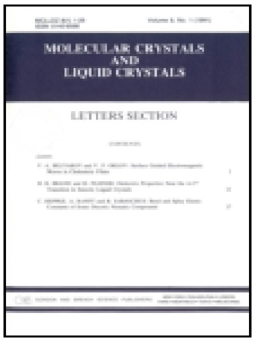

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Mesomorphism Dependence on the Position of Substitution of a Pair of Esters

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ABSTRACT

A novel homologous series of ethylene derivatives of thermotropic liquid crystals has been synthesized. The methoxy to octyloxy derivatives are nematogenic, the decyloxy to tetradecyloxy derivatives are smectogenic, in addition to nematogenic, and the hexadecyloxy homologue is smectogenic only. All the members of the series are enantiotropically mesogenic. Thermotropic behavior was determined by an optical polarizing microscope equipped with a heating stage and Differential Scanning Calorimetry (DSC) study. Analytical and spectral data confirm the molecular structures of homologues (infrared, nuclear magnetic resonance, mass spectra, X-ray, and DSC data). Textures of the nematic phase are threaded or Schlieren and that of smectic phase are focal conic fan-shaped of smectic A or C. Transition curves of the phase diagram behave in a normal manner except one or two deviations from the normal trend. The mesophase range (Sm+N) varies from 3°C to 44°C. The average thermal stability for smectic is 93°C and that for nematic 117.4°C. The LC behavior of the novel series is compared with a structurally similar known series.

KEYWORDS

Enantiotropy; liquid crystals; nematic; smectic; thermotropic

Introduction

An intermediate physical state of a substance between crystalline solid and a true isotropic liquid is called an anisotropic liquid or a liquid crystalline (LC) state. The mesophase, known since 1888 [1], has proved to be of value in applications such as electronic display devices, pharmaceutical preparations from biologically active molecules, medical instruments, engineering and technology, and space research [2–5]. Ester derivatives of benzoic acid and/or cinnamic acid are biologically active molecules, and several materials with or without LC properties have been reported to date [6–10]. The study of LC state is multidisciplinary and studied with different aims and objectives depending on the research group. However, every LC research group requires novel LC substances to continue their research. In order to produce novel LC substances one must have adequate knowledge of molecular geometry, shape, size, polarity and polarizibility, dipole moment, and intermolecular forces conducive to LC state. Therefore, the aim here was to synthesize novel LC substances with three phenyl rings bridged through -COO and -CO-CH=CH- central groups with a view to understanding and establishing the effect of molecular structure on LC properties as a consequence

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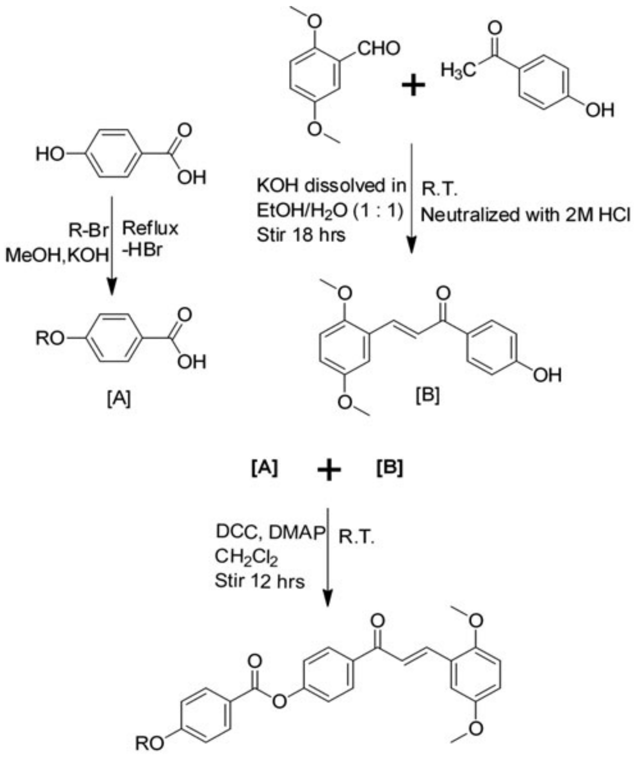

α-4-(4'-n-Alkoxy benzoyloxy) benzoyl β-2",5"-dimethoxy phenyl ethylenes

Where, R= C_nH_{2n+1} and n = 1 to 8 and 10,12,14,16

Scheme 1. Synthetic route to novel series.

of molecular rigidity and flexibility [11–16]. The proposed novel substances may prove their ability and usefulness as anti-inflammatory, anticancer, antioxidant, anti-angiogenis, antitumor, antiradiation-induced oxidative stress and protect against radiation injury, antimalarial and antibacterial agents [17–22].

