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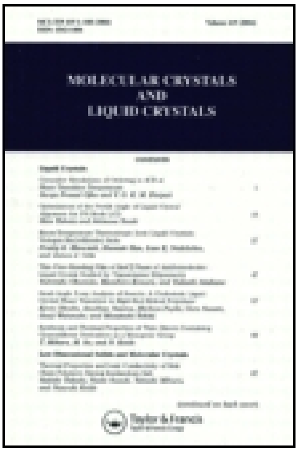

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Study of Liquid Crystalline State and Evaluation of its Properties Through a Novel Homologous Series

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Study of Liquid Crystalline State and Evaluation of its Properties Through a Novel Homologous Series

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A novel homologous series α-4-[4′-n-alkoxy benzoyloxy] benzoyl-β-3″,4″-dimethoxy phenyl ethylenes has been synthesized and studied for liquid crystal (LC) properties to understand and establish the relation between molecular structure and liquid crystalline behavior. Twelve members of series were synthesized. All the members except first member of the series are mesomorphic. The hexyloxy to tetradecyloxy homologoues are smectogenic and nematogenic in character. The ethoxy to pentyloxy and the hexadecyloxy homologues exhibit only nematogenic character with the absence of smectogenic mesophase formation. An odd–even effect is observed for the smectic-nematic and the nematic-isotropic transition curves in the phase diagram. The smectic mesophase showed as either the SmA or SmC. The nematic mesophase shows a threaded or Schlieren type texture. Spectral and analytical data confirms the molecular structures of the homologues. The thermal stabilities for the smectic and the nematic are 115.6°C and 156.6°C. The smectogenic and nematogenic mesophase length vary from 7°C to 28°C and from 7°C to 52°C respectively. The transition temperatures were observed through an optical polarizing microscope equipped with heating stage. Thus, the presently investigated novel homologous series is predominantly nematogenic and partly smectogenic with a middle ordered melting type and a considerable mesophase length. The LC properties of the novel series are compared with structurally similar homologous series.

Keywords Anisotropic liquid; liquid crystal; mesomorphism; nematic; smectic

Introduction

The exhibition of liquid crystal (LC) properties requires suitable magnitudes of anisotropic intermolecular forces of attraction. These attractions are as a consequence of favorable molecular rigidity and flexibility [1–4] resulting from the molecular structure of a substance by appropriate substitution of lateral, terminal, and central groups with phenyl rings. The LC state is exploited in a number of electro-optic, biological, and thermographic applications, hence the need to synthesize new LC substances [4]. The present work is aimed at synthesizing a new homologous series of thermotropic LC compounds, which

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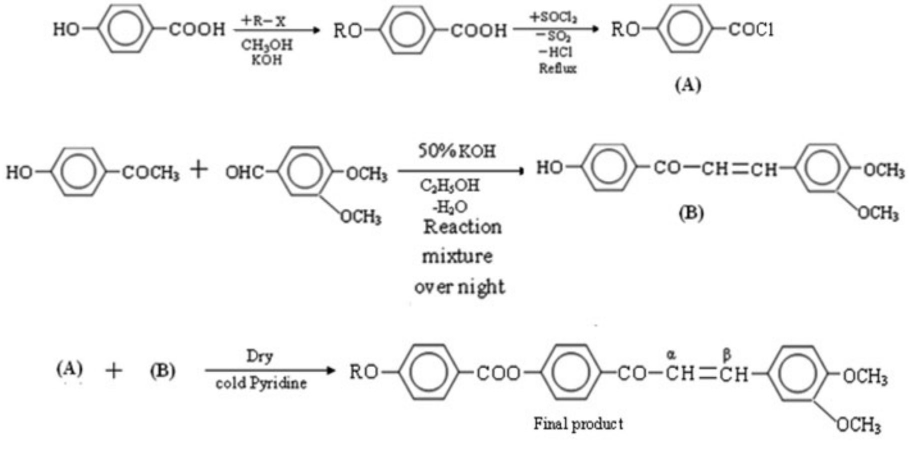
exhibit liquid crystalline properties. The novel molecules are constructed with three phenyl rings bridged through −COO− and −CO−CH=CH− as a rigid core, and n-alkoxy (−OR) and two methoxy (−OCH_3) groups (one at a terminal position and the other as lateral group). Thus, the combined effect of the two highly polar methoxy groups on LC properties with the variation of the number of carbon atoms in the left n-akoxy terminal chain can be studied and evaluated.

