Dependence of Mesomorphism on Molecular Rigidity

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ABSTRACT

A novel smectogenic homologous series of twelve homologues synthesized and studied with a view to understand and establish the effect of molecular structure on liquid crystal properties (LC) and LC behaviors of thermotropic homologues. First (C_1) to last (C_{16}) member of a series exhibited only enantiotropically smectogenic property without showing nematic property which is absent even in the monotropic condition. Transition and melting temperature including textures of homologues were determined by an optical polarizing microscopy equipped with a heating stage, texture of a smectic phase are of the type A or C. Smectogenic phase length ranger between 5.1°C to 22.6°C. Smectic-Isotropic (Sm-I) thermal stability is 153.55°C. Analytical, spectral and thermal data supported molecular structures of homologues. LC behaviors of present novel series are compared with the structurally similar homologous series. Transition curves viz. Cr-Sm and Sm-I transition curves of a phase diagram behaved in normal manner.

Keywords: Smectic; Enantiotropy; Nematic; Liquid crystals; Mesogenic.

1. INTRODUCTION

Liquid crystalline (LC) state [1] either thermotropic or lyotropic are exploited by scientific and technological communities of researchers in the benefit of mankind as a whole, since from its origin. [2,3,4,5,6]. Though the research groups working on LC state have different views, aims and objects, but they need novel LC materials in order to continue their research work in the benefit of people. Therefore, our interest in LC study made limited to synthesize novel LC materials through novel homologous series of LC potentials, which may be useful for the thermotropic or lyotropic action purposes. It is possible to vary molecular moieties by changing number of phenyl or other type of rings and central bridge or bridges related to molecular rigidity and lateral or terminal group or groups related to molecular flexibility. Thus, number of homologous series can be synthesized to provide novel LC materials as a source for farther research with different aims, views and object in different disciplines. Thus present study is aimed to synthesize and provide novel LC materials with a view to understand the effect of molecular structure on LC properties and to establish the relation between LC behaviors and molecular structure [7, 8, 9, 10]. Number of homologous series has been reported till the date [11, 12, 13, 14]. Present investigation consists of a molecule of three phenyl rings bonded through -COO- and -CO-CH=CH- central bridges with flexible terminal end groups -OR ($R=C_nH_{2n+1}$) which varies $n=1,2,\dots,16$ and

unchanging -F, and without any lateral group or groups. Results are to be discussed, compare and interpreted in terms of molecular rigidity and flexibility [15, 16, 17, 18].

2. EXPERIMENTAL

2.1. Synthesis

n-Alkoxy benzoic acids were prepared from 4-hydroxy benzoic acid, by suitable alkylating agents by modified method of Dave and Vora [19]. α -4-Hydroxy benzoyl- β -4' fluoro phenyl ethylene was prepared by usual established method [20] (M.P.-162°C, Yield-75.2%). 4-n-Alkoxy benzoic acids and α -4-hydroxy benzoyl- β -4' fluoro phenyl ethylene were condensed in 1, 3-dicyclohexylcarbodiimide (DCC), 4-dimethyl aminopyridine (DMAP) and CH_2Cl_2 [21] to obtain α -4-(4'-n-Alkoxy benzoyloxy) benzoyl- β -4'' fluoro phenyl ethylenes. Final products were individually decomposed, filtered, washed, dried and purified till the constant transition temperatures obtained.

The synthetic route to the novel homologous series of ethylene derivatives is under mentioned in scheme-1.

Scheme 1. Synthetic route to the novel series.

2.2. Characterization

Some of members of a novel series as the representative member of a series were characterized by elemental analysis (Table-1), Infrared spectroscopy, ^1H NMR spectra and mass spectroscopy. Microanalysis was performed on EuroEA Elemental Analyzer. IR spectra were recorded on Shimadzu FTIR Model-IRAffinity-1S (MIRacle 10), $^1\text{HNMR}$ spectra were recorded on Bruker spectrometer using CDCl_3 as a solvent and mass spectra were recorded on Shimadzu GC-MS Model No.QP-2010.

