Mesomorphism Molecular Rigidity and Flexibility

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Abstract. A novel homologous series of liquid crystalline (LC) behaviors of Schieff's bases: RO-C₆H₄-CH=CH-COO-C₆H₄-N=CH-C₆H₄-OC₂H₅ have been synthesized and studied with a view to understand and establish the effect of molecular structure on LC properties of a novel substances. The members of a novel series are enantiotropically nematogenic (C₁ to C₁₀) or the some of the homologues (C₁₂ to C₁₈) are smectogenic phase nematogenic. Transition temperatures, textures and melting behaviors observed or determined by an optical polarizing microscopy equipped with a heating stage. Thermometric temperatures are varied between 102 °C and 311 °C. Textures of the nematic phases are threaded or schlieren and that of the smectic phases are of the type A or C. Smectic and nematic thermal stabilities are 122.5 °C and 270.7 °C. Total mesophase lengths vary from 111.0 °C to 194.0 °C. Analytical and spectral data confirms the molecular structures of homologues. Some LC properties of present novel series are compared with the structurally similar known series. Transition curves viz. Cr-M, Sm-N and N-I behaved in normal manner. N-I transition curve exhibited odd-even effect. Thus present novel series is partly smectogenic and fully nematogenic with high mesophase length and higher observed melting type.

1. INTRODUCTION

Scientist and technologists working on liquid crystalline state[1] of a substance with different aims, objects and views in the interest of mankind. The LCD products have to avail at an economical cost [2, 3, 4, 5, 6,]. Therefore irrespective of their type of aims, objects, views and goals, or research scientist or technologist always need the novel LC substances for their continuation of research. Therefore present investigation is planned with a view to understand and establish the effect of molecular structure on LC properties [7, 8, 9, 10,] by synthesizing novel LC substances through unexploited moieties. Thus, study will include the availability of novel alternative LC substances to the researchers working in application part. The novel substances will be characterized and then reported with evaluation of thermometric data and will be interpreted and compared with structurally similar series on the basis of molecular rigidity and flexibility [11, 12, 13, 14,]. Number of homologous series have been reported till the date [15, 16, 17, 18, 19, 20, 21, 22,] but present series will consist of three phenyl rings bonded through -CH=CH-COO- and -N=CH- central bridges as well as left and right -OR and -OC₂H₅ end groups.

2. EXPERIMENTAL

Synthesis

4-n-Alkoxybenzaldehydes were synthesized by refluxing 4-hydroxybenzaldehyde (1 equiv.) with corresponding n-alkyl bromides (1 equiv.) in the presence of potassium carbonate (1 equiv.) and acetone as a solvent [23]. The resulting 4-n-alkoxybenzaldehydes were reacted with malonic acid (1.2 equiv.) in the presence of 1-2 drops piperidine as catalyst and pyridine as solvent to yield corresponding trans 4-n-alkoxy cinnamic acids (A) [24]. (E)-4-((4-ethoxybenzylidene) amino) phenol (B) was prepared by an established method [25] M.P.196°C, Yield- 69.2 %. Coupling of compound A and compound B is done by steglichesterification to yield p-(p'-n-alkoxy cinnamoyloxy)-(p''-ethoxy benzylidene) aniline [26].

The synthesis route to the novel homologous series is under mentioned in scheme-1.

Scheme 1: Synthesis route to the novel homologous series

3. 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), ^1H NMR 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.

Analytical data

Table 1: Elemental analysis for (1) Dodecyloxy (2) Tetradecyloxy (3) Octadecyloxy derivatives

Sr. No.	Molecular formula	Elements %Found				Elements %Calculated			
		C	H	O	N	C	H	O	N
1	C ₃₆ H ₄₅ NO ₄	77.75	8.35	11.50	2.49	77.80	8.16	11.52	2.52
2	C ₃₈ H ₄₉ NO ₄	78.10	8.35	10.45	2.36	78.18	8.46	10.96	2.40
3	C ₄₂ H ₅₇ NO ₄	78.59	8.95	10.00	2.14	78.63	8.98	10.00	2.19

Spectral Data:

¹H NMR in ppm for Propyloxy Derivative

1.05 (t, 3.68H, -CH₃ of -CH₂-CH₃ group), 1.45 (t, 3.26H, -CH₂-CH₃ 1.85 (Sextet 3.26H, -CH₂-CH₂-CH₃), 3.95 (t, 2.44H, -O-CH₂CH₂-), 4.10 (q, 2.29H, -O-CH₂CH₃), 6.50 (d, 1.02H, -CH=CH-), 6.90 (q, 4.13H, middle phenyl ring), 7.2 (4.59H, phenyl ring with ethoxy chain), 7.5 & 7.85 (5H, phenyl ring with alkoxy chain), 8.4(s, 1.00H, -N=CH-) The NMR data are reliable with the molecular structure.