Experimental

Synthesis

n-Alkoxy benzoic acids were prepared from 4-hydroxyl benzoic acid by suitable alkylating agents by a modified method of Dave and Vora [23]. α-4-Hydroxybenzoyl β-2′,5′-dimethoxy phenyl ethylene was prepared by a usual established method [24]. 4-n-Alkoxy benzoic acids and α-4-hydroxybenzoyl-β-2′,5′dimethoxy phenyl ethylene were condensed in 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and CH_2Cl_2 [25]. The synthetic route to the series is shown in Scheme 1. Final products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained.

The following chemicals were used “as received” except solvents, which were dried, purified, and distilled prior to use: 4-hydroxy benzoic acid, 4-hydroxy acetophenone, 2,5 dimethoxybenzaldehyde, alkyl bromide (R-Br), methanol, KOH, 1,3-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, dichloromethane, and ethanol.

Table 1. Elemental analysis for (1) ethyloxy, (2) butyloxy, and (3) hexyloxy derivatives

		Elements found (%)			Elements calculated (%)		
Sr. No.	MF	C	H	N	C	H	O
1.	$C_{26}H_{24}O_6$	76.11	6.51	16.85	76.57	6.43	17.00
2.	$C_{28}H_{28}O_6$	77.41	7.02	16.45	77.00	6.80	16.20
3.	$C_{30}H_{32}O_6$	79.86	9.15	12.02	79.58	9.06	11.36

Characterization

Some selected members of the series were characterized by elemental analysis (Table 1), infrared (IR) spectra, ^{1}H NMR spectra, mass spectra, X-ray diffraction (XRD; single crystal). Transition temperatures and textures of nematic and smectic phases were determined by an optical polarizing microscope equipped with a heating stage. Thermodynamic data enthalpy (ΔH) and entropy (ΔS) were determined from differential scanning calorimetry (DSC).

Elemental analyses were performed on a Euro EA elemental analyzer. IR spectra were recorded on a Shimadzu FTIR-8400, ^{1}H NMR spectra were recorded on a BRUKER Avance-III (400 MHz) spectrometer using $CDCl_3$ as a solvent, and mass spectra were recorded on a Shimadzu GC-MS Model No. QP-2010. Phase-transition temperatures and enthalpy changes were measured using a differential scanning calorimeter (Shimadzu DSC-60) at a scanning rate of 10°C min^{-1}. XRD measurements were performed at beamline BL17A. The liquid crystal behavior and the type of textures were determined by a miscibility method on microscopic observations.

Analytical data

Spectral data

^{1}HNMR in ppm for pentyloxy derivative

^{1}H NMR ($CDCl_3$, 400 MHz): 0.86–0.88 (t, 3H, -CH_3 of –OC_5H_{11} group), 1.42–1.45 (m, 4H, polymethylene group of –OC_5H_{11} group), 1.80–1.89(p, 2H, Ar-O-(CH_2)-$\mathbf{CH_2}$), 3.80–3.85 (6H, s, Ar-O-$\mathbf{CH_3}$), 4.00–4.03 (t, 2H, Ar-O-$\mathbf{CH_2}$), 6.84–8.15 (m,11H, Ar-H), 7.61 (d, 1H, chalcone), 8.12 (d, 1H, chalcone). The NMR data are consistent with the molecular structure.

^{1}HNMR in ppm for decyloxy derivative

^{1}H NMR ($CDCl_3$, 400 MHz): 0.88–0.90 (t, 3H, -CH_3 of –$OC_{10}H_{21}$ group), 1.27–1.45 (m, 12H, polymethylene group of –$OC_{10}H_{21}$ group), 1.47–1.50 (p, 2H, Ar-O-(CH_2)$_2$-$\mathbf{CH_2}$), 1.78–1.85 (p, 2H, Ar-O-(CH_2)-$\mathbf{CH_2}$), 3.86 (6H, s, Ar-O$\mathbf{CH_3}$), 4.02–4.05 (t, 2H, Ar-O-CH_2), 6.86–8.11 (m, 11H, Ar-H), 7.35–7.57 (d, 1H, chalcone), 8.08–8.10 (d, 1H, chalcone). The NMR data are consistent with the molecular structure.

