“Mesomorphism Dependence on Molecular Flexibility at Constant Rigidity”

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ABSTRACT

A Novel homologous series of high transition temperature $\text{RO-C}_6\text{H}_4\text{-CH=CH-COO-C}_6\text{H}_4\text{-N=CH-CH=CH-C}_6\text{H}_5$ has been synthesis and studied with a view to understand establish and evaluate the relation between liquid crystal properties and the molecular structure of a substance. A series consists of thirteen homologues. All the homologues are mesogenic. Smectic mesophase commences from C_{12} to C_{18} homologues. Nematic mesophase appears from C_1 to C_{18} homologues. The textures of a nematic phases are of threaded or schlieren and that of the smectic phase are focal conic fan shaped of smectic-A or C type. Transition temperatures and textures were determined by an optical polarizing microscopy equipped with a heating stage. The analytical and spectral data confirms the molecular structures of homologues. Thermal stability for smectic and nematic are 118.5°C and 224.77°C , whose total mesophase length ranger from 73.0°C to 111°C . The liquid crystal properties from homologue to homologue varies in the same series. Some liquid crystal properties of present series are compared with the structurally similar known homologous series. Present novel homologous series is partly smectogenic and fully nematogenic and of higher ordered melting type and high thermal stability.

1. INTRODUCTION

Thermotropic liquid crystalline (LC) material [1] workable at room temperature or high temperature are useful for the manufacture of temperature sensing material in LC devise [2,3,4]. Therefore present investigation was planned with a view to understand and establish the effect of molecular structure on LC behaviors of substance [5,6,7,8,9], by synthesis of homologous series of unexploited moiety. Number of homologous series are reported till the date [10,11,12,13,14,15,16,17,18] but a series with fixed rigidity and varying flexibility of high transitions temperature within working capacity of a hot stage polarizing microscopy for available temperature range up to 250°C to 280°C limit, it was aimed to synthesize a novel series with conjugated double bond structure including three phenyl rings and $-\text{OC}_n\text{H}_{2n+1}$ flexible unit, whose molecular rigidity remain unaltered but molecular flexibility undergo variation from homologue to homologue [19,20,21,22]. The evaluated experimental result will be interpreted and compared with structurally similar known series.

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]. 4-Hydroxy-N-(cinnamylidene) aniline (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 steglich esterification to yield 4-(4'-n-alkoxy cinnamoyloxy)-N-(cinnamylidene) aniline [26].

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

Scheme-1: Synthetic route to the novel series

Where, $R=C_nH_{2n+1}$, $n=1$ to 8, 10, 12, 14, 16 and 18

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), 1HNMR 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) Propyloxy (2) Heptyloxy (3) Dodecyloxy derivatives

Sr. No.	Molecular formula	Elements %Found			Elements %Calculated		
		C	H	O	C	H	O
1	$C_{27}H_{29}NO_3$	78.10	6.99	11.52	78.04	7.03	11.55
2	$C_{30}H_{35}NO_3$	78.79	7.67	10.46	78.74	7.71	10.49
3	$C_{36}H_{47}NO_3$	79.76	8.76	8.89	79.81	8.74	8.86

Spectral Data:**¹H NMR in ppm for Ethyloxy Derivative**

1.42 (t,3H,-CH₃ of -OC₂H₅ group), 4.07 (t,2H,-CH₂-O-), 7.55 (d,1H, -CH=CH-COO-), 7.16 (d,1H, -COO-CH=CH-), 6.49 (t,1H, -N=CH-CH=CH-), 6.92 (d,1H, -N=CH-CH=CH-), 7.83 (d,1H, -N=CH-CH=CH-), 7.38-7.41 (4H, middle phenyl ring), 6.93 & 7.63 (4H, phenyl ring with alkoxy chain), The NMR data are reliable with the molecular structure.

