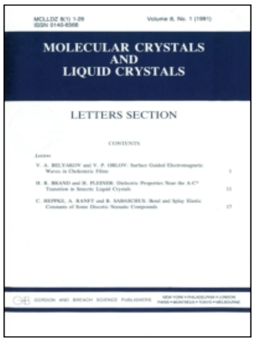
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Synthesis and study of new homologous series of ester-chalcone exhibiting nematic phases

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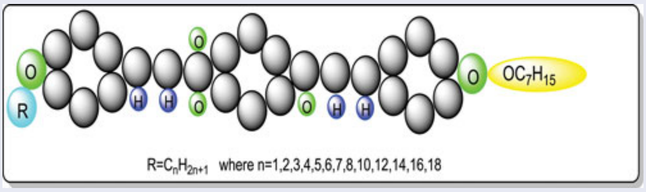
ABSTRACT
A novel homologous series of ester-chalcone have been synthesized and their liquid crystals (LCs) properties are studied. All the homologue shows nematic phase except C_1–C_4 homologue. Classical nematic textures are observed in this homologous series with the help of polarizing optical microscope (POM) equipped with hot stage. The role of flexible methylene group spaces, degree of polymerization and central linkage on the exhibition of all the homologue is discussed. The novel homologous series has been characterized by the standard methods (1HNMR, IR, and elemental analysis).

KEYWORDS
Enantiotropic; liquid crystals; mesomorphic; nematogenic; smectogenic

GRAPHICAL ABSTRACT



Introduction

Chalconyl derivatives are well-known for their antibacterial, antifungal, antimalarial, anticancer, etc. [1–7]. biological properties and many other biological processes in solution or as lyotropic liquid crystals (LC). The liquid crystalline state of the thermotropic type is [8] exploited in LC devices [9–11]. The present investigation is planned with a view to understanding and establishing the relation between thermotropic mesomorphism and the molecular structure of a substance. Secondly, the study will provide novel chalconyl LC materials to scientists and technologists working with LCs. The rigid core of the structure is made up of ring structures (aromatic) bridged through two central groups and the flexible portion is made up of terminal end groups. The novel homologous series consists of three phenyl rings linked through two central bridge –CH=CH–COO and –CO–CH=CH– which act as a rigid core. The left and right terminal end groups of the homologous series are n-alkoxy and -OC_7H_{15}, respectively and these act as flexible units of the homologous series without

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any lateral substitution. The novel compounds will be characterized by analytical and spectral data. Thermometric data will be evaluated and interpreted in terms of molecular rigidity and flexibility depending on molecular structure and then mesomorphic properties and behavior will be compared with structurally similar series. Several ester homologous series with or without chalconyl group have been studied to date [12–21]. Group efficiency order and structure relation with mesomorphism will be derived.

Experimental

Synthesis

Trans 4-n-alkoxy cinnamic acids (A) were prepared by a modified method [22, 23]. $\alpha-4$-Hydroxy benzoyl $\beta-4^{/}$heptyloxy ethylene (B) was prepared by the usual established method [24]. Esters were synthesized through a literature method [25]. Thus, the chalconyl ester homologue derivatives were decomposed filtered, washed with a solution of sodium bicarbonate and sodium hydroxide followed by water and dried and purified until constant transition temperatures were obtained using an optical polarising microscope equipped with a heating stage. Alkyl halides, 4-hydroxybenzaldehyde, 4-hydroxy acetophenone, dicyclohexylcarbodimide, dimethyl amino pyridine, DCM, Ethanol, and acetone required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to a series is shown in Scheme 1.