Experimental

The 4-Hydroxybenzoic acid was alkylated by suitable alkylating agents to form corresponding n-alkoxybenzoic acids by the modified method of Dave and Vora [5]. The alkoxybenzoic acids were converted to the corresponding acid chlorides (A) using freshly distilled thionyl chloride. The α-4-Hydroxy benzoyl-β-3′,4′-dimethoxy phenyl ethylene (B) was synthesized by reacting 4-hydroxyacetophenone and 3,4-dimethoxybenzaldehyde through an established method [6]. Components (A) and (B) were condensed in dry cold pyridine by the gradual addition of (A) to (B). Final products were decomposed, filtered, washed, dried, purified, and recrystallized until constant transition temperatures were obtained. The 4-Hydroxybenzoic acid, alkyl halides, pyridine, 4-hydroxyacetophenone, 3,4-dimethoxybenzaldehyde, MeOH, EtOH, KOH, and thionyl chloride required for synthesis were used as received, except solvents which were dried and distilled prior to use. The synthetic route to the series is shown in Scheme 1.



α-4-[4'-n-alkoxy benzoyloxy] benzoyl-β-3",4"-dimethoxy phenyl ethylene.

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 series.

Characterization

Some selected members of the series were characterized by IR, ^{1}HNMR spectra, and elemental analysis. NMR spectra were recorded using $CDCl_3$ as solvent. Microanalysis was performed on a CHN analyzer, and the results are shown in Table 1. IR spectra were recorded using Perkin–Elmer GX spectrometer. Transition and melting temperatures and

Table 1. Elemental analysis for ethoxy, butoxy, heptyloxy, and decyloxy derivatives

		Elements % found (% Calculated)	
Sr. No.	Molecular formula	C	H
1	$C_{26}H_{24}O_6$	72.10 (72.22)	5.70 (5.56)
2	$C_{28}H_{28}O_6$	73.12(73.04)	6.01 (6.09)
3	$C_{31}H_{34}O_6$	74.25 (74.10)	6.92 (6.77)
4	$C_{34}H_{40}O_6$	76.91 (75.00)	7.28 (7.35)

LC properties were observed on a hot stage polarizing microscope. The textures of the mesophases were determined by a miscibility method.

Analytical Data

NMR in ppm for the Propoxy Derivative

0.870 ($-CH_3$ of $-OC_3H_7$ group), 1.029 ($(-CH_2-)_n$ Polymethylene group of $-OC_3H_7$), 3.980 (Triplet) ($-OCH_2-CH_2-$ of $-OC_3H_7$), 3.964 singlet ($-OCH_3$), 4.075 broad ($-CH{=}CH-$ group), 6.911 and 6.933 ($-CO-CH{=}CH-$ group), 7.892, 7.913, and 8.063 (substituted phenyl ring). The NMR spectrum supports the molecular structure.

NMR in ppm for the Dodecyloxy Derivative

0.871 ($-CH_3$ of $-OC_{12}H_{25}$ group), 1.255($(-CH_2-)_n$ Polymethylene group of $-OC_{12}H_{25}$), 4.067 (Triplet) ($-OCH_2-CH_2-$ of $-OC_{12}H_{25}$), 3.990 singlet ($-OCH_3$), 4.984 broad ($-CH{=}CH-$ group), 6.899 and 7.920 ($-CO-CH{=}CH-$ group), 7.893, 7.914, and 8.954 (substituted phenyl ring). The NMR spectrum supports the molecular structure.