2.3. Analytical data

Table 1. Elemental analysis for (1) Ethyloxy (2) Pentyloxy (3) Octyloxy derivatives.

Sr. No.	Molecular formula	Elements %Found			Elements %Calculated		
		C	H	O	C	H	O
1	$\text{C}_{24}\text{H}_{19}\text{FO}_4$	73.86	4.90	16.36	73.84	4.91	16.39
2	$\text{C}_{27}\text{H}_{25}\text{FO}_4$	75.08	5.80	14.77	74.98	5.83	14.80
3	$\text{C}_{30}\text{H}_{31}\text{FO}_4$	75.98	6.58	13.44	75.93	6.58	13.49

Spectral Data

$^1\text{HNMR}$ in ppm for Methyloxy Derivative

8.1039-8.0817 (d 2H Ar-H), 8.0393-8.0177 (d 2H Ar-H), 7.7423-7.7031 (d 1H H-C=C j Hz), 7.5917-7.5566 (d 2H Ar-H), 7.4101-7.3709 (d 1H H-C=C j Hz), 7.2998-7.2781 (d 2H Ar-H), 7.0661-7.0232 (d 2H Ar-H), 6.9380-6.9158 (d 2H Ar-H), 3.8316 (s 3H -OCH₃). The NMR data are reliable with the molecular structure.

$^1\text{HNMR}$ in ppm for Heptyloxy Derivative

8.0865-8.0644 (d 2H Ar-H), 8.0380-8.0163 (d 2H Ar-H), 7.7424-7.7032 (d 1H H-C=C j Hz), 7.5920-7.5528 (d 2H Ar-H), 7.4103-7.3112 (d 1H H-C=C j Hz), 7.2983-7.2766 (d 2H Ar-H), 7.0663-7.0234 (d 2H Ar-H), 6.9204-6.8821 (d 2H Ar-H), 3.9907-3.9579 (t 2H O-CH₂-), 1.7873-1.7171 (p 2H O-CH₂-CH₂), 1.4385-1.2421 (p 8H -CH₂-CH₂-), 0.8459-0.8119 (t -CH₃). The NMR data are reliable with the molecular structure.

IR in cm^{-1} for Propyloxy Derivative

3066.92 (w, C-H str. of Aromatic ring), 2970.48, 2881.75 (s C-H str. of alkane, sp³ Carbon), 2357.09, 2332.02 (combination of C-H str.), 1728.28 (s C=O str. ester), 1658.84, 1599.04, 1508.38 (C=C str. In Aromatic ring), 1417.73 (m C-H bend. Alkane) 1276.92 (s Aromatic C-O str. and C=C str.), 1170.83, 1074.39, 1016.52, (s Aliphatic C-O str. and so and overtone C-H str.), 829.42, 758.05, 684.75 (m-o-p sub. phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Tetradecyloxy Derivative

3066.92 (w, C-H str. of Aromatic ring), 2920.32, 2848.96 (s C-H str. of alkane, sp³ Carbon), 2357.09, 2332.02 (combination of C-H str.), 1726.35 (s C=O str. ester), 1656.91, 1597.11, 1510.31 (C=C str. in Aromatic ring), 1413.87 (m C-H bend. Alkane) 1263.42 (s Aromatic C-O str. and C=C str.), 1166.97, 1072.46, 1028.09, 985.66, (s Aliphatic C-O str. and

so and overtone C-H str.), 821.70, 640.29, 601.81 (m-o-p sub. phenyl ring). The IR data are consistent with the molecular structure.