Characterization

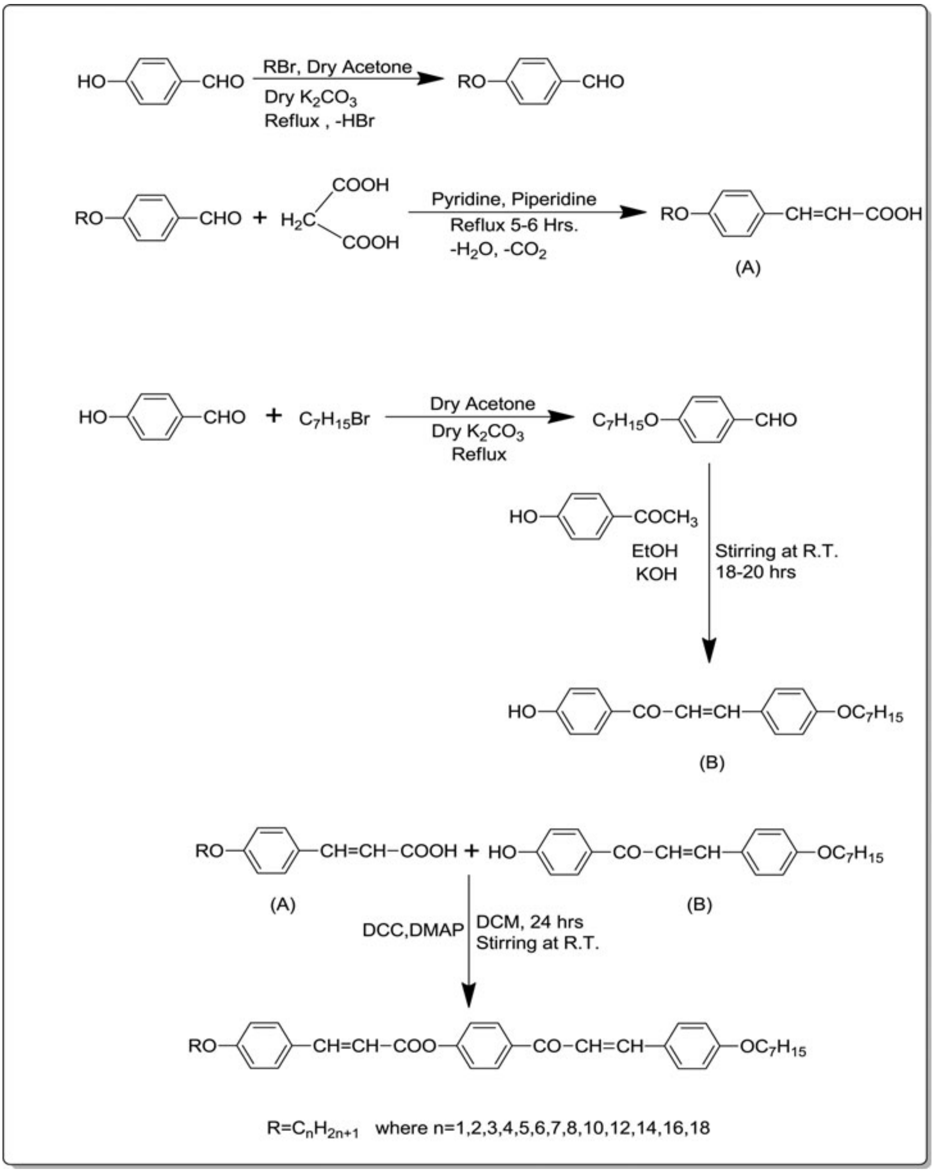
Selected members of the novel homologous series were characterized by Elemental Analysis (Table 1), infrared spectroscopy, ^{1}H NMR spectra. IR spectra were recorded by Perkin-Elmer spectrum GX,^{1}H NMR spectra were recorded on Bruker using $CDCl_3$ as solvent. Microanalysis was performed on a Perkin-Elmer PE2400 CHN analyzer. Transition temperature and LC properties (Textures) were determined using an optical polarizing microscopy equipped with a heating stage. Textures of nematic phase is determined by miscibility method (Table 2).

Analytical data

IR Spectra in cm^{-1} for Heptyloxy and Dodecyloxy Derivatives

Octyloxy: 661(Cis –CH=CH–), 719 Polymethylene (–CH_2-)n of -OC_7H_{15}, 833(–C–H– def. m di-substituted), 757 Polymethylene (–CH_2-) of -OC_7H_{15}, 949 (–C–H– def. hydrocarbon), 1107(–C-O-) Str, 1165,1254 and 1381 (–C-O str in -(CH_2)n chain), 1455 (–C–H– def. in CH_2), 1516 (–C=C-)str, 1604 (–C=O group) 1708 (–COO– ester group), 2848 and 2923 (–C–H str in CH_3).

Dodecyloxy: 658(Cis –CH=CH–), 720 Polymethylene (–CH_2-)n of -$OC_{12}H_{25}$, 817(–C–H– def. m di-substituted), 767 Polymethylene (–CH_2-) of -OC_7H_{15}, 950 (–C–H– def. hydrocarbon), 1110(–C-O-) Str, 1375, 1164, and 1252 (–C-O str in -(CH_2)n chain, 1468(–C–H– def. in CH_2),1513 (–C=C-)str, 1602(–C=O group) 1712 (–COO– ester group), 2849 and 2920 (–C–H str in CH_3).