IR in cm^{-1} for tetradecyloxy derivative

3066 (=C-H Str. of phenyl nucleus), 2929 and 2850 (CH_2 sym. & asym. stra.), 1728 (aromatic C=O Str.), 1604 (aromatic C=C str.), 1510 (C-C aromatic str.),1467 (C-H bend alkanes), 1315 (aromatic and aliphatic C-O str.), 1166 (Ar-O str.),844 (C-H oop. phenyl ring), 758 (C-H oop. bending of phenyl ring). The IR data are consistent with the molecular structure.

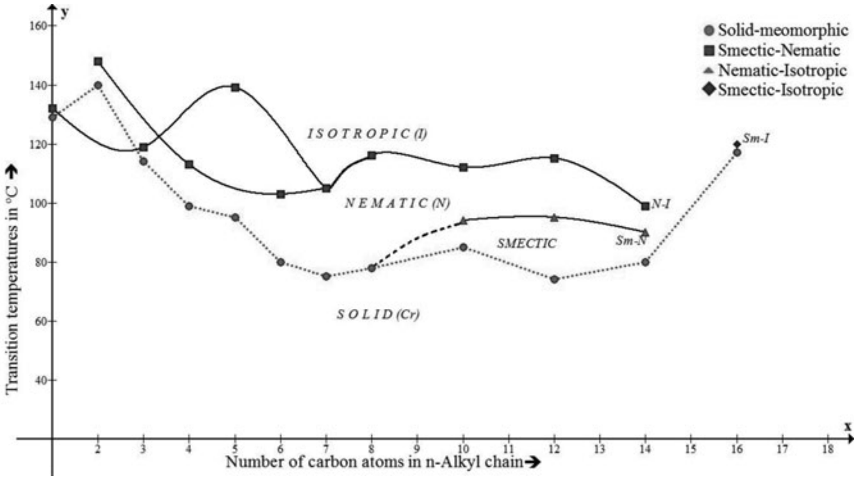

Figure 1. Phase behaviors of series.

IR in cm^{-1} for hexadecyloxy derivative

3074 (=C-H Str. of phenyl nucleus), 2916 and 2850 (CH_2 sym. and asym. stra.), 1778 (aromatic C=O Str.), 1606 (aromatic C=C str.), 1508 (C-C aromatic str.), 1473 (C-H bend alkanes), 1315 (aromatic and aliphatic C-O str.), 1170 (Ar-O str.), 844 (C-H oop. phenyl ring), 759 (C-H oop bending of phenyl ring). The IR data are consistent with the molecular structure.

Mass of propyloxy derivative

m/z (rel. int%): 445 (M)+, 398, 231, 147, 119.

Mass of octayloxy derivative

m/z (rel. int%): 516(M)+, 485, 233, 121, 104.

Texture determination by miscibility method

- Butyloxy derivative (C_4): Threaded nematic
- Hexyloxy derivative (C_6): Schlieren nematic
- Decyloxy derivative (C_{10}): Smectic-A
- Hexadecyloxy derivative (C_{16}): Smectic-C

Results and discussion

The novel homologous series α-4-(4′-n-alkoxy benzoyloxy) benzoyl β-2″;,5″-dimethoxy phenyl ethylene consists of 12 homologues of mesogenic characteristics. The methoxy to octyloxy homologue derivatives are only nemetogenic; the decyloxy to tetradecyloxy homologues are smectogenic, in addition to nematogenic, and the hexadecyloxy homologue is only smectogenic. All phases are generated enantiotropically. The transition temperatures (Table 2(a)), as determined on an optical polarizing microscope equipped with a heating stage, are plotted against the member of carbon atoms present in n-alkoxy chain of n-alkoxy (-OR) terminal end group. Transition curves (N-I, Sm-N, Sm-I, solid-mesomorphic) are obtained on linking with similar or related transition points, showing phase behaviors of a series in a phase diagram (Fig. 1). The solid-mesomorphic transition curve adopts a zigzag path of rising and

Table 2. Transition temperatures in °C.

Compound No.	n-alkyl group C_nH_{2n+1}(n)	Transition temperature Sm	 N	 Isotropic
(a) Transition temperatures in °C of series-1				
1	1	-	129	132
2	2	-	140	148
3	3	-	114	119
4	4	-	99	113
5	5	-	95	139
6	6	-	80	103
7	7	-	75	105
8	8	-	78	116
9	10	85	94	112
10	12	74	95	115
11	14	80	90	99
12	16	117	-	120
(b) Transition temperatures in °C of series-X				
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
(c) Transition temperatures in °C of series-Y				
1	1	-	-	200.0
2	2	-	-	206.0
3	3	-	-	190.0
4	4	-	-	201.0
5	5	-	142.0	170.0
6	6	-	124.0	160.0
7	7	-	123.0	174.0
8	8	-	110.0	169.0
9	10	-	132.0	178.0
10	12	-	120.0	166.0
11	14	-	125.0	152.0
12	16	-	132.0	156.0