¹H NMR in ppm for Hexyloxy Derivative

0.90 (t, 3.05H, -CH₃ of -CH₂-CH₂-CH₃ group), 1.20 (m, 4.23, -CH₂-CH₂-CH₂-1.3 (m, 5.04H, CH₂-CH₂-CH₂), 1.8 (p, 2.0H, -CH₂-CH₂-CH₂-), 4.00 (t, 2.03H, -O-CH₂CH₂-), 4.10 (q, 2.29H, -O-CH₂CH₃), 6.50(d, 1.02H, -CH=CH-) 6.90 (q, 4.13H, middle phenyl ring), 7.2 (4.59H, phenyl ring with ethoxy chain), 7.5 & 7.85 (5H, phenyl ring with alkoxy chain), 8.4(s, 1.00H, -N=CH-) The NMR data are reliable with the molecular structure.

IR in cm⁻¹ for Decyloxy Derivative

2924.09 (C-H str. of alkan), 2854.65 (C-H str. of (-CH₂)_n group of -OC₁₀H₂₁), 1712.79 (C=O str. of carbonyl carbon of ester group), 1627 (C=O str. of α,β unsaturated ketone), 1604.77 (C=C str. of alkene), 1473.62, 1504.48 and 1573.91 (C=C str. of aromatic ring), 995.27 (C-H bending of alkene disubstituted), 1165.00 (C-O str. of ether linkage), 1242.16 (C-O str. of ester group), 1388.75 (C-H bending of alkene). The IR data are consistent with the molecular structure.

IR in cm⁻¹ for butyloxy Derivative

2954.95 (C-H str. of alkane), 2870.08 (C-H str. of (-CH₂)_n group of -OC₄H₉), 1728.22 (C=O str. of carbonyl carbon of ester group), 1627(C=O str. of α,β unsaturated ketone), 1604.77 (C=C str. of alkene), 1473.62, 1504.48, and 1566.20 (C=C str. of aromatic ring), 972.12 (C-H bending of alkene disubstituted), 1165.00 (C-O str. of ether linkage), 1249.87 (C-O str. of ester group), 1388.75 (C-H bending of alkane). The IR data are consistent with the molecular structure.

Mass spectra of Ethyloxy Derivative

m/z (rel.int%): 415 (M)⁺, 240, 212, 183, 175, 147, 119, 91, 65

Mass spectra of Heptyloxy Derivative

m/z (rel.int%): 485 (M)⁺, 245, 212, 183, 147, 119, 91, 77, 57,

4. RESULTS AND DISCUSSION

4-Hydroxy derivatives of a Schiff's base is a liner lath like molecule is a nonmesomorphic (m.p.202 yield 80 %) but on linking it with trans 4-n-alkoxy cinnamic acids yielded mesomorphic derivatives of ester, with high transition temperatures high degree of mesomorphism. C₁ to C₁₈ homologues are nematogenic but C₁₂ to C₁₈ includes smectogenic character in addition to nematic property. Transition temperatures (table-2) as determined from an optical polarizing microscopy equipped with a heating stage are plotted against the number of carbon atoms present in n-alkyl chain bonded to first phenyl ring through oxygen atom. A phase diagram (figure-1) is obtained showing phase behaviors of series through Cr-M, Sm-N and N-I transition curves formed by linking like or related points. A Cr-M transition curve follows a zigzag path of rising and falling with overall descending tendency as series is ascended and behaved in normal established manner. A Sm-N transition curve initially raises from C₁₂ and continued to rise up to C₁₈ without exhibition of odd-even effect. It extrapolated [27, 28, 29, 30] to C₁₀ homologue to determine its ability to exhibit smectic properties. Extrapolated curve merges to Cr-M point which suggests the inability of C₁₀ to form smectic phase. Thus, it behaved in normal manner. An N-I transition curve continuously descended as series is ascended with overall descending tendency and exhibition of odd-even effect. Thus, it behaved in normal expected manner. The textures of nematic phase are threaded or schlieren and that of smectic phase are fan shape or batonates of the type A or smectic-C. The analytical and spectral data confirmed the molecule structures of novel homologues. Thus, a novel homologous series is partly smectogenic and fully nematogenic whose, mesogenic phase length vary from 111 °C to 194 °C and high ordered melting type.

Table 2: Transition temperatures in °C

Compound No.	n-alkyl chain C _n H _{2n+1} (n)	Smectic	Nematic	Isotropic
1	C ₁	-	159	307
2	C ₂	-	164	311
3	C ₃	-	147	295
4	C ₄	-	138	301
5	C ₅	-	140	290
6	C ₆	-	118	290
7	C ₇	-	128	282
8	C ₈	-	125	271
9	C ₁₀	-	106	256
10	C ₁₂	102	109	238
11	C ₁₄	110	115	232
12	C ₁₆	107	131	227
13	C ₁₁₈	109	135	220

Figure 1: Phase behaviors of series

The N-I transition curve for odd and even members merge into each other at the C₇ member of a series and then odd-even effect disappears from and beyond C₇ for higher homologues for which single transition curve prolongs. N-I transition curves for odd member's occupied lower position as compared to a curve for even member.

