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Synthesis and study of benzo-ester homologous series of ethylene derivatives: α -4-[4'-n-Alkoxy cinnamoyloxy benzoyl] β -2''-nitro phenyl ethylenes

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ABSTRACT

Titled homologous series consisting of eleven members is a liquid crystal in nature pentyl to decyl members of the series are liquid crystal (LC) while, rest of the members of the series are nonliquid crystals. Enantiotropic nematogenic mesophase with threaded or schlieren texture persisted for pentyl, hexyl, octyl and decyl derivatives of the series. Smectogenic character is totally absent. Phase behavior of a phase diagram is normal for transition curves. Odd-even effect is observed for nematic-isotropic transition curve. Transition temperatures of the homologues are determined by an optical polarizing microscope, equipped with a heating stage. Analytical data supported the structures of molecules. Liquid crystal properties of the titled series are compared with structurally similar homologous series. Nematic-isotropic thermal stability is 171.5°C. Thus; series is predominantly nonmesogenic and partly nematogenic without exhibition of any smectogenic character.

Key words: Nematic , Liquid crystal , Mesomorphic , Enantiotropy , Smectic.

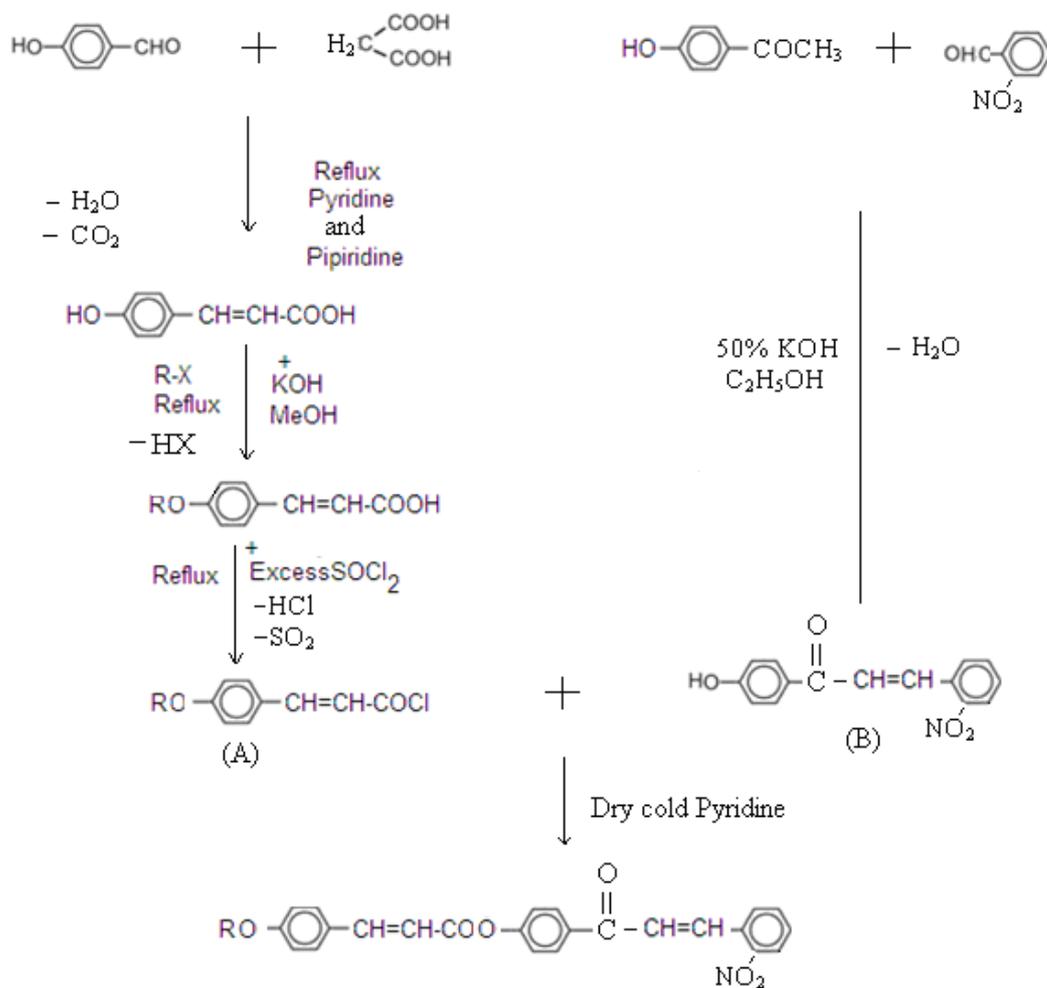
INTRODUCTION

Homologous series with -CH=CH-CO- central group in combination with ester central group are rarely reported till the date. Liquid crystal properties of the substances are varied by changing their molecular moiety which can directly affect molecular rigidity and flexibility. Thus, present series under investigation is planned by altering central group linking middle and third phenyl ring as well as replacing -H by -NO₂ group at ortho position to -CO-CH=CH- central group at third phenyl ring. Thus, variation of molecular rigidity and flexibility carried out for the purpose. This variation can induce mesogenic character of the series. This will be discussed in terms of effect of structure on liquid crystal properties.