Scheme 1. Synthetic route to the series.

^{1}HNMR spectra in $CDCl_3$ in δ ppm for Hexyloxy & Octadecyloxy Derivative

Hexyloxy: 0.83(t, $-CH_3$ of $-C_6H_{13}$), 1.1–1.4(m, n-poly methylene groups of-OC_6H_{13}),1.70 (m, n-poly methylene groups of -OC_7H_{15}), 3.1–3.4 (s,-OCH_2-CH_2-ofOC_7H_{15}), 3.98

Table 1. Elemental analysis for hexyloxy, decyloxy, tetradecyloxy, and hexadecyloxy derivatives.

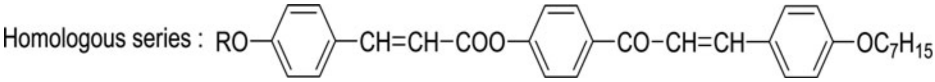
		%Elements found		%Elements theoretical	
Sr. no.	Molecular formula	C	H	C	H
1	$C_{37}H_{44}O_5$	80.98	8.01	81.02	8.02
2	$C_{41}H_{52}O_5$	81.40	8.57	81.45	8.60
3	$C_{45}H_{60}O_5$	81.79	9.05	81.81	9.09
4	$C_{47}H_{64}O_5$	81.95	9.24	81.97	9.30

Table 2. Texture of nematic phase of C_8, C_{12}, C_{14}, C_{18} by miscibility method.

Sr. no.	Homologue	Texture
1	C_8	Threaded
2	C_{12}	Threaded
3	C_{14}	Schlieren
4	C_{18}	Schlieren

(s,-OCH_2–CH_2-of OC_6H_{13}), 6.48 (d,–CH=CH–),6.9–7.2 (s,–CO–CH=CH), 8.09(s, p-disubstituted phenyl ring).

Octadecyloxy: 0.87 (t,–CH_3 of –$C_{18}H_{37}$), 1.2–1.6(m, n-poly methylene groups of-$OC_{18}H_{37}$), 1.75(m, n-poly methylene groups of -OC_7H_{15}), 3.4–3.6(s,-OCH_2–CH_2-ofOC_7H_{15}), 4.04 (s,-OCH_2–CH_2-of $OC_{10}H_{21}$),6.41 (d,–CH=CH–), 6.8–7.3 (s,–CO–CH=CH),8.12 (s, p-disubstituted phenyl ring).



α-3-(4′-n-alkoxycinnamyloxy)benzoyl-β-4″-heptyloxyphenyl ethylenes

Result and discussions

α-4-(4′-n-Alkoxycinnamoyloxy) benzoyl –β-4′-heptyloxyphenyl ethylenes is a non liquid crystal (NLC) compound which on condensation with trans n-alkoxycinnamic acids yielded novel chalconyl derivatives. The C_1 to C_4 homologues are NLCs. The other derivatives are (C_5–C_{18}) are enantiotropic nematogens without exhibition of any smectogenic phases. Transition temperatures (Table 3) were plotted against the number of carbon atoms present in n-alkyl chain of left n-alkoxy group. Transition curves (Figure 1) Cr-I/N and N/I were obtained on linking like or related points, which shows phase behaviors of series. Cr-I/N transition curve adopted zigzag path of rising and falling with overall descending tendency. N-I transition curve initially rises and then falls with overall descending tendency except negligible abnormality at the C_7 homologue. Odd-even effect is observed for N-I transition curve. The N-I transition curve for odd and even numbers merge into each other at the decyloxy C_{10} homologue and then continue as one trend. The single transition curve passes through the

Table 3. Transition temperature of homologous series.