IR in cm^{-1} for the Hexyloxy Derivative

625 (polymethylene $-(CH_2)n-$ group of $-OC_6H_{13}$), 770 (p-substituted phenyl ring), 1170 ($>C{=}O$ group), 1250, 1605 ($-COO$ ester group), 940 ($-CH{=}CH-$ group), 820 (1,2,4-trisubstituted phenyl ring). The IR spectrum supports the molecular structure.

IR in cm^{-1} for the Octyloxy Derivative

645 (polymethylene $-(CH_2)n-$ group of $-OC_8H_{17}$), 730 (p-substituted phenyl ring), 1150 ($>C{=}O$ group), 1260, 16005 ($-COO$ ester group), 960 ($-CH{=}CH-$ group), 845 (1,2,4-trisubstituted phenyl ring). The IR spectrum supports the molecular structure.

Texture by Miscibility Method

Hexadecyloxy:	Schlieren Nematic
Butyloxy:	Threaded Nematic
Hexyloxy:	Smectic-A

Results and Discussion

4-n-Alkoxybenzoic acids (A) are dimeric in which two phenyl rings are bonded through hydrogen bonding. The α-4-Hydroxy benzoyl β-3′,4′-dimethoxy phenyl ethylene (B) is not

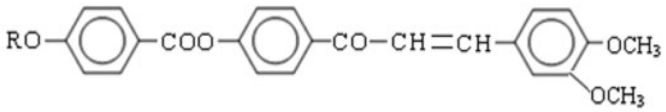
Table 2. Transition temperatures in °C of series 1

Compound No.	n-Alkyl group R = C_nH_{2n+1} (n)	Sm	*N*	Isotropic
1	1	—	—	169.0
2	2	—	134.0	167.0
3	3	—	153.0	160.0
4	4	—	140.0	164.0
5	5	—	145.0	158.0
6	6	110.0	117.0	166.0
7	7	102.0	115.0	167.0
8	8	104.0	118.0	168.0
9	10	92.0	120.0	159.0
10	12	95.0	119.0	140.0
11	14	90.0	105.0	138.0
12	16	—	100.0	136.0

Sm = Smectic; *N* = Nematic.

Homologous series: α-4-[4′-n-alkoxy benzoyloxy] benzoyl-β-3″,4″-dimethoxy phenyl ethylenes.

liquid crystalline. However, on condensing, components (A) through acid chloride and (B) resulted in liquid crystalline homologues from ethoxy to hexadecyloxy. All the members of the novel series except first member are enantiotropically mesogenic in character. The hexyl to tetradecyl homologues exhibit smectogenic and nematogenic properties, while the ethoxy to pentyloxy and the hexadecyloxy homologues exhibit only the nematic phase. The transition temperatures (Table 2) of the homologues as determined from an optical polarizing microscope equipped with a heating stage were plotted versus the number of carbon atoms in the left n-alkoxy terminal chain. The solid-smectic, smectic-nematic, and nematic-isotropic transition curves were obtained as a phase diagram to show the phase behavior of the series (Fig. 1). The solid-isotropic or mesomorphic transition curve follows a zig–zag path of rising and falling values with an overall descending tendency and behaves in the usual manner. The smectic–nematic transition curve initially rises, passes through a maxima and then descends in a normal manner with the exhibition of an odd–even effect. The curve is extrapolated [7] to the hexadecyloxy homologue which merges in the solid-nematic transition temperature, which indicates that the smectogenic mesophase ceases to appear at solid-nematic transition temperature, i.e., the smectogenic phase length is zero for the hexadecyloxy homologue. The nematic–isotropic transition curve is descended as the series is ascended with the exhibition of an odd–even effect, and behaves in the normal established manner. The odd–even effect diminishes as series is ascended and the curves for the odd and even homologues merge into each other at the decyloxy homologue for smectic phase and/or nematic phase at the octyloxy homologue in the curve. The smectic and nematic mesophase ranges from 07°C to 28°C and from 07°C to 52°C respectively. Thus, the mesomorphic properties from homologue to homologue in the same series vary with the number of carbon atoms present in the left n-alkoxy terminal chain. The nematic mesophase commences from the third member and the smectic mesophase commences from the seventh member of the series in the 4-n-alkoxybenzoic acids [8] from which presently investigated series is synthesized, in which the nematic and smectic mesophase commences earlier from the ethoxy (second member) and hexyloxy homologue respectively. The non-mesomorphic tendency of the methoxy homologue (first member) is attributed to the rigidity