Sm = Smectic, Nm = Nematic.

falling values and behaves in a normal manner. The Smectic–Nematic transition curve shows a descending tendency and behaves in a usual established manner. A point of Sm-I transition temperature does not match with the descending trend of Sm-N transition curve and deviates from the normal behavior. The Nematic–isotropic (N-I) transition curve shows mainly normal descending behavior as the series is ascended with the exhibition of an odd-even effect and a deviating trend at the pentyloxy homologue. Curves for odd and even members merge at the heptyloxy (C_7) homologue and progresses as a single curve up to the tetradecyloxy (C_{14}) homologue.

Thus, the odd-even effect diminishes as the series is ascended. The Sm-N transition curve is extrapolated [26,27] to the octyloxy (C_8) homologue to predict its latent transition temperature (LTT) for smectic keeping in view the trend of Sm-N transition curve, which merges into the point of solid-nematic transition temperature (78°C). Initial members of a series are nematogenic (C_1 to C_8), upper middle members are smectic and nematic (C_{10} to C_{14}), and

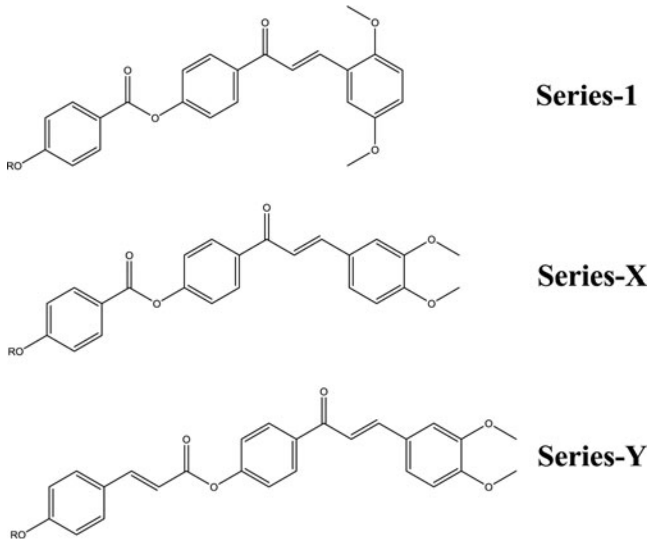

Figure 2. Structurally similar series.

last (C_{16}) member is only smectogenic. Thus, novel series follows normal trend of mesophase sequence, with a little bit deviating tendency at pentyloxy (C_5) and hexadecyloxy (C_{16}) derivatives. Sm-N and N-I thermal stabilities are 93°C and 117.4°C respectively, whose smectogenic phase length varies between 9°C and 21°C and the nematogenic phase length varies between 3°C and 44°C. Thus, novel series is predominately nematogenic and partly smectogenic of middle-ordered melting-type, or a novel series of the present investigation is entirely mesomorphic. Thus, mesomorphic properties of the present series vary from homologue to homologue.

α-4-Hydroxy benzoyl β-2′,5′-dimethoxy phenyl ethylene (m.p.: 205–210°C, yield 68–70%) is a non-mesogenic. However, mesogenic property is induced on linking it with the 4-n-alkoxy benzoic acids through their corresponding acid chlorides. The molecular length and breadth of final ester derivatives are increased. Hence, the molecular polarity and polarizibility are enhanced according to dipole moment acting across the long molecular dipole–dipole interactions, dispersion forces, etc. related to suitable magnitudes of anisotropic forces of end-to-end and lateral attractions because of resultant molecular rigidity and flexibility required to induce mesogenic behaviors in a substance. All the members of a novel series under the influence of heat resist individually the externally exposed thermal vibrations for

Table 3. Average thermal stability (°C).

Series	1	X	Y
Smectic–nematic	93.0	115.6	–
Commencement of smectic phase	[C_{10}-C_{14}]	[C_6-C_{14}]	–
	C_{10}	C_6	
Nematic–isotropic	117.4	156.6	163.1
Commencement of nematic phase	[C_1-C_{14}]	[C_2-C_{16}]	[C_5-C_{16}]
	C_1	C_2	C_5
Phase length range in °C	03 to 44 = 41	07 to 67 = 60	24 to 59 = 35

