Study of mesomorphism changing on terminal side chain with different Thioalkyl group

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Keywords: Mesomorphism, Liquid crystal, Smectic, Nematic, Thermotropic

ABSTRACT: A novel mesomorphic series is RS-C₆H₄-COO-C₆H₄-CO-CH=CH-C₆H₄-OC₁₈H₃₇(n) (para) of chalconyl ester play double role thermotropic as well as lyotropically bioactive is synthesized and studied with a view to understand and establish the effect on mesomorphism when changing on left thioalkyl chain. the relation between mesomorphism and molecular structure on the basis of molecular rigidity and flex Novel series consists of thirteen homologues of which four homologues (C₁ to C₃) are non liquid crystal and the rest of the homologues (C₅ to C₁₈) are thermotropically enantiotropic nematic absences with smectic property. Thermometric transition temperatures and textures of nematogenic phase are determined by an optical polarizing microscopy equipped with a heating stage (POM). Textures of nematic phase schilieren and threaded type. Cr-N/I and N-I transition curves behaves in as manner with negligible abnormality at C₁₈ homologue in phase diagram of a series. Analytical and spectral data conforms the molecular structure of homologues. Thermal stability for nematic is 123.2 °C whose degree of mesomorphism vary minimum from 4.0°C to a maximum of 24.0 °C, and hence novel series is of middle ordered melting type.

1. INTRODUCTION

The study of LC [1] property of a substance have played an important role from the point of view of utility in LC devices and pharmaceutical preparations. Also liquid crystal is most important field in material science. it is well known that the mesomorphic properties of liquid crystal can largely be influenced by the structural variation in terminal substituents likely R, OR, Thioalkyl groups. (2-6) Hence, present investigation is planned to synthesize novel chalconyl derivatives through novel homologous series and to characterize homologues by thermometric, elemental analysis, IR and H¹NMR spectra, LC properties like thermal stability, degree of mesomorphism etc. with a view to understand the effect of molecular structure on LC properties [7,8,9,10]. Normally chalconyl moiety exist as nonmesomorphic properties but when its coupled with alkoxy, Thioalkyl, alkoxy of acid or acid chloride it's become as mesomorphic derivative. Chalcone basis liquid crystal material have been reported as biological active substance its giving a antimicrobial antifungal activity However our present investigation will be limited to novel thermotropic LC materials only. This thermotropic LCs consisted of 3 phenyl rings linked with thio central bridge – COO-, -CO-CH=CH- and two flexible terminal end groups viz. varying –C_nH_(2n+1) S- and their Liquid crystal behaviours are discussed and interpreted in terms of molecular rigidity and flexibility. [11,12,13,14]

2. EXPERIMENTAL

General:

IR spectra were recorded as KBr pellets on a Buck-M500 spectrometer. ^1H NMR were recorder on Gemini-200 using CDCl_3 as a solvent and TMS(Tetra methyl Silane) as internal standard. Elemental analysis was performed on Euro Vectro EA 3000A. The phase transitions were observed with polarized optical microscope (POM) equipped with hot plate. Textures of nematic phase determined by miscibility method, thermodynamic quantities enthalpy (ΔH) and entropy ($\Delta S = \Delta H/T$) are qualitatively discussed.

Synthesis of n-thio alkyl benzoic acid:

Taking 15mmol of Marcapto benzoic acid in ethanol, 17.5 mmol alkyl helide in an. K_2CO_3 as base reflux this mixture at 100-130 °C 24 hrs. than cool the mixture add 20-25 ml water followed by ether evaporated the product is Crystalized in ethanol.

Synthesis of chalconyl moiety:

α -4-Hydroxy benzoyl β -4 -octadecyloxy phenyl ethylene (B) was prepared by usual established method [15].

