“Study of the Effects of lateral Substitution (Bromo) on Mesomorphic Behaviours of Chalconyl Ester Derivatives”

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Abstract: Novel homologous series: RO-C₆H₄-COO-C₆H₃-Br-CO-CH=CH-C₆H₄-OC₁₈H₃ (n) (ortho bromo to -COO-) is synthesized and studied with a view to understand and establish the relation between mesomorphic properties and the molecular structure with reference to lateral substitution of bromine

-Br at middle phenyl ring. Chalconyl homologous series consists of thirteen homologues between (C₁ to C₁₈). Nematogenic mesomorphism commences from C₅ homologue and continues up to C₁₈ homologue in enantiotropic manner. Transition and melting points were determined by an optical polarizing microscopy (POM) equipped with a heating stage. Textures of nematic phase are threaded or schlieren. Transition curve Cr-N/I behaved in normal manner. N-I transition curve exhibited odd-even effect up to C₈ homologue. It (N-I) rises and fall with negligible deviations from its normal descending tendency which appears in case of homologues C₁₀ to C₁₈. Thermal stability for nematic is 142.89 °C and the mesophase lengths vary minimum 8.0 °C to maximum 26.0 °C at the C₇ and C₈ homologue respectively. Liquid Crystal properties of present series are evaluated and compared with structurally analogous series and relative group efficiency order derived. Thus, present series is predominantly nematogenic with absence of Smectic property. Analytical and spectral data supported molecular of homologues.

Introduction:

Thermotropic liquid crystal (LC) of chalconyl ester with long n- alkoxy chain as tail end group [1] have been proposed to synthesize and study, because of their dual importance to act as LC material and potentiality as to act as anti- malarial, anti- cancer, anti- bacterial, anti- oxidant etc.[2,3,4,5,6,7]. Present proposed investigation is planned with a view to understand and establish the effect of molecular structure on thermo tropic LC properties [8,9,10,11] of laterally substituted – Br group at the middle phenyl ring as a consequence of molecular rigidity and flexibility [12,13,14,15]. Number of chalconyl ester homologous series have been reported till the date [16,17,18,19,20,21,22,23]. The properties of proposed series of novel chalconyl derivatives will be compared with other known series and the group efficiency order will be derived. Novel substance may be useful for the scientists and technologist who are working on LC state with different aims and objects other than present object to extend or to continue their research in the benefit of mankind and societies.

Experimental:

Synthesis:

4-Hydroxy benzoic acid was alkylated using suitable alkylating agent (R-X) to convert it into 4-n-alkoxy benzoic acids (A) by modified method of Dave and Vora [24], α -3- Bromo -4 Hydroxy benzoyl β -4 - n-octadecyloxy phenyl ethylene (B) was prepared by usual established method [25]. 4-n-Alkoxy benzoic acids and α -3- Bromo -4 Hydroxy benzoyl β -4 - n-Octadecyloxy phenyl

ethylene were condensed in 1, 3-dicyclohexylcarbodiimide (DCC), 4-dimethyl amino pyridine (DMAP) and CH_2Cl_2 [26] to obtain α -4-(4'-n-Alkoxy benzoyloxy) benzoyl- β -4''-n-Octadecyloxy 3-bromo phenyl phenyl ethylene. Final products were 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 series

Characterization:

Representative homologues of a series were characterized by elemental analysis, Infra red spectroscopy, ^1H NMR spectra, IR spectra were recorded by Perkin-Elmer spectrum GX, ^1H NMR spectra were recorded on Bruker using CDCl_3 as solvent. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyser (Table-1). Transition temperature and LC properties (Textures) were determined using an optical polarising microscopy equipped with heating stage. Textures of nematic phase determined by miscibility method (Table-2) thermodynamic quantities enthalpy (ΔH) and entropy ($\Delta S = \Delta H/T$) are qualitatively discussed.