definite range of temperature. They misaligned at an angle of 90° or less than 90° with a floating surface, depending upon suitable magnitudes of anisotropic intermolecular adhesion to maintain mesophase formation with certain degree of entropy (ΔS). The molecules of the present series are under observation through heating stage polarizing microscopy but some homologues are observed by DSC. Methoxy (C_1) to octyloxy (C_8) members maintained only statistically parallel orientational order of molecules of definite entropy limit, while floating on the surface prior to isotropic temperature with appearance of nematic phase. However, on continued exposure to thermal vibrations beyond certain limit, the molecules under examination, from and beyond isotropic temperature, are randomly oriented in all possible directions with high order of disorder or high value entropy ($\Delta S = \Delta H/T$). However, on cooling the same, with appropriate rate of cooling the same, the nematic mesophase appears from and below isotropic temperature until solidification. The molecules from decyloxy (C_{10}) to hexadecyloxy (C_{16}) homologues bear lamellar packing of molecules in their crystal lattices, which allows the molecule to be set perpendicular to floating surface to build up two- or three-dimensional network and acquires layered arrangement of crystal structure. However, sliding layered arrangement of molecules is maintained under the exposed thermal vibrations for some range of temperature with exhibition of smectic phase. C_{10}, C_{12}, and C_{14} homologues exhibited smectic phase for the same temperature range and then adopted nematic phase for higher range of temperature up to isotropic temperature in irreversible manner on heating and cooling. C_{16} homologue adopts only smectogenic behavior due to high degree of its intermolecular anisotropic forces of attractions. Disappearance of dimerization of n-alkoxy benzoic acids through esterification is attributed to the breaking of hydrogen bonding between two molecules of 4-n-alkoxybenzoic acids. Normal behavior of solid-mesomorphic and Sm-N transition curves of a phase diagram is understandable, but the deviating trend of N-I transition curve at the pentyloxy (C_5) and unmatched tendency (Sm-I) of hexadecyloxy (C_{16}) homologue with Sm-N transition curve requires some specific understandings. The upper N-I transition curve may fall progressively, while the lower curve rises to the early maxima before it falls and merges with the upper curve as alternation diminishes. Such behavior has been reported earlier for including certain aldonitrones [28]. Therefore, exceptional behavior of C_5 homologue may occur for its exceptional magnitudes of molecular rigidity and flexibility. The deviating trend of Sm-I transition temperature of C_{16} homologue may be attributed to the under certainty of the status of longer n-alkyl chain of left n-alkoxy terminal end group, and may cause exceptional variations of suitable magnitudes in anisotropic forces of intermolecular attractions. The exhibition of odd-even effect by N-I transition curve is due to the sequentially and progressively added methylene unit or units to n-alkyl chain bonded through oxygen atom with a first phenyl ring. The diminishing of odd-even effect for longer n-alkyl chain is attributed to its coiling or bending or flexing, or coupling of major axis of a molecular core structure affecting suitable magnitudes of anisotropic forces of end-to-end attractions because of varying molecular flexibility and rigidity operating mesomorphic behavior of a substance. The changing mesomorphic property from homologue to homologue in the present series is attributed to the changing molecular length, molecular polarity and polarizibility, dipole moment across the molecular axis, etc. due to the changing number of methylene units, i.e. changing molecular flexibility, keeping right terminal/lateral end groups unchanged, which are also contributing to the total molecular flexibility, and hence causing expected or unexpected variations in the type and the degree of mesomorphism. Smectic and nematic average thermal stability of the present series are 93°C and 117.4°C respectively. These values are relatively lower than the normal expected values, reflecting the lower magnitudes of intermolecular anisotropic forces of intermolecular attractions due to two polar

-OCH_3 groups set at 2 and 5 positions of third phenyl ring. -OCH_3 groups at 2 and 5 positions are linked to two carbons of the same phenyl ring situated at an angle of 180° from each other. Therefore, the C-OCH_3 bond polarities and resulting dipole moment are equal in magnitudes of C-OCH_3 but opposite in directions, as bond polarity, dipole moment, dipole–dipole interactions and polarizibility are vector quantities whose effectiveness depends upon the direction in which they operate. Thus, such parameters governing LC behaviors being equal in magnitudes and opposite in directions cancel the effectiveness of each other caused by two -OCH_3 groups substituted at positions 2″, 5″ on phenyl ring of targeted molecule. Thus, contribution of dipole moment across the long molecular axis is reduced, affecting transition temperatures, which results into lowering of average thermal stabilities for smectic and nematic phases.

The liquid crystal properties or behaviors of the present investigated novel homologous series-1 are compared with the chosen structurally similar isomeric known series-X [28(ii)] and series-Y [29] as shown in Fig. 2; transition temperatures of series-X and Y are shown in Tables 2(b) and (c).