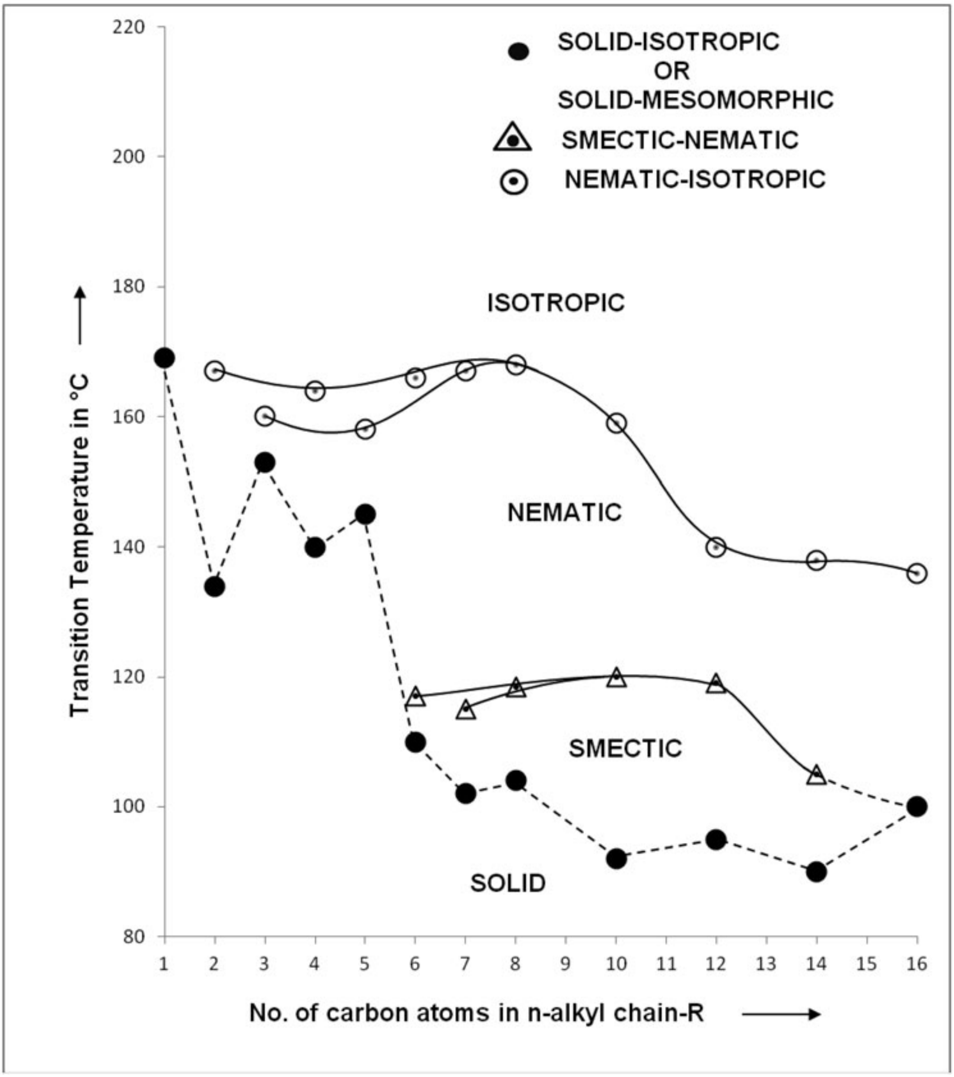


Figure 1. Phase behavior of series.