Analytical data:**Table 1: Elemental analysis for Ethoxy, Pentyloxy, Decyloxy, Dodecyloxy derivatives.**

Sr. No.	Molecular formula	Elements found %			Elements calculated %		
		C	H	Br	C	H	Br
1	C ₂	70.16	7.8	11.12	70.07	7.6	11.12
2	C ₅	70.90	8.10	10.59	70.95	8.01	10.51
3	C ₁₀	72.00	8.60	9.8	72.20	8.5	9.6
4	C ₁₂	72.60	8.5	9.20	72.64	8.7	9.31

IR Spectra (KBr) in cm⁻¹ for Octyloxy, Tetra decyloxy Derivatives:

Octyloxy: 514 (-CH-Br str), 763 Poly methylene (-CH₂-)n of -OC₈H₁₇, 831(-C-H- def. m di-substituted-Para), 778 Polymethylene (-CH₂-) of -OC₁₈H₃₇, 985 (-C-H- def. hydrocarbon), 1024 and 1110(-C-O-) Str, 1253 and 1301 and 1423, 1485 (-C-O str in -(CH₂)n chain), 1508 (-C-H- def. in CH₂), 1575 (-C=C-)str, 1602 (-C=O group), 1743 (-COO- ester group), 2852 and 2923 and 3064 (-C-H str in CH₃).

Tetradecyloxy: 518 and 675 (-CH-Br str), 722 and 762 Polymethylene (-CH₂-)n of -OC₁₄H₂₉, 835 and 850(-C-H- def. m di-substituted-Para) Benzene, 989 (-C-H- def. hydrocarbon), 1027, 1074, 1114, 1172 (-C-O-) Str, of C₁₈H₃₇, 1384 and 1321 and 1303, 1257 (-C-O str in -(CH₂)n chain, 1481 (-C-H- def. in CH₂), 1512 and 1581 (-C=C-)str, 1606 and 1616 (-C=O group), 1730 (-COO- ester group), 2858 and 2927 and 3033 (-C-H str in CH₃).

¹H NMR spectra in CDCl₃ in δ ppm for Pentyloxy & Hexyloxy Derivative:

Pentyloxy: 0.90(t, -CH₃ of -C₅H₁₁), 1.31-1.76(m, n-poly methylene groups of -OC₅H₁₁), 1.55-1.76(m, n-poly methylene groups of -OC₁₈H₃₇), 4.10-4.20(s, -OCH₂-CH₂-of -OC₁₈H₃₇), 4.0-4.2(s, -OCH₂-CH₂-of -OC₅H₁₁), 7.58 and 8.20(s, -CO-CH=CH), 8.8-8.9 (s, p-di substituted phenyl ring).

Hexyloxy: 0.88(t, -CH₃ of -C₆H₁₃), 1.3-1.43(m, n-poly methylene groups of -OC₁₈H₃₇), 1.5-1.7(m, n-poly methylene groups of -OC₆H₁₃), 4.1(s, -OCH₂-CH₂-of -OC₆H₁₃), 4.1-4.4(s, -OCH₂-CH₂-of -OC₁₈H₃₇), 6.94-7.15 (s, substituted benzene), 6.9-7.2(s, -CO-CH=CH), 7.5-7.7(s, p-substituted phenyl ring).

Table 2: Textures of Nematic phase by miscibility method for C₇, C₁₀, C₁₆, C₁₈.

Sr. No.	Homologue	Texture
1	C ₇	Threaded
2	C ₁₀	Threaded
3	C ₁₆	Schlieren
4	C ₁₈	Schlieren

Results and Discussion:

α-3- Bromo -4- hydroxyl benzoyl -β- 4' n- octadecyloxy phenyl ethylene (m.p- 85 °C, yield-74 %) is a nonmesomorphic component, which on condensation with dimaric n- alkoxy benzoic acid yielded mesomorphic homologues from C₅ to C₁₈ as enantiotropically nematogenic without exhibition of smectogenic property. The transition temperatures as determined using an optical polarizing microscopy equipped with a heating stage of mesogenic homologues are relatively lower than the corresponding n- alkoxy acids. Transition curves Cr-N/I and N-I showing the phase behaviours of novel series in a phase diagram (figure.1) are obtained by linking points plotted for the number of carbon atoms present in n- alkyl 'R' chain of left -OR group versus the transition temperatures as recorded in table - 3

Table 3: Transition Temperatures in °C for Homologous series:

Homologous series: α -4-(4'-n-Alkoxy benzoyloxy) benzoyl- β -4'' -n- octadecyloxy 3- bromo phenyl ethylene.