		Transition temperatures in°C		
Sr.no	R = n-alkyl group	Smectic	Nematic	Isotropic
1	C1	—	—	127.0
2	C2	—	—	134.0
3	C3	—	—	123.0
4	C4	—	—	120.0
5	C5	—	82.0	112.0
6	C6	—	78.0	118.0
7	C7	—	69.0	97.0
8	C8	—	73.0	100.0
9	C10	—	72.0	101.0
10	C12	—	76.0	108.0
11	C14	—	65.0	102.0
12	C16	—	71.0	113.0
13	C18	—	67.0	110.0

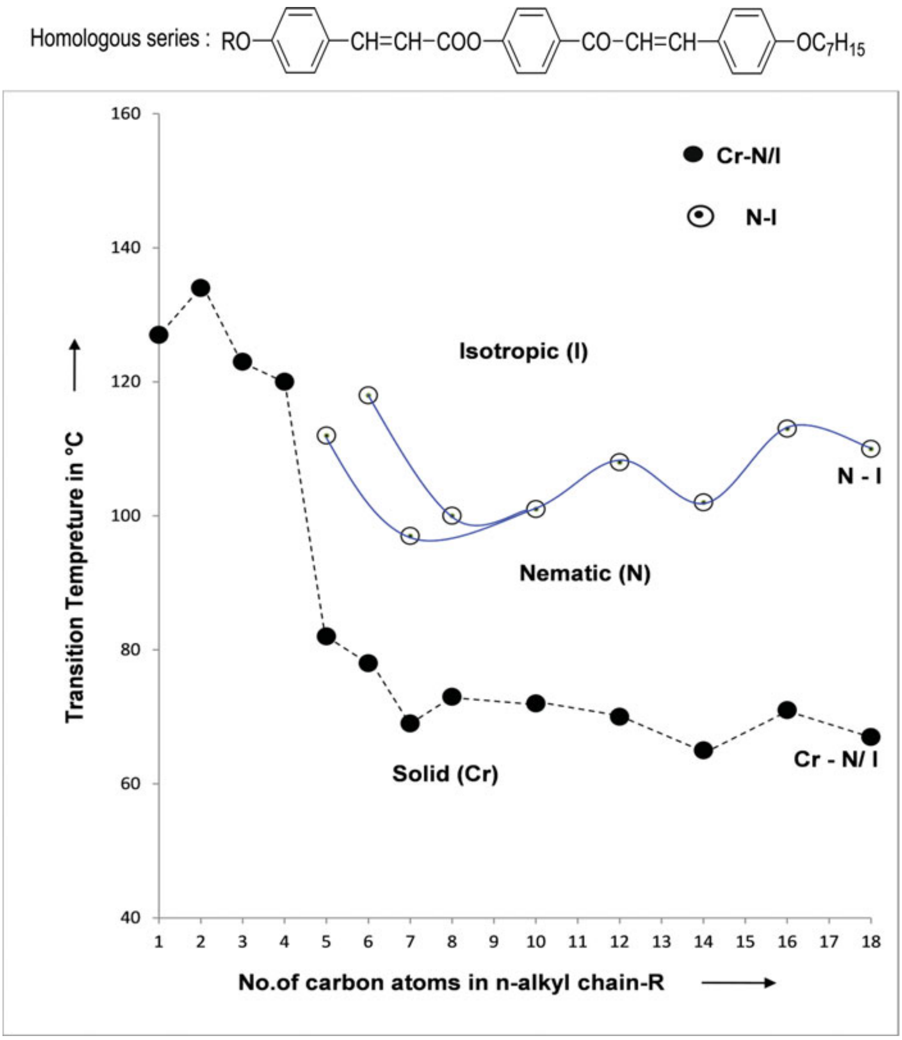


Figure 1. Phase behavior of series.

C_{12} and continues with a negligible fall at C_{18} homologue and negligible abnormality from descending tendency at C_7 homologue. Thus, N-I transition curve behaved almost in normal manner. N-I transition curve for even members occupies higher position than curve (N-I) for odd members. The nematogenic mesomorphism commences from the pentyloxy (C_5) homologue and continues up to the octadecyloxy homologue (C_{18}).

