and pyridine, required for the synthesis were used as received except solvents which were dried and distilled prior to use.



Scheme 1. Synthetic route to the series.

Characterization

Some of the selected homologues of the novel homologous series were characterized for the determination of molecular structures by infra red [IR] and ^{1}HNMR (Nuclear magnetic resonance) techniques. Microanalysis was performed on a Perkin Elmer PE 2400 CHN analyzer. IR spectra were recorded on a Perkin–Elmer spectrum GX instrument, and ^{1}HNMR spectra was recorded on a Bruker instrument using $CDCl_3$ as a solvent. The mesogenic properties and transition temperatures of the series were investigated using an optical polarizing microscope equipped with a heating stage. Thermodynamic quantity

Enthalpy (ΔH) and Entropy (ΔS) are qualitatively discussed instead of using differential scanning calorimeter scan. The textures of the smectic and the nematic mesophases were determined by a miscibility method.

Analytical Data

Spectral Data:

NMR in ppm for the Propyloxy Derivative. 0.850 ($-CH_3$ of $-OC_3H_7$ group), 1.243 ($-CH_2-$ of $-OC_3H_7$), 4.001 ($-OCH_2-$ of $-OC_3H_7$), 7.611 ($-CO-CH=CH-$ group), 6.9 to 8.04 (p-substituted phenyl ring). NMR supports the structure.

NMR in ppm for Octyloxy Derivative. 0.879 ($-CH_3$ of $-OC_8H_{17}$ group), 1.332 ($-CH_2-$ of $-OC_8H_{17}$), 4.02 ($-OCH_2-$ of $-OC_8H_{17}$), 6.9 ($-CO-CH=CH-$ group), 6.91 to 8.13 (p-substituted phenyl ring). NMR supports the structure.

IR in cm^{-1} for Pentyloxy Derivative. 700 polymethylene group of $-OC_5H_{11}$, 760 $-Cl$ group, 870 p-substituted phenyl ring, 1180 ($-CO-$ of $-OC_5H_{11}$ group), 1240, 1440, 1605 $-COO-$ ester group), 975 ($-CH=CH-$ group). IR supports the structure.

IR in cm^{-1} for Tetradecyloxy Derivative. 680 polymethylene group of $-OC_{14}H_{29}$), 750 $-Cl$ group, 860 (p-substituted phenyl ring), 1150 ($-CO-$ of $-OC_{14}H_{29}$ group), 1200, 1280, 1600 ($-COO-$ ester group). IR supports the structure.

Texture by Miscibility Method

- Hexyl—Nematic—Threaded
- Decyl—Nematic—Schlieren

Results and Discussion

Hydrogen bonding of dimerized 4-n-alkoxybenzoic acids break on esterification. The ethylene derivative [B] is nonmesomorphic, but on esterification with acid chlorides the enantiotropic nematic phase appears in seven homologues. The transition temperatures of the novel homologues were plotted against the number of carbon atoms in n-alkyl terminal chain. The phase diagram (Fig. 1) consists of two transition curves. The solid-isotropic or nematic transition curve adopts a zigzag path of rising and falling values as the series is ascended with an overall descending tendency and behaves in a normal manner. The nematogenic mesophase commences from the pentyl homologue derivative of the series. The nematic-isotropic transition curve descends as the series is ascended with minor exceptional behavior at the decyl homologue derivative with the exhibition of short ranged odd–even effect. The nematic-isotropic transition temperatures varies between 168°C and 138°C with a short range nematogenic mesophase length and a 149.4°C thermal stability. Thus, the novel series is entirely nematogenic with a middle ordered melting type. The texture of nematic mesophase is of the threaded or Schlieren type. The smectogenic character of the novel series is totally absent.

The methyl to butyl and the hexadecyl homologues are nonmesogenic and sharply melt to the isotropic liquid phase without passing through an intermediate state of matter. These five homologues are unable to resist the thermal vibrations exposed upon them. The

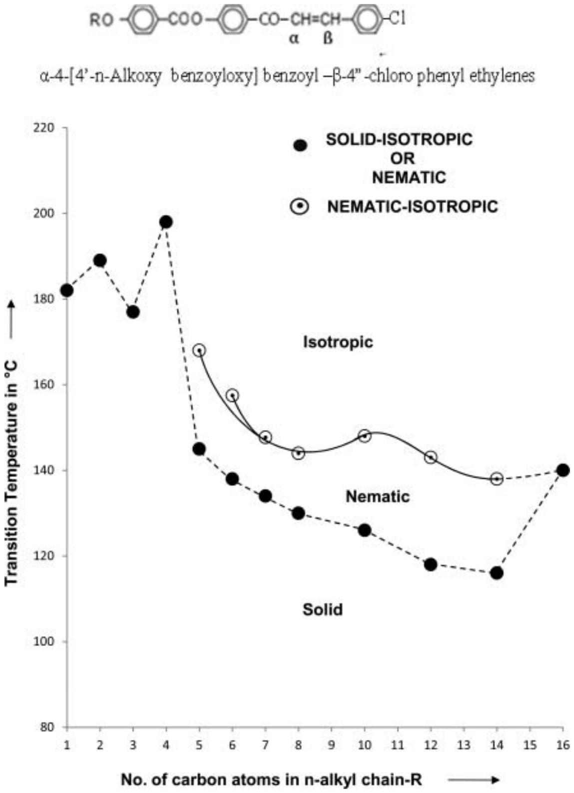


Figure 1. Phase behavior of series.