of the very short unit, which causes unsuitable magnitudes of anisotropic intermolecular forces of attractions [4]. Thus, the first member of the present series melts sharply and directly into the isotropic liquid without passing through a LC phase. The molecules from the ethyl to hexadecyl homologue derivatives are coaligned at an angle of less than 90° with the plane of the surface resisting the exposed thermal vibrations between two or more temperatures, i.e., from t_1 to t_2 and/or from t_2 to t_3 forming a smectic and/or a nematic mesophase. If the sample substance under examination floats with a statistically parallel

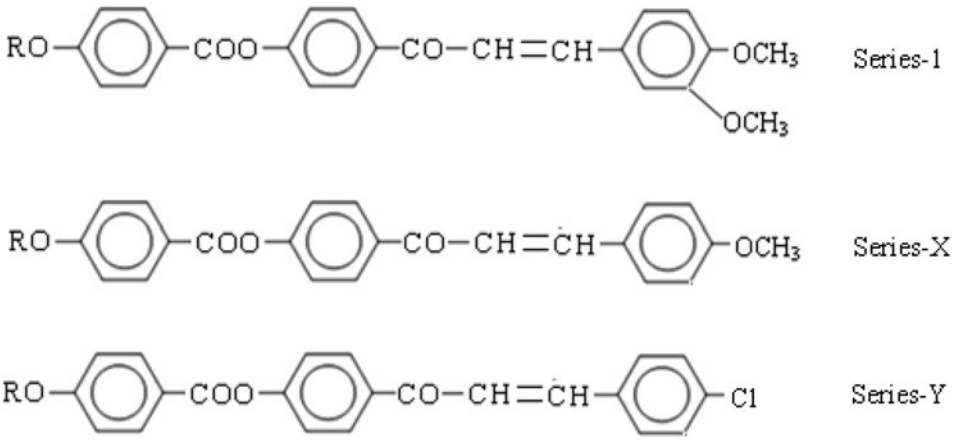


Figure 2. Structurally similar series.

orientational order of the molecules then a nematogenic mesophase persists between two temperatures. If the molecules arrange themselves in a sliding layered manner in a floating condition containing a lamellar packing of molecules in their crystal lattices, then a smectogenic mesophase persists. Thus, the ethoxy to pentyloxy and hexadecyloxy homologues exhibit a nematic mesophase only and the hexyloxy to tetradecyloxy homologues exhibit smectogenic mesophase formation in addition to the nematogenic mesophase formation. From and beyond the isotropic temperature, the molecules are randomly oriented in all possible directions with high disorder. The odd–even effect in the mesomorphic or isotropic (Sm−N or N−I) transition curve is attributed to the progressive addition of a methylene group to the left n-alkoxy terminal chain. The disappearance of the odd–even effect for the higher homologues is attributed to the longer left n-alkoxy terminal chain, which may coil, bend or flex or couple to lie with the major axis of the core. Thus, the present series is predominantly nematogenic and partly smectogenic with a middle ordered melting type and a moderate mesophase length. The mesomorphic properties of the present homologous series 1 is compared with other structurally similar homologous series X[9] and Y[10] as shown in Fig. 2.

Homologous series-1, X and Y are identical in all respects except their right terminal end groups which are 3″,4″-dimethoxy, 4″-methoxy and 4″-Cl respectively. Three phenyl rings are bonded through two central groups −COO− and −CO−CH=CH− contributing to the molecular rigidity and the n-alkoxy (−OR) left terminal end group contributes to the molecular flexibility [1–3], and these are identically and commonly present to the series selected under comparison. However, varying the right hand flexible terminal end group causes a variation in the overall molecular rigidity and flexibility [1–3]. This variation generates the difference in mesomorphic properties and the degree of mesomorphism. The commencement of smectic and/or nematic mesophase, thermal stabilities, smectogenic, and nematogenic character from homologue to homologue for the same series and series to series are shown in Table 3.