Coupling of A&B:

Solution of 4n-thio alkyl benzoic acid 10 mmol, 10mmol Chalcone, DCC(55mmol), in 50 ml dry DCM along with solid DMAP as catalyst (2.5mmol) were magnetically stirred at room temperature for 12 hrs. the product was filtered out remove the solvent the crude was recrystallized from hot ethanol untill constant transition temperature were observed.[16]

Reaction scheme:

Scheme: 1 Synthetic route to the series

Analytical data:**Table: 1 Elemental analysis for Pentoxy, Decyloxy, Tetradecyloxy, Hexadecyloxy derivatives.**

Sr. No.	Molecular formula	Elements found %			Elements calculated %		
		C	H	S	C	H	S
1	C ₅	77.20	8.88	4.6	77.36	8.80	4.5
2	C ₁₀	78.50	9.25	4.10	78.12	9.3	4.16
3	C ₁₄	78.69	9.84	3.70	78.64	9.7	3.88
4	C ₁₆	78.50	9.80	3.50	78.87	9.85	3.75

IR Spectra (KBr) in cm⁻¹ for Heptoxy, Octadecyloxy Derivatives:

Heptoxy: 718 Polymethylene (-CH₂)_n of -OC₇H₁₅, 835(-C-H- def. m di-substituted-Para), 788 Polymethylene (-CH₂-) of -OC₁₈H₃₇, 947 (-C-H- def. hydrocarbon), 1050 and 1010(-C-O-) Str, 1365 and 1303 and 1255, 1200 (-C-O str in -(CH₂)_n chain), 1427 and 1465 (-C-H- def. in CH₂)1530 (-C=C-)str, 1610 and 1670 (-C=O group), 1730 (-COO- ester group), 2865 and 2935 (-C-H str in CH₃).

Octadecyloxy: 770 Polymethylene (-CH₂)_n of -OC₁₈H₃₇, 845(-C-H- def. m di-substituted-Para), 915, 925(CH=CH-Group), 948 (-C-H- def. hydrocarbon), 1057 (-C-O-) Str, 1365 and 1310 and 1249, 1165 (-C-O str in -(CH₂)_n chain, 1388 and 1360 (-C-H- def. in CH₂), 1530 (-C=C-)str, 1635 and 1681 (-C=O group), 1735 (-COO- ester group), 2854 and 2916 (-C-H str in CH₃).

¹H NMR spectra in CDCl₃ in δ ppm for Ethoxy & Hexyl Derivative:

Ethoxy: 0.88(t, -CH₃ of -C₁₈H₃₇), 1.27(q, CH₃ of C₂H₅), 1.31-1.76(m, n-poly methylene groups of -OC₁₈H₃₇), 2.84(s, -CH₂ group in C₂H₅), 3.8-4.0 (s, -OCH₂-CH₂- of -OC₁₈H₃₇), 6.31-6.50, (s, -CH=CH-group), 7.5-7.9(s, -CO-CH=CH), 8.8-8.9 (s, p-di substituted phenyl ring).

Hexyl: 0.83(t, -CH₃ of -C₁₈H₃₇), 0.88(t, -CH₃ of -OC₆H₁₃), 1.29-1.60 (m, n-poly methylene groups of thio alkyl chain -SC₆H₁₃), 2.94(s -SC₆H₁₃ group) 3.9(s, -OCH₂-CH₂- of OC₆H₁₃), 4.1-4.4(s, -OCH₂-CH₂- of OC₁₈H₃₇), 6.21-6.30(s CH=CH-), 6.9-7.2(s, -CO-CH=CH), 7.5-7.7(s, p-substituted phenyl ring).

Texture determination by miscibility method :

C₁₀, C₅ and C₇.... Thread Nematic

C₁₆ and C₁₈ Schlieren Nematic.