unfavorable molecular rigidity and flexibility without an ordered molecular arrangement in floating condition means that the molecules are randomly oriented in all possible directions and show a sharp melting point. The pentyl to tetradecyl homologoues are nematogenic because the molecules resist thermal vibrations exposed upon them for a definite range of temperatures. The molecules lie on the surface at an angle less than 90° withstanding the exposed thermal vibrations and a statically parallel orientational order of molecules is maintained between two temperatures enantiotropically (or monotropically) in a floating condition. The statically parallel orientational order of the molecules in a floating condition shows the formation of a nematogenic mesophase by suitable magnitudes of anisotropic forces as a consequence of favorable molecular rigidity and flexibility [1–4]. Absence of lamellar packing of the molecules in their crystal lattices precludes a sliding layered arrangement of molecules in a floating condition. Hence, the smectogenic character is absent. The nematogenic mesophase length varies from a minimum of 14°C at the seventh and eighth homologue to a maximum of 25°C for the dodecyloxy homologue. Thus, it is a series with narrow phase length. The appearance of an odd–even effect and a variation of mesogenic properties from homologue to homologue in the same novel series is attributed to the progressively and sequentially added methylene unit at the n-alkyl terminal chain. The mesogenic properties of the present series 1 are compared with two other structurally similar homologous series-X [8] and Y [9] as shown in the Fig. 2.

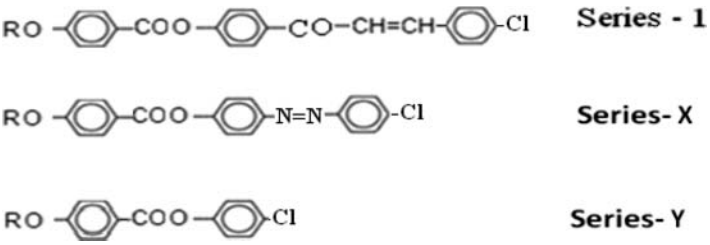


Figure 2. Structurally similar homologous series.

Homologous series 1 and X under comparison are identical in all respects with three phenyl rings, and left and right sided terminal end groups of —OR and —Cl respectively, and a central group of —COO— linking the first and middle phenyl rings. However, both series (1 and X) differ in respect of central group —CO—CH=CH— and —N=N— linking middle and third phenyl rings. Therefore, the observed difference of mesogenic properties and degree of mesomorphism is attributed to the differing features between series 1 and X. The effects due to three phenyl rings, that is, molecular aromaticity, central group —COO—, and functional group polarity due to —OR and —Cl terminal end groups remains the same; but the molecular length, length to breadth ratio, and other parameters relating differing features of molecules, that is, magnitudes of anisotropic forces of intermolecular lateral and terminal attraction as a consequence of resulted molecular rigidity and flexibility [1–4] vary considerably, which causes variations in mesogenic properties and the degree of mesomorphism. Homologous series 1 and Y are identical in all respects of —COO— central group linking two phenyl rings, two terminal end groups —OR and —Cl, but they differ in respect of molecular length due to the presence and absence of $-C_6H_4-CO-CH=CH-$ molecular moiety in series 1 and Y respectively. This differing feature of series 1 and Y causes differences in magnitudes of mesogenic properties and the degree of mesomorphism as a result of varying molecular rigidity and flexibility [1–4]. Table 3 represents thermal stabilities and commencement of mesophase or mesophases etc. for the series 1, X, and Y selected for a comparative study.