Mass spectra of Butyloxy Derivative

m/z (rel.int%): 418(M)+, 241, 177, 165, 121, 101, 93, 76, 65, 44

Mass spectra of Hexyloxy Derivative

m/z (rel.int%): 446(M) +, 241, 205, 162, 121, 101, 93, 76, 65, 44

3. RESULTS AND DISCUSSION

α -4-Hydroxy benzoyl β -4' fluoro phenyl ethylene is a non-liquid crystal component of the homologues. However smectic type mesomorphism is indeed on linking it with 4-n-alkoxy benzoic acids by steglich esterification. Dimerization of n-alkoxy benzoic acid disappears on esterification. Transition temperatures (Table-2) as determined from an optical polarizing microscopy were plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminally situated and group (Figure-1). Transition curves Cr-Sm and Sm-I are drawn smoothly linking like or related points as shown in a phase diagram showing phase behaviors of a series. Cr-Sm transition curve follows partly zigzag path of rising and falling in usual established manner with overall descending manner as series is ascended. Sm-I transition curve behaved normal manner with exhibition of odd even effect. Sm-I transitions curves for odd and even numbers merges into each other at the butyloxy (C_4) homologue of a series and then it prolong as a single curve till C_{16} homologue. Thermal stability for smectic is 153.55°C and the mesophase length ranges from 5.1°C (C_{12}) to 22.6°C at the C_{16} member of a series. Smectogenic mesophase formation commences from very first member (C_1) to the lost (C_{16}) member of a series in enantiotropic manner without exhibition of nematic property. Thus, present novel series is fully smectogenic with middle ordered melting type.

Table 2. Transition temperatures in $^\circ\text{C}$.

Compound No.	R=n-alkyl chain C_nH_{2n+1}	Transition temperatures in $^\circ\text{C}$		
		Sm	N	Isotropic
1	1	177.8	-	189.0
2	2	167.7	-	173.5
3	3	148.8	-	160.2
4	4	147.2	-	154.8
5	5	145.1	-	152.4
6	6	142.8	-	149.0
7	7	139.3	-	145.0
8	8	137.6	-	149.5
9	10	135.1	-	143.1
10	12	143.8	-	148.9
11	14	122.7	-	137.2
12	16	117.4	-	140.0

Sm, Smectic; N, Nematic

Figure 1. Phase Behavior of Series.

Linking of dimeric n-alkoxy benzoic acid by steglich esterification with α -4-hydroxy benzoyl β -4'-fluoro phenyl ethylene increased molecular length, polarity and polarizability, rigidity and flexibility and suitable magnitudes of anisotropic forces of intermolecular lateral and end to end attractions to such an extent that, lamellar packing of molecules occur in solid crystalline state. Thus, molecules of each homologue (C_1 to C_{16}) disaligned of angle ninety degree to from focal conic networking as layers. Such layers are slides over one another under the influence of exposed thermal vibrations with different magnitudes of resistivity depending upon enthalpy (ΔH) value acquired during formation, which maintains thermal stabilization and resistivity towards exposed heat and caused to appear smectic mesophase formation throughout the series. However, the residual forces of end to end attractions is insufficient for all the homologues to maintain statically parallel orientational order of molecules in floating condition on the surface to exhibit nematic phase, but directly converted to isotropic state in which the molecules of homologues (C_1 to C_{16}) randomly oriented in all possible directions with high order of disorder or high entropy ($\Delta S = \Delta H/T$). Isotropic melt on cooling reacquire smectic phase by passing monotropic nematic mesophase formations. Thus, only smectogenic mesomorphic phase is exhibition enantiotropic manner directly and transform in to crystalline state without exhibition of monotropic nematic mesophase formation. Disappearance of dimerization of n-alkoxy benzoic acid is attributed to the breaking of hydrogen bonding between two molecules by esterification process. Disappearance of odd-even effect from and beyond C_4 homologues in Sm-I transition curve is attributed to the coiling or flexing or bending or coupling of longer n-alkyl chain (C_5 to C_{16}) with major axis of the core structure of the molecules. Average thermal stability indicates transition and melting temperatures above 100°C . However, smectogenic mesophase stabilize after between 5.1°C and 22.6°C . Thus, thermal stability facilitated for majority of homologues is low which is operated by

paramagnet dipolemoment across the long molecular axis, dipole-dipole interactions, electronic interactions, dispersion forces etc. conducive to mesophase formation. Thus, series under discussion is fully smectogenic with absence of nematogenic character. Some mesomorphic properties of presently investigated novel homologues series-1 are compared with structurally similar known homologous series- X [22] and Y [23] as under in figure -2.