Compound No	n-alkyl chain C_nH_{2n+1}	Transition Temperatures in(°C)		
		Smectic	Nematic	Isotropic
1	C_1	-	-	170.0
2	C_2	-	-	185.0
3	C_3	-	-	158.0
4	C_4	-	-	152.0
5	C_5	-	118.0	138.0
6	C_6	-	130.0	148.0
7	C_7	-	132.0	140.0
8	C_8	-	128.0	138.0
9	C_{10}	-	131.0	148.0
10	C_{12}	-	128.0	143.0
11	C_{14}	-	134.0	152.0
12	C_{16}	-	140.0	155.0
13	C_{18}	-	98.0	124.0

Homologous series: α -4-(4'-n-Alkoxy benzoyloxy) benzoyl- β -4'' -n- octadecyloxy 3- bromo phenyl ethylene.

Figure 1: Phase behavior of the series

The Cr-N/I transition curve adopted a zig-zag path of rising and falling and finally descended in normal manner. N-I transition curve exhibited odd even effect from C₅ to C₈ homologue with merging of N-I transition curves at C₈ homologue. Then N-I transition curve negligibly rises and falls with overall normal descending tendency of negligible rising abnormality transition curves for odd and even members are extrapolated to C₄ and C₃ homologues to highlight the odd-even effect and to predict their nematogenic transition temperatures [27,28,29,30]. N-I transition curve prolong as a single transition curve from and beyond merging of transition curve showing odd – even effect upto C₈ homologue for longer n- alkyl chain (R') of –OR. Thermal stability for nematic is 142.89 °C and mesomorphase length lower to upper varies from 8.0 to 26.0 °C at the C₇ and C₁₈ homologues. It is middle order melting type series. Textures of a nematic phase are threaded or schlieren. Mesomorphic properties from homologue to homologue varies with varying number of carbon atoms in n- alkyl chain 'R' of –OR keeping – OC₁₈H₃₇ (n) tail end group unchanged. Mesogenic behaviors of present series are compared with structurally analogous series to derive group efficiency order as depended on molecular structure as a consequence of resulted molecular rigidity and flexibility. The absence of mesomorphic behaviours of C₁ to C₄ homologues is due to their high crystallizing tendency which arises from low magnitude of dispersion forces and the dipole dipole interaction, which causes unsuitable magnitude of anisotropic forces of intermolecular cohesion and closeness. Laterally substituted polarizable –Br group, which increases intermolecular distance and decrease intermolecular attractive forces but at the same time the molecular polarizability increases intermolecular cohesion, Therefore, two opposing forces which are operated for the same reason of lateral substitution. Thus, resultant effect which will be operative of suitable

magnitudes will depend upon the predominantly of the factor (closeness or polarizability) operating in opposite direction for the same reason which facilitated nematic phase. The exhibition of nematogenic mesophase formation by C_5 to C_{18} homologues is attributed to the intermolecular suitable forces of end to end and lateral cohesion and closeness as a consequence of favorable molecular rigidity and flexibility as depended molecular structure, which facilitated and maintained floating of molecules of C_5 to C_{18} homologues on the surface as statistically parallel orientational order for some degree of temperature difference, causing appearance of nematic phase. In exhibition of smectic mesophase formation is attributed to the absence of sliding layer molecular arrangement in floated condition under exposed thermal vibrations due to unsuitable magnitude of intermolecular lateral attraction irrespective of presence of laterally substituted $-Br$ functional group. The lowering of transition temperature of novel homologues as compared to corresponding n - alkoxy acids is attributed to breaking of hydrogen bonding through esterification process. The exhibition of odd-even effect is due to the sequentially added methylene unit or units at the n - alkoxy ($-OR$) group. The diminishing of odd-even effect from and beyond C_8 homologue is attributed to the coiling or bending or flexing or coupling of longer n - alkyl chain with major axis of the core structure of a molecule of higher homologues. The negligible deviation of N-I transition curve of present series is attributed to unusual status and unusual unexpected behaviours of n - alkyl chain of 'R' and $-C_{18}H_{37}$ end under exposed thermal vibrations. The variation in mesogenic properties from homologue to homologue in the same series is attributed to changing number of methylene units, which causes alteration in molecular length, length to breadth ratio, permanent dipole moment across the long molecular axis magnitude of intermolecular forces of cohesion and closeness causing variation in magnitude of dispersion forces as a result of effective molecular rigidity and flexibility depending on molecular structure, its size and geometrical shape and the ratio of the polarity to polarizability.