The LC behaviors from homologue to homologue in the same series undergoes variations. Thermal stability for nematic is 108.0°C whose LC phase length varies from 27.0°C to 43.0°C at the C_8 and C_{18} homologue, respectively. Thus, it is a middle ordered melting type series of medium ranged liquid crystallinity. Lowering if transition temperatures of present novel homologues as compared to corresponding dimeric trans n-alkoxycinnamic acids is attributed to the breaking of hydrogen bonding between two molecules of aromatic acid by esterification process. Alterations of transition points are attributed to odd and even number of carbon atoms in alkyl (R) of -OR group. Thenonmesomorphicity of C_1–C_4 homologues is attributed to low magnitudes of intermolecular dispersion forces and low dipole-dipole interactions as a consequence of unfavourable molecular rigidity and flexibility, which induces unsuitable magnitudes of intermolecular end to end and/or lateral cohesion and closeness as well as high crystallising tendency. As a result of this, the molecules of C_1–C_4 are unable to resist exposed thermal vibrations and melted sharply to the isotropic state without passing through LC state. The absence of smectogenic character throughout a novel series is due to absence of lamellar packing molecules through inadequate intermolecular lateral cohesion. However, residual intermolecular anisotropic forces of end to end attractions and closeness are strong enough to disalign the molecules of C_5–C_{18} at an angle less than ninety degree on floating surface and resists the exposed thermal vibrations for some temperature difference and maintained the molecular arrangement in statistically parallel orientational order to show the formation of nematic phase as a consequence of end to end favourable magnitudes of cohesion and closeness. The molecules of homologue either from rigid crystalline state or nematogenic mesophase, transform into isotropic state, at an isotropic temperature, at which the molecules are randomly orient in all possible direction with high order of disorder or randomness or high entropy. But on cooling the isotropic mass from and below isotropic temperature, the nematic mesophase reappears in reversible manner exactly at a temperature at which, it had appeared. Odd-even effect observed for N-I transition curve is due to the sequentially and progressively added methylene unit or units at the left -OR group. The odd-even effect disappears from and beyond C_{12} homologue and N-I transition curve prolonged as a single transition curve for the higher homologues of longer n-alkyl chair ‘R’ of left -OR group, because, longer n-alkyl chain may coil or bend or flex or couple to lye with major axis of the core structure and hence, the alteration diminishes as series is ascended from and beyond C_{12} homologue. The negligible abnormality from normal descending tendency at C_7 homologue and rising tendency of deviation of N-I transition curve at the C_{14} homologues are attributed to the uncertainty in the status of n-alkyl chain R of -OR and n-alkyl chain of common longer tail end group -OC_7H_{15}(n) (Para) of linear shaped molecules of homologues. Moreover an unique homologue of -OR equal to -OC_7H_{15} and tail end -OC_7H_{15} i.e. in case of a homologue in which terminal end groups are identically same, the vector sum of all bonds of -OC_7H_{15} group will be exactly equal in magnitudes and opposite in directions contribute to ZERO polarity. Therefore the effectiveness of molecular polarity and polarizability may reflect to molecular flexibility showing more or less or negligible deviation at an unique homologue involving identically same n-alkoxy terminal end groups in chalconyl ester derivatives. In case of the rest of the homologues other than $C_{14}$the group polarity difference between -OR and -OC_7H_{15}(n) reflects the molecular flexibility, descending tendency of each homologue of a present novel series. The variations in LC properties from homologue to homologue in the same novel series is attributed to the sequentially added methylene unit or units to n-alkoxy group (-OR) which alters molecule lengths, permanent dipole moment across the long molecular axis, length to breadth ratio, ratio of the polarity to polarizability, intermolecular cohesion and closeness due to varied dispersion forces, dipole-dipole interactions etc. Thus, variation in LC properties of presently investigated homologous series are altered due to attraction of molecular flexibility keeping unaltered molecular rigidity throughout the same series. The LC properties of novel series 1 are compared with the structurally analogous or similar series A [26] and B [27] as shown in Fig. 2.

Homologous series 1 and A are identical with respect to three phenyl rings, central bridge linking middle and third phenyl ring, left and right terminal end groups for the same homologue from series 1 to series A. But they differ with respect to central bridges –CH=CH–COO– and –COO– linking first and middle phenyl rings for the same homologue fro series 1 to series A. Thus, combine effect of molecular rigidity plus flexibility vary for the same homologue from series to series and from homologue to homologue in the same

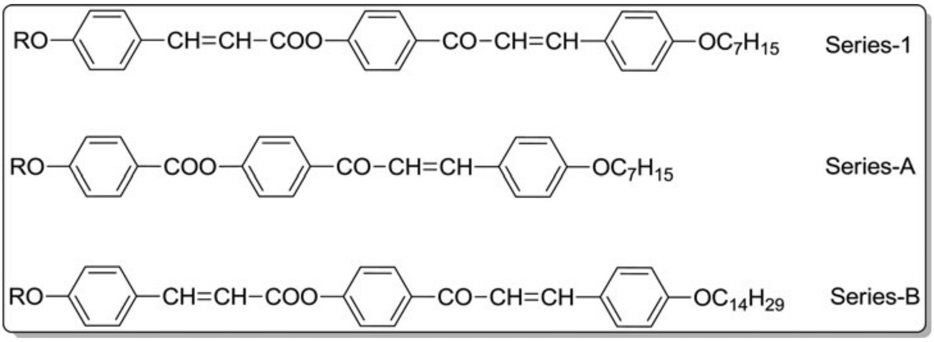


Figure 2. Structurally similar series.