¹H NMR in ppm for Pentyloxy Derivative

0.88 (t,3H,-CH₃ of -OC₅H₁₁ group), 1.27-1.30 (m,4H, CH₃-CH₂-CH₂-CH₂-CH₂-), 1.81 (p,2H,-CH₂-CH₂-O-), 4.00 (t,2H,-CH₂-O-), 7.55 (d,1H, -CH=CH-COO-), 6.47 (d,1H, -COO-CH=CH-), 6.51 (t,1H, -N=CH-CH=CH-), 7.18 (d,1H, -N=CH-CH=CH-), 7.85 (d,1H, -N=CH-CH=CH-), 7.27-7.28 (4H, middle phenyl ring), 6.92 & 8.28 (4H, phenyl ring with alkoxy chain). The NMR data are reliable with the molecular structure.

IR in cm⁻¹ for Butyloxy Derivative

3039 (C-H str. of alkene disubstituted), 2931 & 2870 (C-H str. of (-CH₂)_n group of -OC₄H₉), 1712 (C=O str. of carbonyl carbon of ester group), 1627 (C=O str. of α,β unsaturated ketone), 1597 (C=C str. of alkene), 1504 & 1419 (C=C str. of aromatic ring), 1396 (C-H bending of alkene disubstituted), 1288 (C-O str. of ether linkage), 1141 (C-O str. of ester group), 979 & 833 (C-H bending of alkene). The IR data are consistent with the molecular structure.

IR in cm⁻¹ for Decyloxy Derivative

3058 (C-H str. of alkene disubstituted), 2924 & 2854 (C-H str. of (-CH₂)_n group of -OC₁₀H₂₂), 1720 (C=O str. of carbonyl carbon of ester group), 1627 (C=O str. of α, β unsaturated ketone), 1631 (C=C str. of alkene), 1604, 1504 & 1474 (C=C str. of aromatic ring), 1334 & 1288 (C-H bending of alkene disubstituted), 1249 (C-O str. of ether linkage), 1130 (C-O str. of ester group), 979 & 833 (C-H bending of alkene). The IR data are consistent with the molecular structure.

Mass spectra of Methyloxy Derivative

m/z (rel.int%): 383 (M)⁺, 302, 222, 203, 161, 133, 115, 90, 77

Mass spectra of Heptyloxy Derivative

m/z (rel.int%): 468 (M)⁺, 245, 222, 192, 147, 115, 91, 77

3. RESULTS AND DISCUSSION:-

4-Hydroxy derivative of a schiff's base HO-C₆H₄-N=CH-CH=CH-C₆H₅ on linking with trans 4-n-alkoxy cinnamic acids yields an ester homologous series of high transition temperatures and high thermal stability. All the members of series are nematogenic C₁₂ to C₁₈ homologues exhibited added smectogenic character. Transition temperatures (Table-2) as determined from an optical polarizing microcopy were plotted versus the number of carbon atoms present in n-alkyl chain of the left n-alkoxy terminal end group and a phase diagram obtained, showing phase behaviors of series as shown in figure-1. Cr-M transition curve adopted a zigzag path of rising and falling with overall descending tendency. Sm-N transition curve rises up to last number of homologue without exhibition of odd-even effect. N-I transition curve is continuously descended from C₁ to C₁₈ as series is ascended with exhibition of odd-even effect. Thus, Cr-M, Sm-N, and N-I transition curve of a phase diagram behaved in normal expected manner. Odd- even effect is N-I transition curve ceases to appear from and beyond C₇ homologue and then a single N-I transition curve propagates. Till the last C₁₈ homologue. Analytical and spectral data supported the structure of the molecule. Textures of some selected members were determined by miscibility method. The mesogenic property from homologue to homologue in the same series varies as series is ascended. Thus, presently investigated novel series is partly smectogenic and fully nematogenic with high ordered melting type and high (73.0 to 111.0) mesogenic phase length range. Smectic and nematic thermal stability are 118.5 °C and 224.77 °C, whose smectic mesophase length very from 04 °C to 17.0 °C and nematic mesophase length very from 56 °C to 111 °C.