MATERIALS AND METHODS

Synthesis: Cis-p-n-Alkoxy cinnamic acid and its corresponding acid chloride (A) was prepared by a modified method of Dave and Vora [4] α -4-Hydroxy benzoyl β -2'Nitro phenyl ethylene (B) was prepared by usual established [6c] method. Component (A) and (B) were condensed in dry cold pyridine [6,7] p-Hydroxy acetophenone, ortho nitro benzaldehyde, p-hydroxy benzaldehyde, malonic acid, Alkyl halides, pyridine, piperidine,

thionylchloride, KOH, methanol, ethanol and other chemicals required for synthesis were used as received. The synthetic route to the series is outlined in scheme-1 as under.



Scheme:1 Synthetic route of the series.

Characterization

Some selected representative members of the series were characterized by elemental analysis, infrared [IR] and ¹HNMR spectra. C, H, N. Analysis was carried out by Perkin Elmer PE 2400 Analyzer. IR spectra were recorded on Perkin Elmer spectrum GX. ¹HNMR spectra were recorded on Bruker using CDCl₃ as solvent. Liquid crystal properties were determined through hot stage polarizing microscopy. Textures of the nematic mesophase were determined by miscibility method. Thermodynamic properties ΔH and ΔS are qualitatively discussed.

Table: 1 Elemental analysis for Propyloxy, Butyloxy, Pentyloxy and Dodecyloxy Derivatives.

Molecular formula	Element % found (% calculated)		
	C	H	N
C ₂₇ H ₂₃ NO ₆	70.83 (70.89)	5.10 (5.03)	3.11 (3.06)
C ₂₈ H ₂₅ NO ₆	71.38 (71.34)	5.35 (5.31)	3.03 (2.97)
C ₂₉ H ₂₇ NO ₆	71.80 (71.75)	5.52 (5.57)	2.86 (2.89)
C ₃₆ H ₄₁ NO ₆	74.17 (74.10)	7.10 (7.03)	2.45 (2.40)

Homologous Series: α -4-[4'-n-Alkoxy Cinnamoyloxy] benzoyl- β -2''- Nitro Ethylenes