series. Homologous series 1 and B are identical with respect to three rings, two central bridges and left terminal end group except right handed tail end groups, -OC_7H_{15} and -$OC_{14}H_{29}$ for the same homologue from series 1 to series B and from homologue to homologue in the same series as a consequence of combined effect of molecular rigidity plus flexibility whose magnitudes decides the possibility of inducing LC property and its thermotropic behaviour.Table 4 represents some thermotropic behavior of presently investigated novel chalconyl homologous series 1 and the series chosen for comparative study.

Table 4 represent that,

- All the three series 1, A and B under comparative study are nematogenic only without exhibition of Smectic property.
- Mesomorphism commences from C_5 homologue in case of series 1 and A, but it commences from C_6homologue of a series B.
- Thermal stability of a series 1 is higher than the series A and B.
- The degree of mesomorphism of all the series are almost nearer or in increasing order from series B to A to 1.

The suitable magnitudes of anisotropic forces of end to end intermolecular cohesion and closeness as a consequence of favourable molecular rigidity and flexibility which arranges molecules of all the homologous series (1, A and B) to float on the surface with statistically parallel orientational order for different degree of mesomorphism, depending upon individual varying magnitudes of molecular polarities and polarizability. Thus, only nematic mesophase formation occurs with absence of smectic phase, due to absence of inadequate magnitudes of environmental situation and forces of cohesion as required for exhibition of smectogenic character. Thus, smectogenic character fails to facilitate in all the series 1, A and B under comparative study. The extent of molecular noncoplanarity for all the series 1, A and B are equivalent but it slightly differs for the difference of –CH=CH– unit in case of series A. The observed difference for thermal stabilities is attributed to the unusual and unexpected molecular status of n-alkyl chain of both ended n-alkoxy terminals -OR and -OC_7H_{15} depending

Table 4. Relative thermal stability in °C.

Series	1	A	B
smectic-isotropic or smectic-nematic Commencement of Smectic phase	—	—	—
Nematic-Isotropic Commencement of Nematic phase	108.0 (C_5–C_{18}) C_5	102.0 (C_5–C_{18}) C_5	99.75 (C_6–C_{18}) C_6
Total upper and lower mesophase length range in °C C_i–C_j	27–43 C_8–C_{18}	14–2 C_{12}–$C_{7/16}$	19–34 C_6–C_8

upon resultant differing polarity difference of -OR and -OC_7H_{15} which induces thermal resistivity, degree of mesomorphism and transition temperatures of homologues. Thus, thermal stabilities and upper and lower mesophase lengths ranges of series 1, A and B are not much differed in magnitudes.

Conclusions

- Presently investigated chalconyl ester series is partly nematogenic whose degree of mesomorphism is shorter and of low melting type without exhibition of smectogenic property.
- The group efficiency order derived on the basis of (i) thermal stability (ii) early commencement of mesophase and (iii) higher degree mesomorphism are as under.
    - (i) Smectic Series 1 = Series A = Series B
    - (ii) NematicSeries 1 > Series A > Series B
    - (iii) Nematic Series 1 = Series A > Series B
    - (iv) Nematic Series 1 > Series A > Series B
- Mesomorphism is very sensitive and susceptible to the molecular structure as a consequence of molecular rigidity or/and molecular flexibility.
- Present novel compounds may be useful for the devices to be operated at room temperature or low temperature and their biological activity as antifungal or antibacterial etc. may be exploited in agricultural production to control and reduce the consumption of insecticides and pesticides.
- Homologous series with longer n-alkyl chains bonded to third phenyl ring through oxygen atoms as tail end group are nematogenic only of low degree of mesomorphism.
- Difference of group polarities at the two terminal end groups decides the mesogenic behavior of individual homologue and the same homologous series as a whole.
- Present study support and raised credibility to the conclusions drawn earlier.

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