Table-2. Transition temperatures in °C

Compound No.	n-alkyl chain C_nH_{2n+1} (n)	Sm	N	Isotropic
1	1	-	144	255
2	2	-	167	260
3	3	-	148	245
4	4	-	136	241
5	5	-	138	238
6	6	-	122	233
7	7	-	125	230
8	8	-	118	227
9	10	-	112	213
10	12	105	109	202
11	14	106	113	200
12	16	108	125	195
13	18	110	127	183

Sm- Smectic; N- Nematic

Figure-1. Phase Behavior of Series

Three phenyl rings and two central bridges bearing conjugated double bond constitute molecular rigidity. Only progressive addition of methylene units undergoes variations, which varies molecular flexibility from homologue to homologue in the same series. Thus, variation in mesomorphic properties from homologue to homologue in the same series is attributed to changing molecular flexibility at constant molecular rigidity. The suitable magnitude of anisotropy forces of intermolecular cohesion and closeness as a consequence of favorable fixed molecular rigidity and the varying molecular flexibility from homologue to homologue in the same series due to increasing molecular length by $-CH_2-$ unit causes gradual increase in the permanent dipole moment of the molecules across the long molecular axis, dispersion forces, dipole-dipole interactions etc. which maintains the floating of the molecules in only statistically parallel orientational order under exposed thermal vibration for inducing only nematic phase from very first member C_1 to C_{10}

homologue. However, on increasing the n-alkyl chain length from and beyond C₁₂ homologue, the molecular length and induced molecular polarizability factor of the molecular commence to exhibit and occupy sliding layered arrangement of molecules in addition to an arrangement of molecules floating in statistically parallel orientational order for definite and different ranges of temperatures to induced smectic phase in addition to nematic phase from C₁₂ to C₁₈ homologues depending upon magnitude of their thermal resistivity. Hence, induced polarity and polarizability from and beyond C₁₂ homologue occupied lamellar packing of molecular in their crystal lattices to provide sliding layer molecular arrangement under the influence of exposed thermal variations. Exhibition of odd-even effect by N-I transition curve is attributed to sequentially added methylene unit up to C₇ homologue. Disappearance of odd-even effect from and beyond C₇ homologue is attributed to the coiling or bending or flexing or coupling of longer n-alkyl chain with the main axes of the core structure of a molecule. The changing trend in liquid crystalline behaviors from homologue to homologue in present series is attributed to the changing magnitudes of flexibility as occurred by added methylene unit at the n-alkoxy chain bonded to first phenyl ring through oxygen atom. The liquid crystal properties of present homologous series-1 are compound with the structurally similar known homologue series-X (27) and series-Y (28) as shown in figure-2.

Figure-2. Structurally similar series.

Homologue series-1, X and Y are identical with respect to three phenyl rings, one of the central bridge -CH=CH-COO- and a flexible left n-alkoxy terminally situated end group for the same homologue from series to series. However, they differ from each other by the central groups – N=CH-CH=CH-, -CO-CH=CH- and -CH=CH-COO-CH₂- linking middle phenyl ring and a tail phenyl ring. Therefore molecule rigidity of the series-1, X and Y are changing for the series under comparative study, keeping molecular flexibility same, for the same homologue from series to series, though molecular rigidity of individual series remains unaltered from homologue to homologue in the same series but alter molecular flexibility. The changing trend in same mesogenic properties are mentioned in table-3.

Table-3 indicate that,

- Homologous series-1 of present investigation and series-Y are smectogenic in addition to nematogenic and series-X is only nematogenic.
- Smectic thermal stability of series-1 is lower than series-Y.
- Nematic thermal stability of present series is higher than series-Y and X i.e. nematic thermal stability is in decreasing order from series-1 to series-Y to series-X.
- Smectic mesophase commences late from C₁₂ member of present series-1 but it commences earlier from C₆ member of series-Y, but it does not commences till the last member of series-X.
- Nematic mesophase commences from very first member of a series-1 and from C₃ and C₅ members of a series Y and X.
- Total mesophase length range is the highest for present series-1 and the lowest for series-X and intermediate valued series-Y.