3. RESULTS AND DISCUSSION

The novel Homologous series of present investigation is formed by The condensation of n-thio alkyl chain and the α -4-Hydroxy benzoyl β -4'-octadecyloxy phenyl ethylene (M.P 74°C, Yield 72%). The transition temperatures of novel chalcony ester derivatives of a series are nematogenic LC from and beyond C₃ homologue (C₄ to C₁₈) with absence of smectic property. C₁ to C₃ homologue are nonmesomorphic. Transition temperatures (table-2) as determined from an optical polarizing microscopy were plotted versus the number of carbon atoms present in n-thioalkyl chain bonded to first phenyl ring through sulfur atom (-SR). A phase diagram is obtained from Cr-N/I and N-I transition curves by linking like or related transition points. Cr-N/I transition curve adopted zigzag path of rising and falling with descending tendency and behave in normal manner.

Table: 2 Transition Temperatures in °C for Homologous series:

Homologous series: α -4-(4'-n-thioalkoxy benzoyloxy) benzoyl- β -4''-octadecyloxyphenyl ethylenes

Compound No.	n-Alkyl chain $\text{C}_n\text{H}_{2n+1}$	Transition Temperatures in(°C)		
		Smectic	Nematic	Isotropic
1	C_1	-	-	139.0
2	C_2	-	-	135.0
3	C_3	-	-	128.0
4	C_4	-	126.0	138.0
5	C_5	-	120.0	124.0
6	C_6	-	110.0	126.0
7	C_7	-	114.0	120.0
8	C_8	-	111.0	120.0
9	C_{10}	-	105.0	120.0
10	C_{12}	-	102.0	118.0
11	C_{14}	-	100.0	120.0
12	C_{16}	-	108.0	122.0
13	C_{18}	-	100.0	124.0

α -4-(4'-n-thioalkoxy benzoyloxy) benzoyl- β -4''-octadecyloxyphenyl ethylenes

Figure: 1 Phase behavior of the series

N-I transition curves for odd (C_5 , C_7) and even ($C_6 \dots C_8$) members are matching into each other at the C_{10} homologue and then gradually ascended up to C_{18} homologue as a single transition curve from and beyond C_{10} homologue. Thus, it exhibits odd-even effect and deviated negligibly from and beyond C_{12} homologue from normal descending tendency. Textures of nematogenic homologues are threaded or schlieren as determined by miscibility method. Analytical and spectral data confirms the molecular structures of homologues. Odd member's N-I transition curve occupied lower position as compared to even member's transition curve. The mesogenic (LC) properties from homologue to homologue cause variations keeping $-OC_{18}H_{37}$ tail end constant and changing $-SR$ tail group at the left hand side. Thermal stability for nematic phase is 123.2°C , with low degree of mesomorphism, which varied from 4.0°C to 24.0°C . Disappearance of dimerization of aromatic acids and the lowering of transition temperatures of resultant chalconyl esters derivatives are attributed to the breaking of hydrogen bonding between acid molecules by way of esterification process. The inhibition of any sort of mesophase formation by C_1 to C_3 homologues is attributed to their inability to resist exposed thermal vibration due to unsuitable magnitudes of intermolecular anisotropic end to end or/and lateral forces of cohesion and closeness as emerging from low dispersion forces and low dipole-dipole interactions, which induces high crystallizing tendency in a substance to transform into isotropic liquid sharply from crystalline state on heating and on cooling the same from isotropic liquid to directly solid crystalline state without passing through an intermediate state of existence called as LC state. However, the molecules of C_4 to C_{18} homologues