The mesogenic behaviors of present novel series are compared with the structurally analogous series-X [31] as mention below in figure.2.

Figure:2 Structurally Similar Series

Homologous series-1 of present investigation and a homologous series- X selected for comparative study are identical with respect to three phenyl rings, two central bridge $-COO-$ and $-CO-CH=CH-$ left and right flexible terminal end group, but they differ with respect to laterally substituted $-Br$ group which is present in series- 1 but is absent in series-X. Thus, the combined effect of molecular rigidity and flexibility for the same homologue from series to series and from homologue to homologue in the same series differs in magnitude. Thus, the magnitudes of mesogenic properties and the degree of mesomorphism depend upon the differing features of the molecular structures of series under comparison. Following table-4 represents the some differing features like type of mesophase exhibited commencement of mesophase, thermal stability, total mesophase lengths (lower and upper) etc as recorded below.

Table 4: Relative thermal stability in °C

Series →	Series -1	Series-X
Sm-I or Sm-N Commencement of Smectic phase	-	-
Nematic-isotropic (N-I) Commencement of nematic phase	142.89 (C ₅ - C ₁₈) C ₅	122.0 (C ₅ -C ₁₈) C ₅
Total mesomorphism in °C	08.0 to 26.0 C ₇ C ₁₈	7.0 to 38.0 C ₇ C ₁₂

- Homologous series 1 and X under comparative study are enantiotropically nematogenic without exhibition of smectic property.
- Thermal stability for nematic is raised by 20.89 units by introduction of –Br lateral group at ortho position to the –COO- central bridge and meta position to –CO-CH=CH- group.
- The nematogenic mesophase identically commences from C₅ homologue for both the series-1 and X under comparison.
- A total mesophase length of present series-1 is relatively lower than a series-X.

The exhibition of only nematic phase by the both series-1 and X is attributed to only by end to end attraction of suitable magnitudes require for an environmental molecular arrangement under floating condition under the influence of exposed thermal vibration. The laterally substituted –Br group at the middle phenyl ring which should have raised intermolecular lateral attractions by operating polarizability factor more than the polarizability to be played by linear molecule of series-X. However it seems that, the reduction or decrease in intermolecular attraction by the increasing with of molecules of series-1 is compensated through acting of polarizability factor by increasing molecular width of series-1, due to laterally substituted –Br group. Thus, the magnitudes of intermolecular attractions by polarizable nature enhanced in case of series-1 to such an extent that it raises thermal stability for nematic by 20.89 unit as compared to the corresponding nematic thermal stability of series-X, but at the same time, the resistivity towards exposed thermal vibration undergo reduction from 7.0 to 38.0 of series-X to 8.0 to 26.0 °C of series-1 under comparative study. The commencement of nematic phase which take place in series-1 and X in equal manner i.e. mesophase commence from C₅ homologue in both series which suggest that, irrespective –Br lateral substitution, the molecular co planarity or non co –planarity are almost equal. i.e. presence of Bromo like lateral substitution does could not attain the extent of molecular noncoplanarity. Thus, the combined effect of molecular rigidity and flexibility in case of present series-1, is sufficient to facilitate nematic phase from C₅ to C₁₈ but the intermolecular forces of attraction are insufficient to cause lamellar packing of molecules in crystal lattice of series -1, which fails to exhibit smectogenic character. Hence, the thermal stability is raised but the upper mesophase length of series-1 is reduced, keeping commencement of mesophase unaltered from C₅ homologue in case of series-1 and X.

Conclusions:

From above result and discussion we concluded that the novel chalconyl based series only nematogenic in nature with absence of Smectogenic property. The thermal stability of series -1 is higher than the series –X. the lateral bromo group increasing the nematogenic properties but in novel series no homologue exist smectic properties. Mesomorphic properties of series -1 is less than the series –X.

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