Table -3. Average thermal stabilities in °C

Series →	1	X	Y
Smectic-Isotropic or Smectic-Nematic	118.5 (C ₁₂ -C ₁₈)	-	176.8 (C ₆ -C ₁₄)
Commencement of Smectic mesophase	C ₁₂	-	C ₆
Nematic-Isotropic	224.77 (C ₁ -C ₁₈)	155.4 (C ₅ -C ₁₆)	219.3 (C ₃ -C ₁₆)
Commencement of nematic phase	C ₁	C ₅	C ₃
Total Mesophase length range (Sm+N)	73.0 (C ₁₈) to 111.0 (C _{1&6})	11.0 (C ₁₆) to 48.0 (C ₆)	22.0 (C ₁₆) to 76.0 (C ₄)

The -CH=CH- unit is commonly attached with differing central bridges of series-1, X, and Y under comparative study. The remaining parts of the differing central bridges are -N=CH-COO- and -COO-CH₂- in series-1, X and Y respectively. Therefor observed difference in mesomorphic behaviors among the series-1, X and Y is attributed to the remaining changing part of uncommon central bridges containing common -CH=CH- unit. -N=CH-, -CO- and -COO-CH₂- units have different atomic arrangement in the space bonded to -CH=CH- unit. Therefore, magnitudes of molecular rigidity vary from series to series for the same homologue. Hence, the magnitude of molecular polarity and polarizability, thermal resistivity towards externally exposed thermal vibration, heat content (ΔH), thermal stability for smectic and/or nematic, the molecular geometry and their related extent of molecular non-coplanarity related with early or late commencement of mesophase, thermal resistivity, suitable magnitudes of anisotropy forces of intermolecular cohesion and closeness or the degree of dispersion forces etc. differ for the same homologue from series to series under comparison. Thus, thermal stability for smectic and its commencement differs to considerable extent, i.e. a series-Y with higher smectic thermal stability commence early commencement of smectic phase and vice versa. Similarly, the pattern for nematic thermal stability and commencement of nematic phase is followed.

4. Conclusions

- Ester homologous series of present investigation is partly smectogenic and fully nematogenic with high ordered melting type and high degree of mesomorphism.
- A series with relatively high thermal stability for a mesophase (smectic or nematic) has early commencement of mesophase formation and vice versa.
- The combined effect of the molecular rigidity and flexibility operates a phenomenon of mesomorphism depending on the molecular structure.
- Phenomena of mesomorphism are very sensitive and susceptible to a molecular structure.
- Present thermotropic LC homologues may be useful for the study of binary systems to operate the LC devise workable above 100 °C and below 200 °C as temperature sensing material in heavy industrials projects and machinery. Ester may be useful for the growth of fruits and flowers.
- Present investigation support the conclusions drawn earlier and raises the credibility to the exiting literature of LC; related to molecular structure.

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Reference:

- [1] Naemura, S. (2001). Advance LCD technologies, *Displays*, 22 (1), 1.
- [2] Kim, W.S., Elston, S.J., & Raynes, F.P. (2008). *Display*, 29, 458-463.
- [3] Talwa, I., Dr. Salnana Shahi, Ramteke, V. & Syed, I. (2012). "Liquid crystal Pharmaceutical Application: A Review", "IJPRAS" International journal of Pharmaceutical Research and Allied Science, 1(2), 06-11.
- [4] Hertz, E., Laorel, B., & Faucher, O. (2011). *Nature photon*, 5, 78-79.
- [5] Gray, G. W., & Windsor, P.A. (1974). *Liq. Cryst. Plastic Cryst.*, Ellis Horwood: Chichester, U.K., 1 (4), 103-153.
- [6] Gray, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystal*. Academic Press: London.
- [7] Imrie, C.T. (1999). Liquid crystal dimers, *Structure*, Bond, 95, 149-192.
- [8] Gray, G. W., & Windsor, P. A. (1974). *Liq. Cryst. and Plastic Cryst.*, The role of liquid crystals in life processes by Stewart G.T., 1, 308-326.
- [9] Mrie, C.T. & Luckhurst, G.R. (1998). Liquid Crystal dimers and oligomers: Handbook of liquid crystal, low molecular liquid crystals, 2B, Demus, D., Goodly, J.W., Spiess, H.W. and Vill, V., Wiley-VCH, Weinheim, 801-833.
- [10] Demus, D. (1988). 100 years of Liquid Crystal Chemistry, *Mol. Cryst. Liq. Cryst.*, 165, pp. 45-84.
- [11] Demus, D. (1989). Plenary lectures 100 years of Liquid Crystal Chemistry, Thermotropic liquid crystals with conventional and unconventional molecular structure, *Liq. Cryst.*, 5, pp. 75-110.
- [12] Doshi et al (i) Suthar, D.M. & Doshi, A.V. (2013). *Mol. Cryst. Liq. Cryst.*, 575, 76-83. (ii) Chuhan, H.N. & Doshi, A.V. (2013). *Mol. Cryst. Liq. Cryst.*, 570, 92-100. (iii) Chudhari, R.P., Chuhan, M.L. & Doshi, A.V. (2013). *Mol. Cryst. Liq. Cryst.*, 575, 88-95.
- [13] Suthar, D.M., Doshi, A.A., & Doshi, A.V., (2013). *Mol. Cryst. Liq. Cryst.*, 582, 79-87.
- [14] Travadi, J. J., Bhoya, U. C., & Doshi, A. V. (2012). "Determination of Transition Temperatures of Non-mesomorphism by extrapolation method in Binary Systems", *Mol. Cryst. Liq. Cryst.*, 552, 10-15.
- [15] Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, 552, 104-110.
- [16] Patel, B.H., & Doshi, A. V. (2014). *Mol Cryst. Liq Cryst.*, 605, 23-31.
- [17] Patel, B.H., & Doshi, A. V. (2015). *Mol Cryst. Liq Cryst.*, 607, 78-86.
- [18] Patel, B.H., & Doshi, A. V. (2015). *Mol Cryst. Liq Cryst.*, 608, 38-46.
- [19] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Mc Donnell, D. G. (1993). *Liq. Cryst.*, 15, 123.
- [20] Collings, P.J., & Hird, M. (1998). "Introduction to liquid crystals chemistry and physics", Taylor and Francis Ltd, U.K.
- [21] Marcos, M., Omenat, A., Serrano, J. L. & Ezcurra, A. (1992). *Adv. Mater.*, 4, 285.
- [22] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, 14, 741.
- [23] Aurangzeb Hasan, Asghar Abbas and Muhammed Nadeem Akhtar, (2011). *Molecules*, vol.16, pp. 7789-7802.
- [24] (a) Jordan, Angela, (2007). *Journal of Labelled Compounds and Radiopharmaceuticals*, 50(5-6), pp. 338-341. (b) Yang, Xian-Hui (2012). *Bioorganic & Medicinal Chemistry*, 20(3), pp. 1181-1187.
- [25] Patel, R. B., Patel, V. R., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, 552, 3-9.

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- [26](a) Greene, T. W.; Wuts, P. G. M. (1991). *Protective Groups in Organic Synthesis*, 2nd Ed.; John Wiley and Sons: New York. (b) Kocienski, P. J. *Protecting Groups*; Georg Thieme: Stuttgart, 1994.
- [27] Hauhan, H.N & Doshi, A.V. (2012). *Der Pharma Chemica*, 4(3), 977-983.
- [28] Patel, B.H., & Doshi, A. V. (2014). *Mol Cryst. Liq cryst.*, 605, 42-51.

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