disalign at an angle less than ninety degree as a consequence of favorable molecular flexibility, which resisted exposed thermal vibrations due to suitable magnitudes of anisotropic end to end forces of intermolecular attractions, and causes to arrange the molecules in statistically parallel orientational order under floated condition on surface, depending upon enthalpy (ΔH) value of LC state within definite range of temperature, called as mesophase length of a homologue. Thus, nematogenic mesophase formation occurs excluding the possibility of smectic mesophase formation which is supposed to form prior to nematic mesophase occurrence. however due to insufficient magnitude of intermolecular lateral forces of attractions as required for lamellar packing of molecules in their crystal lattices of rigid crystalline state is deficient and hence, smectogenic mesophase formation is missing through out to series under dictions Odd-even effect observed for N-I transition curve of phase diagram is attributed to the odd and even number of carbon atoms present in n-thioalkyl (-SR) chain of the left n-thio alkoxy group. The disappearance of odd-even effect from and beyond C₁₀ homologue of the longer n-alkyl chain is attributed to the unusual status of the an alkyl chain, which may coil or bend or flex or couple to lie with the major axes of the core structure of molecules, resulting into end to end attraction and intermolecular distance almost equivalent. Hence a single transition curve appears with diminishing tendency of odd-even effect. The changing trend in mesomorphic properties from homologue to homologue in same series is attributed to the seqrrantial addition of methylene units at the left n-alkoxy terminal (-OR) end groups which alters molecular length, molecular polarity and polarizability, molecular flexibility, permanent dipole moment across the long molecular axis, dipole dipole interaction, magnitude of intermolecular dispersion forces of cohesion and closness etc. including uncertainty in the status of an thioalkyl chain(-SR) of -SR group. The LC properties of present novel series are compared with structurally analogous series as mentioned below in figure-2.

Figure:2 Structurally Similar Series

The novel chalconyl based Homologous series 1, X and Y are identical with respect to three phenyl rings, central -CO-CH=CH and left n-thio alkoxy terminal end group for the same homologue from series to series. Homologous series 1 and X, are identical with respect to first central bridge -COO- and second central bridge with -CO-CH=CH- group when the series Y differ with respect to -CH=CH-COO- and the -CO-CH=CH- group. In this 3 series the series 1 and X only the difference in left side thio alkyl chain and series 1 and Y differ from first central linkage that is -CH=CH-COO- group and thioalkyl and alkyl group(-RS & -OR) group. all above other, respect except right side flexible tail end group -OC₁₈H₃₇, which differs in molecular flexibility for the same homologue from series to series. Homologous series 1 and X are identical in all respect for the same homologue except a central bridge linking first and middle phenyl rings viz. -COO- and -CO-CH=CH-. Here we study the effect on mesomorphic behaviour when oxygen replaced by sulfur atom.

The appearance of this phenomenon in the mesomorphic compound depend on the molecular structure. Increased in thio alkyl chain lengths should have most common two effect.

1. Increasing the intermolecular attractions between the side of the molecule, because of the polarizability of each added methylene groups.
2. Decreases the intermolecular terminal attraction because of increasing separation of the molecules containing the dipolar units.

Thus, the difference of LC properties and the degree of mesomorphism can be correlated with differing features and differing magnitudes of molecular rigidity and/or flexible of molecular structure among the series 1, X and Y respectively for the same homologue from series to series and homologue to homologue in the same series. Some thermotropic LC properties are mentioned below for the comparative study in table-3

Table: 3 Relative thermal stability in °C

Series	1	X	Y
Sm-I or Sm--N Commencement of Smectic phase	-	-	-
Nematic-isotropic (N-I) Commencement of nematic phase	123.2 (C ₄ -C ₁₈) C ₄	122.0 (C ₅ -C ₁₈) C ₅	121.88 (C ₅ -C ₁₈) C ₅
Total degree of mesomorphism in °C Ci to Cp	04.0 to 24.0 C ₈ C ₁₄	7.0 to 38.0 C ₇ C ₁₂	04.0 to 34.0 C ₁₀ C ₁₆

Table-3 indicates that,

- Homologous series 1, X and Y under comparison are nematogenic only with absence of smectogenic properties from series to series.
- Mesomorphic properties (Nematic) commences from C₃ homologue for series1 and X&Y where as, it commence from C₅ homologue of a series-X &Y.
- Thermal stability of series-1 and X& Y are almost nearer to each other.
- Degree of mesomorphism of series 1 and X are almost equivalent but it is lower for a series-Y than series 1 and X.