Figure 2. Structurally similar series.

Homologous series-1 and series-X and Y selected for comparative study are identical with respect to three phenyl rings, a central bridge $-\text{COO}-$ linking first and middle phenyl ring and the left n-alkoxy terminal end group for the same homologues. However, they differ with respect to either central bridges (series 1 and X) or terminally situated tail group (series-1 and Y). Homologous series 1 and X differ by central bridges $-\text{CO}-\text{CH}=\text{CH}-$ and $-\text{N}=\text{N}-$ keeping tail group $-\text{F}$ intact whereas series 1 and Y differ by a tail group $-\text{F}$ and $-\text{Cl}$ respectively, keeping central bridge $-\text{CO}-\text{CH}=\text{CH}-$ unchanged. Therefore, molecular rigidity differs for series 1 and X but molecular flexibility for the same homologues remains unaltered; where as molecular flexibility alters for the series 1 & Y, but molecular rigidity remains unaltered. However, suitable or unsuitable magnitudes of anisotropic forces of intermolecular attraction to stabilize or destabilize liquid crystalline state depend upon the combine effect of molecular rigidity and flexibility. The combined effect of molecular rigidity and flexibility varies from homologues to homologue in the same series or for the same homologue from series to series. Thus, variation in mesomorphic behaviors and the degree of mesomorphism depend upon the charging part of molecules, operating molecular rigidity or flexibility responsible for suitable magnitudes of anisotropic forces of intermolecular end to end and /or lateral attractions. Following table-3 represents some LC properties of Series 1, X and Y in comparative manner.

Table 3. Average thermal stabilities in $^{\circ}\text{C}$.

Series $\rightarrow$	1	X	Y
Smectic-Isotropic or Smectic-Nematic	153.55 ($\text{C}_1\text{-C}_{16}$)	116.80 ($\text{C}_8\text{-C}_{16}$)	-
Commencement of Smectic mesophase	C_1	C_8	-

Nematic-Isotropic	-	189.70 (C ₁ -C ₁₀)	149.4 (C ₅ -C ₁₄)
Commencement of nematic phase	-	C ₁	C ₅
Total Mesophase length range (Sm+N)	5.1(C ₁₂) to 22.6(C ₁₆)	15.0(C ₁₆) to 103.0 (C ₆)	14.0 (C ₈) to 25.0 (C ₁₂)

On comparing the mesomorphic behaviors of homologous series-1 of present investigation and the series-X and Y chosen for comparison;

○Series-1 is only smectogenic, series-X is smectogenic in addition to nematogenic and a series-Y is only nematogenic.

○Smectic thermal stability of series-1 is higher than a series-X and Y.

○Nematic thermal stability of series-X is greater than the series-Y and 1.

○Smectic mesophase commences earlier for the series-1 (C₁) and later from C₈ of the series-X, whereas it does not commence till the last member of a series-Y.

○Nematic mesophase commences from C₁ and C₅ homologues for the series-x and Y respectively, but it does not commence till the last member of a series-1.

○Total mesophase length range (Sm+N) is the highest for series-X and then for series-1 and then lowest of series-Y.