Homologous series-1 and series-X are identical with respect to three phenyl rings and two central bridges -COO- and -CO-CH=CH- constituting molecular rigidity. In addition, these are identical with respect to flexible end groups, -OR and two methoxy groups, for the same homologue from series to series. However, both series under comparison differ with respect to the positional substitution of two -OCH_3 groups bonded to third phenyl ring on 2″, 5″ (series-1) and 3″,4″ (series-X) positions respectively. Therefore, magnitudes of molecular flexibility cause variations of suitable magnitudes in the anisotropic forces of intermolecular end-to-end and lateral attractions, responsible for possibility, type, and degree of mesophase formation. Homologous series-1 and series-Y are identical but they are not isomeric to each other because a central group -CH=CH-COO- linking the first and second phenyl ring of series-Y differ from a central group -COO- of series-1 under identical condition. Moreover, in addition to difference in central bridges, two methoxy groups set an angle of 60° of series-Y in comparison with series-1, in which two -OCH_3 groups set at an angle 180° affect the magnitudes of vector quantity dipole moment across major molecular axis; dipole–dipole interaction and dispersion forces also cause variations. The central bridge vinyl carboxylate -CH=CH-COO- of series-Y and carboxylate -COO- of series-1 are comparable. However, vinyl carboxylate -CH=CH-COO- has greater length than -COO-. Therefore, it causes more non-coplanarity due to a twist obtained, as the oxygen atoms of vinyl carboxy group bump into the non-bonded adjacent hydrogen atoms of aromatic rings. Thus, because of these effects, the mesomorphic-isotropic thermal stabilities, i.e. liquid crystal properties and the degree of mesomorphism, depend upon the varying parts and their varying magnitudes of differing molecular structures. Table 3 presents the comparative data of average thermal stabilities, commencement of mesophase or mesophases, degree of mesomorphism, etc. for series-1, X, and Y under comparative study as mentioned below.

Table 3 clearly indicates the following:

- Isomeric homologous series-1 and X have exhibited smectogenic and nematogenic mesophase but a non-isomeric series-Y exhibited only nematogenic mesophase with absence of smectogenic character.
- Smectic thermal stability of presently investigated novel series-1 is lower (93.0) than an isomeric series-X (115.6).
- Nematic thermal stabilities are in increasing order from series-1 to series-X to series-Y.
- Smectic mesophase commences late from decyloxy (C_{10}) homologue in the present novel series-1, whereas it commences earlier from hexyloxy (C_6) homologue derivative of

Table 4. DSC data for C5, C8, and C12 homologues at a heating rate of 10°C per minute

Homologue	Transition	Transition Temp, *t* (°C)	ΔH ($J\,g^{-1}$)	Absolute temp (°K) T = t + 273	$\Delta S = \Delta H/T$
C_5	Cr ΔS_1 N	97.43	88.04	370.43	0.2376
	N ΔS_2 I	138.16	0.85	411.16	0.00206
C_8	Cr ΔS_1 N	75.71	59.67	348.71	0.1711
	N ΔS_2 I	–	–	–	–
C_{12}	Cr ΔS_1Sm	–	–	–	–
	Sm ΔS_2 N	93.21	87.15	366.21	0.2379
	N ΔS_3I	116.2	3.55	389.42	0.0091

(—): Missing transitions.

isomeric series-X and does not commence till the last (C_{16}) member of series-Y.

- Nematic mesophase commences earliest from first member (C_1) of the present novel series-1, from second member (C_2) of isomeric series-X, and late from the pentyloxy (C_5) homologue member of non-isomeric series-Y.
- Total mesomorphic phase length range is highest for series-X (60), lowest for series-Y (35), and intermittent (41) to series-X and Y for series-1 of the present investigation.