Exhibition of only nematic property in case of series.1 and X and Y is depended upon the difference of polarities of flexible tail end group –SR and –OR and –OC₁₈H₃₇. Hence magnitude of flexibility difference occurred due to n-thio alkoxy (-RS where R=C₁₈H₃₇) tail end group for the same homologue from series-1 to series-X which reduces nematic thermal stability and the degree of mesomorphism. The extent of molecular noncoplanarity difference as occurred due to unusual status of n-thioalkyl chain of tail end group –OC₁₈H₃₇ have operated early (C₅) commencement of series-1 and X respectively. Now on comparing the molecular structure of series-1 and X in which the central bridge linking first and middle phenyl ring –COO- only differs keeping rest of the molecular parts including both terminal tail end groups(-SR and –OC₁₈H₃₇) unaltered. Therefore, left side chain -SR of series-1 is replaced by –OR- of series-X&Y, which contributes partly to the difference of molecular rigidity. The negligible difference of thermal stability (123.2& 122.0°C) is also attributed to the negligible difference of molecular rigidity due to presence of common left group -SR which minimize the difference of effectivity of lengths between –SR- and –RO- group as a consequence of minor difference molecular rigidity, due to replacement of central ester group. In all these homologous series under comparative study, the molecules of mesogenic homologues exhibited nematogenic mesophase formation is attributed to the disalignment of molecules at an angle less than ninety degree which resists exposed thermal vibrations and arrange molecules to float on the surface with statistically parallel orientational order, But the angle of molecular disalignment with floating surface which vary from series to series and homologue to homologue as a consequence of the magnitudes of changing molecular rigidity and/or flexibility of different magnitudes which affects to the molecular resistivity toward exposed thermal vibrations. Thus, nematogenic property vary for the same homologue from series to series and from homologue to

homologue in the same series. The negligible deviation from normal descending behaviours of N-I transition curve for a homologue, bearing same polar group present at the both terminal end groups is attributed to the vector sum of polarities of all bonds in equipolar unique group which is equal in magnitudes but opposite in directions which nullifies the effect of each other. This factor affects flexibility of a homologue and induces more or less or negligible deviation in N-I or M-I transition curve.

4. CONCLUSIONS

New chalconyl derivatives with a thioalkyl chain on the terminal of the benzene ring were synthesized. The study indicates the lengths of thioalkyl chain has an effect on the mesomorphic properties i.e. the temperature range of the nematic phase and melting points decreasing with increasing the thioalkyl chain. However, the large size of the sulfur atom prevents the smectic phase from appearing. The thermotropic LC properties evaluated and compared with the structurally similar known homologous series with view to understand the relations between LC properties and molecular structure depending on changing left side groups of different polarities.

- Homologous series of present investigation is nematogenic only with normal degree of mesomorphism and of middle order melting type.
- An unique homologue of a chalconyl ester series with equipolar both terminal end groups show more or less or negligible deviation from normal descending tendency.
- The group efficiency order derived on the basis of (a) thermal stability (b) early commencement LC phase and (c) Degree of mesomorphism for nematic are as under.

Nematic

(a) Series 1 $\approx$ series-X > series-Y

(b) series-1 = series-X > series-Y

(c) series-1 $\approx$ series-X > series-Y

- A phenomena of mesomorphism is very sensitive and susceptible to molecular structure depending upon the suitable magnitude of molecular rigidity and/or flexibility.
- Study of binary systems of present investigation may prove its utility in LC devices and exploitation of biological activity of present compounds may prove their importance in pharmaceutical preparation.
- Present investigation supports and raises the credibility to the conclusions drawn earlier.

Acknowledgement

Authors acknowledge thanks to Dr. R. R. Shah, principal of K. K. Shah Jarodwala Maninagar Science College, Ahmedabad. Authors are also thankful to Dr. A. V. Doshi, Ex-principal of M.V.M. Science & Home Sci. College - Rajkot for his constant support, inspirations and help, as and when needed during the course of present investigation. Authors thank to NFDD Centre for the analytical and spectral services.

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