The absence of nematic property in resent novel series is attributed to the relative rigidity offered by a central groups -CO-CH=CH- and -N=N- which links the phenyl rings through at least one multiple bond. But, -CO-CH=CH- is longer than -N=N- which increases molecular polarity, polarizability and the permanent dipole moment across the long molecular axis. The stereochemistry of the units through preserve the linearity of the molecule, but usually result in more and less thermally stable mesophase for the homologues of series-1 and X respectively. From this comparison, it is clear that, due to increased length of uncommon central bridges and common tail group -F, the homologues of series-1 resist the forces of thermal break down well enough to yield smectic phase from very first member of a series-1 and from octyloxy member (C₈) of a series-X. Thus, all the homologues of series-1 and the higher homologues of series-X (from and beyond C₈) do get exhibited smectic mesophase formation earlier (series-1) and later (series-X) relatively at higher and lower temperatures respectively; resulting into high and low thermal stability for smectic. Thus, lamellar packing of molecules facilitated smectic mesophase formation as a consequence of molecular rigidity difference between series-1 and X. Thus, display of only smectic property in absence of nematic property in case of series-1 indicates that, the forces holding the plane of the layers together in the rigid crystal are weaken relatively to the attraction between the molecules within a given layer at solid-mesomorphic transition temperature and the layers may become free to slide and rotate over one another giving smectic phase for series-1 and X. However on heating the smectic phase to a higher temperature, the intermolecular end to end forces between the sides of the molecules weaken to such an extent for the homologues of series-1 and X, that resultant intermolecular cohesive forces do not permit the molecules to slide out of the layers and statistically parallel orientation are not permitted for all homologues of series-1 (C₁ to C₁₆) but permitted for maintenance of nematic phase of homologues C₈, C₁₀ of

series-X and its lower homologues C_1 to C_6 in absence of smectic phase, because, C_{12} , C_{14} and C_{16} are only smectogenic. Thus, only smectic property exhibited by series-1 and partly only nematic (C_1 to C_6), partly only smectic (C_{12} , C_{14} , C_{16}) and partly smectic plus nematic (C_8 , C_{10}) which exhibited by series-X. Absence of lamellar packing of molecules in the crystal lattice of series-Y, in which -F is replaced by -Cl as flexible tail group, the changing molecular flexibility, and keeping rigidity same as series-1 permit only statistically parallel orientational order of molecules (C_5 - C_{14}) and hinders lamellar packing of molecules thought the series-Y. Therefore size of tail group (-Cl > -F) play an important role in mesomorphic behaviors of structurally dissimilar unit of a molecules. Early commencement of the smectic phase in comparison of series-1 and X is related with less noncoplanarity of the molecules. Inequality of the extent of noncoplanarity results into smectogenic mesophase formation and lamellar packing of molecules early or late, depending upon changing unit of comparing molecular structures. Total mesophase length range variations depend upon the resistivity of exposed thermal vibrations from series to series for the same homologue as a consequence of changing molecular rigidity and flexibility which are thermodynamically related with enthalpy change of transition mesomorphic to mesomorphic or Cr-M or M-I (ΔH) of individual homologue of the same series and for the same homologue from series to series. Thus, highest thermal resistivity of series-X and the lowest thermal resistivity of series-Y as well as intermittent thermal resistivity of present series under comparative study follow thermo dynamical concept.

4. CONCLUSIONS

- A novel homologous series consisted of three phenyl rings and two central bridges -COO- and -CO-CH=CH- with para substituted -OR and -F tail groups is fully smectogenic without exhibition of nematic property.

- Replacement of a central group -CO-CH=CH- by -N=N- can induce partly smectic and predominantly nematic property.

- Replacement of tail group -F by -Cl induces only nematic property or eliminates smectic property. Thus, size of tail group of same group of periodic table affects mesomorphic characteristics.

- Liquid crystal properties are very sensitive and susceptible to molecular structure.

- Present investigation is useful in the study of binary system and pharmaceutical treatment as well as agricultural growth.

- LC properties and the degree of mesomorphism are the function of molecular structure as a consequence of molecular rigidity and flexibility.

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