All three homologous series under comparison bear laterally substituted -OCH_3 group or groups. Therefore, their intermolecular distances parted somewhat more or less depending on position and polarity of laterally substituted group or groups and magnitudes of intermolecular anisotropic end-to-end and lateral forces of attractions, which are affected because of changing molecular rigidity and flexibility. Generally, enhancement in intermolecular distance reduces intermolecular attractions and depresses mesomorphic isotropic transition temperatures as well as the possibility of facilitating tendency of LC phase formation. However, it also increases intermolecular forces of end-to-end and lateral attractions by increasing molecular polarizibility through increasing molecular width. Thus, two opposing effects of intermolecular forces (reducing and enhancing) are operated at a time for the same reason (i.e. increasing molecular width). Hence, the resulting magnitudes of anisotropic forces of intermolecular end-to-end or/and lateral attractions depend upon the predominance of any one or other (second) effect. Thus, the possibility of facilitating smectic or/and nematic mesophase formation depends upon resulting effects out of the two opposing effects operated at a time. Now comparing the exhibition of mesophase formation in isomeric series-1 and X, the two methoxy groups at positions 2″, 5″ in series-1 are at 180° to each other; and those at positions 3″, 4″ in series-X are at 60° to each other. The bond polarity of C-OCH_3 bonds is equal in magnitudes for all the series under comparative study. However, bond polarity being a vector quantity, the value of resultant bond polarities, i.e. vector sum of two identical bonds, depends upon the angle between two identical bonds. The vector sum of two C-OCH_3 bond polarities, although being equal in magnitudes, acting in opposite directions to each other, is zero or cancels each other for an angle of 180° between two -OCH_3 for the molecules of the presently investigated novel series-1, thus affecting total molecular polarity, flexibility, dipole moment, dipole–dipole interactions, intermolecular dispersion, and anisotropic forces of attraction. However, two C-OCH_3 bonds in the molecules of series-X being at an angle of 60°, the vector sum of two bond polarities are not equal to zero. Therefore, the magnitudes of anisotropic forces of intermolecular end-to-end and lateral attractions of series-X are greater than series-1. Thus, both isomeric series, although containing two C-OCH_3 polar bonds, have contributed differently to molecular polarities and polarizibility. However, both

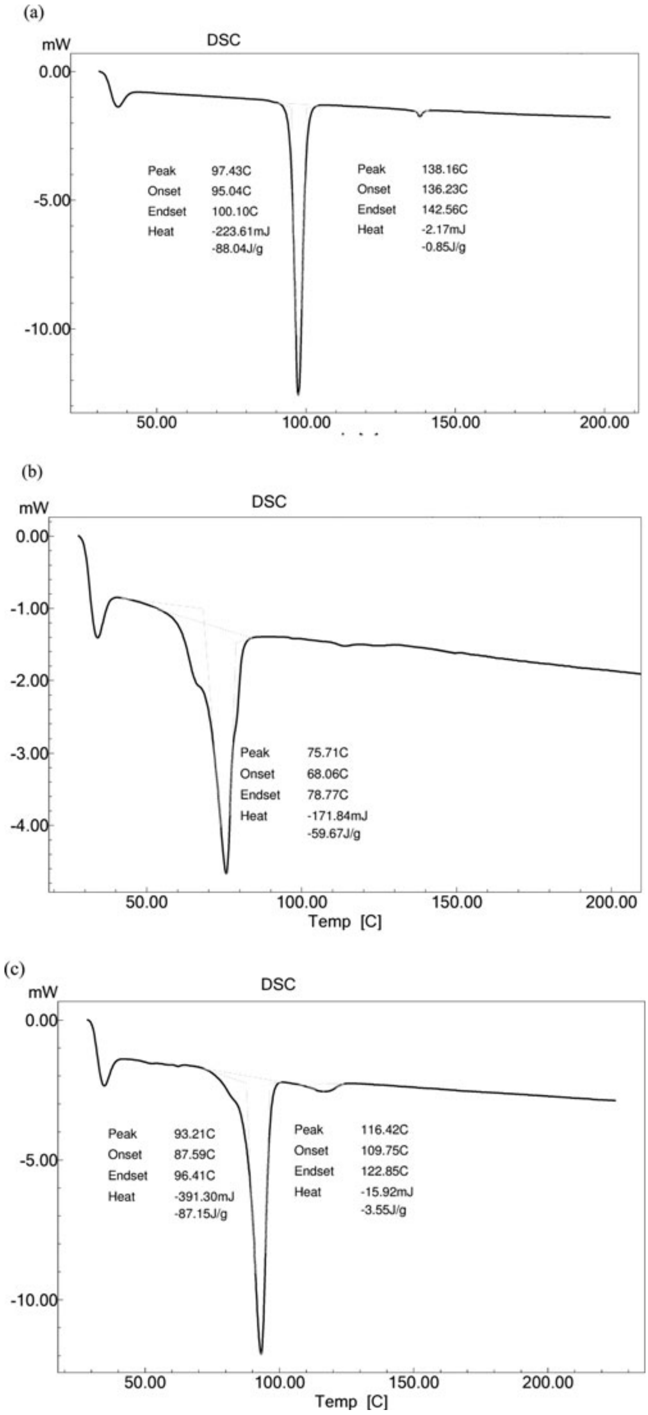

Figure 3. (a) DSC thermogram for pentyloxy derivative; (b) DSC thermogram for octyloxy derivative; (c) DSC thermogram for dodecyloxy derivative.