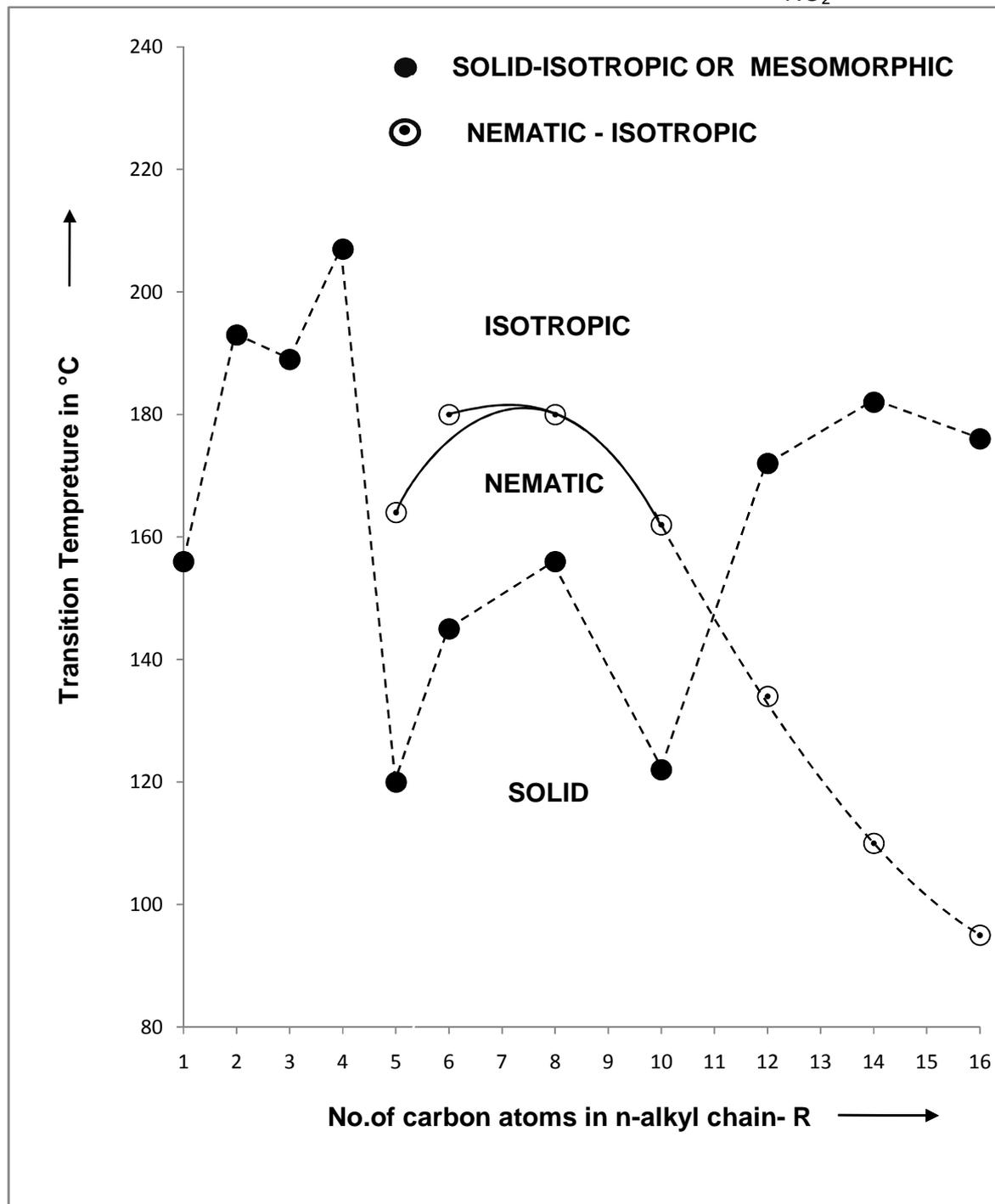
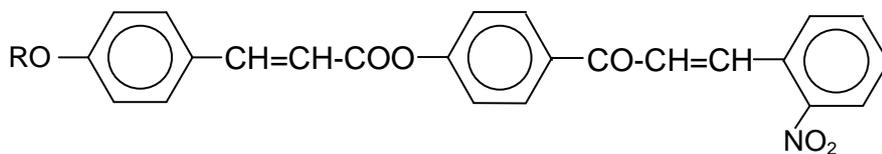


Figure:1 State behavior of the series.

Analytical data:**NMR in PPM for Decyloxy derivative:**

0.806 (-CH₃ of OC₁₀H₂₁), 1.708 (-CH₂)_n of OC₁₀H₂₁), 3.93 (Triplet-OCH₂-CH₂), 6.81 to 7.86 (m, p-sub. Phenyl ring) 7.75-CO-CH=CH- NMR confirms the structure.

NMR in PPM for Tetradecyloxy derivative:

0.941(-CH₃ of OC₁₄H₂₉) 1.1721 (-CH₂)_n of OC₁₄H₂₉) 3.778(Triplet-OCH₂-CH₂ of OC₁₄H₂₉) 6.94(broad) (-CH=CH-) 6.96 to 8.14(m, p-sub. Phenyl ring) 7.31-CO-CH=CH- NMR confirms the structure.

IR in Cm⁻¹ for Hexyloxy derivative:

640 & 760 (m-sub. Phenyl ring), 820 (p-sub. Phenyl ring), 1160 (C-O of alkoxy-OC₆H₁₃), 1420 (-NO₂ group), 1600, 1680 (-COO-group)-930 (-CH=CH-) 685 (polymethylene of C₆H₁₃) IR confirms the structure.

IR in Cm⁻¹ for Octyloxy derivative:

680(m-sub. Phenyl ring), 820 (p-sub. Phenyl ring), 1170 (C-O of alkoxy-OC₈H₁₇), 1025(-CH=CH-) 1210 & 1600(-COO group), 1430 (-NO₂ group) IR confirms the structure.