Table 3 indicates that homologous series 1 is entirely nematogenic while series Y is entirely smectogenic. This observed difference can be attributed to the presence or absence of the $-C_6H_4-CO-CH=CH-$ molecular moiety of series 1 and Y respectively. The presence of the $-C_6H_4-CO-CH=CH-$ section of the molecules increases the molecular length and restricts the lamellar arrangement of molecules in their crystal structure due to the changing of molecular rigidity in such a manner that the end to end intermolecular attractions increase to such an extent, that lamellar molecular arrangement does not occur

Table 1. Elemental analysis for butyloxy, heptyloxy, and dodecyloxy derivatives

		Elements % calculated (% found)	
Sr. no.	Molecular formula	C	H
1	$C_{26}H_{23}O_4Cl$	71.81 (71.52)	5.29 (5.04)
2	$C_{29}H_{29}O_4Cl$	73.03 (73.12)	6.10 (6.44)
3	$C_{32}H_{35}O_4Cl$	74.06 (74.68)	6.75 (6.98)

Table 2. Transition temperatures of series in °C

Compound no.	n-alkyl group ($-C_nH_{2n+1}$)	Transition temperatures in °C		
		Sm	*Nm*	Isotropic
1	1	—	—	182.0
2	2	—	—	189.0
3	3	—	—	177.0
4	4	—	—	198.0
5	5	—	145.0	168.0
6	6	—	138.0	157.0
7	7	—	134.0	148.0
8	8	—	130.0	144.0
9	10	—	126.0	148.0
10	12	—	118.0	143.0
11	14	—	116.0	138.0
12	16	—	—	140.0

Sm = smectic, *Nm* = nematic.

and only a statically parallel orientational order of the molecules is maintained in a floating condition under the influence of heat. The absence of such a molecular section as mentioned above in series Y allows a sliding layered arrangement of molecules in a floating condition under identical conditions of applied heat, which induces only smectogenic properties in the series Y. Thus, the smectogenic character commences from the heptyl homologue derivative of a series, but it does not commence until the hexadecyl homologue of series 1. On comparing the homologous series 1 and X, it is seen from Table 3 that series 1 is entirely nematogenic, while series X is predominatly nematogenic and partly smectogenic. Series 1 is a middle ordered melting type whose N-I thermal stability is 149.4°C, while, series X is high melting type whose smectic and nematic thermal stabilities are 148.8°C and 217.6°C. The smectic and nematic mesophase formation commences from the hexyl and methyl homologues respectively (Series X). Though the end groups in both the series under comparison are identical but, a central group linking the middle and third phenyl rings which are $-CO-CH=CH-$ and $-N=N-$ are different. This variation causes a difference

Table 3. Average thermal stabilities in °C

Series	Average transition temperatures in °C		
	Series (1)	Series (X)	Series (Y)
Smectic-nematic or smectic-isotropic		148.8 (C_6–C_{16})	104.7 (C_{12}–C_{18})
Commencement of smectic mesophase	—	C_6	C_7
Nematic-isotropic	149.4 (C_5–C_{14})	217.6 (C_1–C_{10})	—
Commencement of nematic mesophase	C_5	C_1	

in molecular length, molecular polarity, and polarizabilty, magnitudes of anisotropic forces of intermolecular attractions as a consequence of varying molecular rigidity of series 1 and X. Thus, lamellar arrangement of molecules occurs in the crystal structure which enables a sliding layered molecular arrangement in a floating condition under the influence of heat in case of series X while it does not occur for series 1. Moreover, the stronger rigidity and intermolecular end-to-end attractions of series X, resists the thermal vibrations above the smectic-nematic transition temperature from the very first member of series X for a definite temperature range. The molecules of a sample homologue from the methyl to the decyl homologues of the series resist thermal vibrations due to stronger end-to-end attractions up to the isotropic temperature forming a nematogenic mesophase in addition to a smectogenic mesophase in case of series X in comparison with series 1. The commencement of the smectic phase does not occur until the last homologue of a series 1 while it occurs from the sixth member of series X. This difference in the commencement of the smectic phase depends upon the extent of the relative noncoplanarity [7] caused by the molecules of series 1 and X. The central group —N=N— maintains more linearity in the molecule than a —CO—CH=CH— group. Hence, the molecules of series X are less noncoplanar than the molecules series 1. As a result of this, lamellar packing of the molecules causes a sliding layered molecular arrangement in floating condition. Thus, smectic and nematic group efficiency order derived on the basis of thermal stability are under mentioned in the conclusions. The odd–even effect diminishes as the series is ascended for higher homologues from and beyond the seventh homologue because the longer n-alkyl terminal chain may coil, bend, or flex or couple to lie [4] with major axis of the core.

Conclusions

(1) Group efficiency order for smectic as central group—N=N— > —CO—CH=CH— > —CO—CH=CH— (series X) (series Y) (series 1) Group efficiency order for nematic as a central group—N=N— > —CO—CH=CH— > —CO—CH=CH—
(2) (series X) (series 1) (series Y) Group efficiency of a central group with reference to early commencement of smectic phase and nematic phase. —N=N— > —CO—CH=CH—
(3) Central group —CO—CH=CH— is nematogenic.
(4) Central group —N=N— increases molecular rigidity if molecular flexibility is same.
(5) Central group —CO—CH=CH— restricts the lamellar packing of molecules in their crystal lattices.
(6) Molecular rigidity and flexibility of a molecule are the deciding factors for mesophase formation.

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