On comparing the presently investigated series 1 and series X, the thermal stability for the smectic and nematic of series 1 are lower by just 2.4°C and 0.4°C respectively. The smectic mesophase commences from hexyloxy and heptyloxy homologues, which is earlier by one homologue in series 1 than series X. The nematic mesophase commences

Table 3. Average thermal stability in °C

Series ⟶	1	X	Y
Smectic-Nematic Or Smectic-isotropic	115.6	118.0	—
Commencement of Smectic phase	(C_6-C_{14}) C_6	(C_7-C_{14}) C_7	
Nematic-Isotropic	156.6	157.0	194.4
Commencement of Nematic phase	(C_2-C_{16}) C_2	(C_5-C_{16}) C_5	(C_5-C_{14}) C_5

earliest from the ethoxy homologue of series 1 which commences later from the pentyloxy homologue in the case of series X and Y. The smectogenic mesophase is absent in series Y, but is present in series 1 and X. The maximum smectic and nematic mesophase lengths of series X are 21°C and 46°C respectively, whereas for series 1 they are 28°C and 52°C respectively. Thus, the mesophase length in series 1 is higher than series X under comparison of the two and one methoxy end group(s) contained by series 1 and X respectively. The above differences in LC properties of series 1 and X are attributed to the additional methoxy group substituted at the ortho position (3″-methoxy) to a right terminal (4″-methoxy) end group, which broadens the molecule. Series X is linear and series 1 is nonlinear, hence the extent of suitable magnitudes of anisotropic intermolecular forces of attractions as a consequence of molecular rigidity and flexibility complements [1–4] each other. The balance of intermolecular attractions of series 1 is affected by molecular polarizability due to the molecular width resulting from two opposing forces operating at a time. Thus, the end-to-end attractions give statistically parallel orientational order of molecules and the lamellar packing arrangement of molecules facilitates a sliding layered arrangement of the molecules in a floating condition as also seen in series 1. However, the values of the smectic and nematic thermal stabilities are little affected (56.6 and 57.0). The difference observed for the mesophase length is obvious, as the polarities of two $-OCH_3$ (series 1) group must be more than one $-OCH_3$ group, which enables the difference in resisting capacity of exposed thermal vibrations. The absence of a smectogenic property of series Y indicates absence of lamellar packing of molecules in their crystal lattices. Moreover, early commencement of the smectic phase of series 1 is attributed to the extent of molecular non-coplanarity caused by the 3″-methoxy group as compared to the one $-OCH_3$ and $-Cl$ terminal end group of series X and Y respectively. The nematic thermal stability of series Y is higher than for the series X and 1. Thus, variations in mesomorphic properties from series to series for the same homologue is attributed to the varying right handed terminal end group of fixed polarity [11]. The group efficiency order derived on the basis of (a) thermal stability and (b) the early commencement of smectic and nematic mesophase are mentioned in the conclusion.

Conclusions

1. Group efficiency order derived on the basis of

(a) Thermal stability is:

For smectic: $4''{-}OCH_3$ (Methoxy) $> 3'',4''(-OCH_3)_2$ (Di-methoxy) $> -Cl$ (Chloro)

For nematic: $-Cl$ (Chloro) $> -OCH_3$ (Methoxy) $> 3",4"(\text{-}OCH_3)_2$ (Di-methoxy)

(b) Early commencement of:

For smectic: $3'',4''(-OCH_3)_2 >$ (Di-methoxy) $-OCH_3$ (Methoxy) $> -Cl$ (Chloro)

For nematic: $3'',4''(-OCH_3)_2 >$ (Di-methoxy) $-OCH_3$ (Methoxy) $= -Cl$ (Chloro)

2. The novel homologous series is predominantly nematogenic and partly smectogenic.
3. Variations in mesomorphic properties from homologue to homologue in the same series and from series to series for the same homologue depend upon sequential addition of a methylene unit and varying the terminal end group of fixed polarities respectively.
4. Extension of a phenyl ring (aromaticity) enhances the mesogenic tendency and the early commencement of the mesophase.
5. Favorable molecular rigidity and flexibility facilitate suitable magnitudes of anisotropic intermolecular forces of attractions.
6. Molecular rigidity and flexibility determines the formation of the liquid crystalline state.

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