High transition temperatures and high degree of mesomorphism is attributed to the three phenyl rings and their linking through $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{N}=\text{CH}-$ central bridges bearing conjugated double bonds which increases molecular rigidity, to a considerable extent. Moreover, the highly polar common $-\text{OC}_2\text{H}_5$ tail end group and left changing $-\text{OR}$ group increases molecular flexibility and consequently end to end intermolecular dispersion forces are also enhanced, which induces nematogenic character through out the novel series under discussion. As molecular size is progressively raised, the strengthening of intermolecular forces of attractions is favorable to build up lamellar packing of molecules form and beyond C₁₂ homologue to induce smectogenic character in addition to nematogenic character. The late commencement of a smectic phase from C₁₂ homologue is attributed to the extent of molecular noncoplanarity which arises from changing $-\text{OR}$ terminal end group which properly first to the extent of noncoplanarity of molecule. The appearance of odd-even effect is attributed to the sequential addition of methylene unit or units to the left n-alkoxy terminal end group. The disappearance of add and even effect from and beyond C₇ homologue is attributed to the coiling, bending, flexing or coupling of the longer n-alkyl chain with the principle axes of a core structure of a molecule. Alternation of transition temperatures are due to odd and even number of carbon atoms in n-alkyl chain of the left n-alkoxy terminal end group. Changing trend in number of methylene unit causes variations in mesomorphic properties from homologue to homologue in the same series. The mesomorphic properties of presently investigated novel series are compared with known homologous series as shown in figure-2.

Figure 2: Structurally similar series

Homologous series 1 and X [31] are identical with respect to three phenyl rings, central bridge $-\text{CH}=\text{CH}-\text{COO}-$ and the part of second central bridge $-\text{N}=\text{CH}-$ linking middle and third phenyl ring as well as left n-alkoxy terminal end group for the same homologue from series to series. Thus, they differ with respect to $-\text{CH}=\text{CH}-$ unit of a second central bridge in part, which contributes more or less to the total molecular rigidity and a tail end group $-\text{OC}_2\text{H}_5$ (series-1) which contributes more or less to the total molecular flexibility. Thus, variations in mesomorphic behaviors between the series under comparative study will depend upon the varying features of series-1 and X. Following table-3 represent some mesomorphic properties of presently investigated series-1 and a series-X chosen for comparative purpose as under.

Table 3: Relative thermal stabilities in $^{\circ}\text{C}$

Series	1	X
Smectic-isotropic Or Smectic-nematic Commencement of smectic phase	122.5 ($\text{C}_{12} - \text{C}_{18}$) C_{12}	118.5 ($\text{C}_{12} - \text{C}_{18}$) C_{12}
Nematic-isotropic commencement of nematic phase	270.7 ($\text{C}_1 - \text{C}_{18}$) C_1	224.77 ($\text{C}_1 - \text{C}_{18}$) C_1
Total mesophase length Range in $^{\circ}\text{C}$	111 to 194 $\text{C}_{18} \quad \text{C}_7$	73 to 111 $\text{C}_{18} \quad \text{C}_1, \text{C}_6$

Looking to the above table,

- Homologous series 1 and X are smectogenic plus nematogenic.
- Smectogenic and/or nematogenic properties commences from C_{12} and C_1 homologue for both series under comparative study.
- Smectogenic and nematogenic properties exhibited between ($\text{C}_{12} - \text{C}_{18}$) and ($\text{C}_1 - \text{C}_{18}$) in case of both series 1 and X under comparison.
- Thermal stabilities for smectic and nematic as well as total mesophase length range are in decreasing order from series 1 to series X.

It is clear from above information that elimination of $-\text{CH}=\text{CH}-$ unit of second central bridge (series - 1) though reduces molecular rigidity and the simultaneously introduction of $-\text{OC}_2\text{H}_5$ polar group at the Para position of third phenyl ring increases molecular flexibility and the end to end attractions. Therefore thermal resistivity of series - 1 for the same homologue from series to series against externally exposed thermal vibrations exceeds the corresponding values of series - X. Thus, corresponding transition temperatures, thermal stability and total mesophase length of presently investigated homologous series - 1 are higher than a series - X chosen for comparison, otherwise commencement of smectic and nematic phase and the homologues between which mesophase exhibition take place and the type of mesophase shown resembled, are exactly same for series 1 and X, their magnitudes differed by decreasing molecular rigidity by the elimination of $-\text{CH}=\text{CH}-$

CH=CH- unit of a central bridge and simultaneously increasing molecular flexibility by introducing –OC₂H₅ highly polar group as tail end group in series – 1. Thus, replacement or displacement or elimination of a polar functional group or groups or a part of group brings a great change in mesogenic properties or behaviours and the degree of mesomorphism.

5. CONCLUSIONS

- Homologous series of present investigation is partly smectogenic and fully nematogenic with high degree of mesomorphism and higher ordered melting type.
- Even a small change in molecular structure causes great change in molecular rigidity and or flexibility and consequently mesogenic properties and their magnitudes alters to a very great extent.
- Mesomorphism and degree of mesomorphism are very sensitive and susceptible to molecular structure.
- Present novel substances may be useful for the manufacture of LC device to be operated at high temperature as temperature indicator in heavy machinery.
- Present study very well supports the conclusions drawn earlier and raises the credibility to the early views.

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