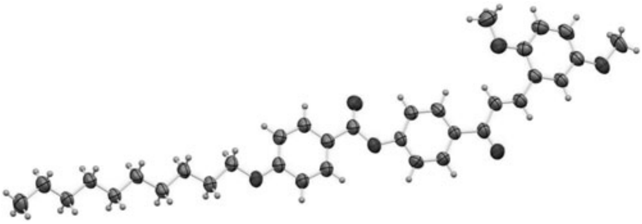

Figure 4. X-ray diffractogram of C10 homologue.

isomeric series exhibited smectic mesophase in addition to nematic mesophase formation, but their thermal stabilities for smectic and nematic, commencement of smectic and nematic phases, degree of mesomorphism, etc. are different because of differing molecular rigidity and flexibility depending on molecular structure. Cancellation of two -$COCH_3$ bond polarities (180°) lower Sm-N and N-I transition temperatures, and hence the corresponding thermal stabilities for smectic and nematic mesophases of the present series-1 as compared with isomeric series-X occur at the cost of the commencement of mesophase, which commences late by one homologue, i.e. from the second member of series-X and from the first member of series-1. The molecules of homologous series-Y have their two -OCH_3 groups bonded with two carbons at a bond angle of 60°, and equally affect the factors related to mesomorphism of series-X, but the effect due to the presence of longer vinyl carboxy -CH=CH-COO- group in comparison with shorter carboxy -COO- group strengthens the end-to-end attractions. Therefore, lamellar packing of molecules in series-Y is hindered, and simultaneously statistically parallel orientational order of molecules is favored in floating condition under the influence of exposed thermal vibrations as a consequence of increased molecular rigidity by -CH=CH-COO- more than -COO central bridge. Thus, the N-I transition temperature of series-Y is higher than that of series-1 at the cost of smectic mesophase formation. Therefore, smectic mesophase is missing for the molecules of series-Y, and nematic thermal stability is highest among the series under comparative study. The late commencement of nematic phase in series-Y (from C_5) as compared with series-1 (from C_1) is attributed to the suitable magnitudes of end-to-end intermolecular closeness required to resist exposed thermal vibrations to suitable and facilitative mesophase for definite temperature range as a consequence of favorable molecular rigidity in combination with molecular flexibility. Thus, changing trend of LC properties for the same homologue from series to series depends upon the changing position of the same pair of polar groups with respect to the same central group linking middle and third phenyl ring. The extrapolation [10(iv),30] of Sm-N transition curve to octyloxy (C_8) homologue keeping in view the trend of the curve, it matches with the solid-nematic transition point, indicating that there is no possibility of existence of smectic mesophase from and prior to octyloxy (C_8) homologue derivative.

The transition temperature (in °C and °K) with associated enthalpy changes (in J g^{-1}) of C_5, C_8, and C_{12} homologues from DSC measurements are summarized in Table 4. The homologues selected for the DSC study are enantiotropically mesogenic and undergo crystal-mesomorphic small-isotropic transitions recorded during heating. DSC thermogram of selected homologues is shown in Fig. 3.

An X-ray diffraction study of decyloxy (C_{10}) homologue carried out for molecular arrangement is depicted with related data in Fig. 4. A typical layer structure is observed for smectic-A phase. A sharp diffraction peak implies the formation of layered structure.

Conclusions

- The LC properties of a substance from homologue to homologue in the same series and for the same homologue from series to series depend upon the molecular structure of a substance because of changing magnitudes of molecular rigidity and/or flexibility.
- Molecular rigidity and flexibility are very sensitive and susceptible to molecular structure.
- The group efficiency order derived on the basis of (i) thermal stabilities, and (ii) the early commencement of smectic and nematic phases are as under:
  - (i) Smectic $3'',4''$dimethoxy with -COO-(series-X) > $2'',5''$dimethoxy with -COO-(series-1) > $3'',4''$methoxy with-CH=CH-COO-(series-Y).
    Nematic Series-Y > series-X > series-1.
  - (ii) Smectic Series-X > series-1 > series-Y.
    Nematic Series-1 > series-X > series-Y
- Carboxy:-COO- central group is smectogenic and vinyl carboxy:-CH=CH-COO central group is nematogenic.
- Presently investigated novel series-1 is predominantly nematogenic and partly smectogenic with middle ordered melting type and middle ordered range of mesophase length.
- Present study reveals that the mesophase range is greatly affected by the positional substitution of the same pair of functional group at the same phenyl ring and by changing central group between first and middle phenyl rings.

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