Texture: Pentyl - Threaded
Decyl - Schilieren

Table -2 Transition temperatures of series in °C

Sr.no	n-alkyl group -C _n H _{2n+1}	Transition temperatures in °C		
		Sm	Nm	Isotropic
1	1	-	-	156.0
2	2	-	-	193.0
3	3	-	-	189.0
4	4	-	-	207.0
5	5	-	120.0	164.0
6	6	-	145.0	180.0
7	8	-	156.0	180.0
8	10	-	122.0	162.0
9	12	-	-	172.0
10	14	-	-	182.0
11	16	-	-	176.0

Sm- Smectic Nm-Nematic

RESULTS AND DISCUSSION

On condensing nonliquid crystal components Cis-p- n-Alkoxy cinnamic acids and their corresponding acid chlorides (A) with a 4- Hydroxy benzoyl β.2'-nitrophenyl ethylene (B) resulted. pentyloxy to decyloxy homologues as liquid crystal substances. Rest of the homologues are nonliquid crystals of the series. A phase diagram (Figure-1) showing phase behavior of a titled series is obtained by plotting transition temperatures (Table-2) of homologues versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy group. Phase diagram indicates that, solid-isotropic or nematic transition curve follows a zigzag path of rising and falling tendency from methyl to decyl derivative of the series and then it adopts overall rising tendency as series is ascended. Nematic-isotropic transition curve initially rises and then it showed descending tendency as series is ascended in normal manner; with exhibition of odd-even effect.

Nonliquid crystal behavior of methyl to butyl and dodecyl to hexadecyl derivatives of a series is attributed to their high crystallizing tendency, arising as a consequence of their resultant molecular rigidity and flexibility [1,2,3] which are responsible to cause isotropic or anisotropic forces of attractions. The molecules of above mentioned nonmesomorphic homologues are unable to resist thermal vibrations exposed upon them due to their inadequate molecular polarity and polarizability causing unsuitable magnitudes of anisotropic intermolecular forces of end to end attractions. Hence, the molecules of nonmesomorphic homologues are sharply transformed into isotropic liquid at their melting point without passing through an intermediate state of existence, called as "Liquid crystal". The thermodynamically high order of molecular disorder or entropy value (ΔS) occur at which molecules are randomly oriented in all possible directions disorderly in uncontrolled manner. Pentyloxy to decyloxy homologues showed

nematogenic property because molecules of these homologues are able to resist exposed thermal vibrations within definite range of temperature ; during which molecules arrange themselves in statistically parallel orientational two dimensional order in floating condition due to the suitable magnitudes of anisotropic forces of intermolecular end to end attractions generated. However, beyond certain limit of temperature, molecules acquire isotropic state after melting temperature under the influence of externally supplied heat from thermodynamic surroundings whose magnitude exceeds the internal energy or enthalpy (ΔH) value of a system (homologue). Absence of smectogenic character of a presently investigated series is attributed to the absence of lamellar packing of molecules in the crystal lattices of the homologues concerned. The presence of $-\text{NO}_2$ group in ortho position , widens or broadens the molecular width[5]. This can reduces the intermolecular attractions due to increased width on one hand, and enhances intermolecular attractions due to increased molecular polarizability on other hand . Thus, two opposing forces are operating at a time. Hence, the observed resultant net effect depends upon the predominating effect out of two opposing effects. Thus, predominating effect in present series must be due to increased intermolecular distance(width) which reduces intermolecular forces of overall attractions, because present series shows poor extent of liquid crystal including absence of smectogenic mesophase as well as showing of nematogenic mesophase formation by only four members out of eleven members of the series. Nematogenic mesophase ranges from 24°C to 40°C at the pentyloxy and octyloxy homologue respectively. Thus, series is partly nematogenic and majorly nonmesomorphic . Nematic-isotropic transition curve is extrapolated [6] to hexadecyl derivative to predict latent transition temperature (LTT) for nematic of nonmesomorphic dodecyl , tetradecyl and hexadecyl derivatives . Thus , probable LTT for nematic are 135°C , 110°C and 94°C respectively , though nematic phase is not realizable practically because before phase appear, substance undergo early crystallization due to their high crystallizing tendency. Liquid crystal properties of present series including average thermal stability (table-3) are compared with structurally similar (or isomeric) series as mentioned below in figure-2.

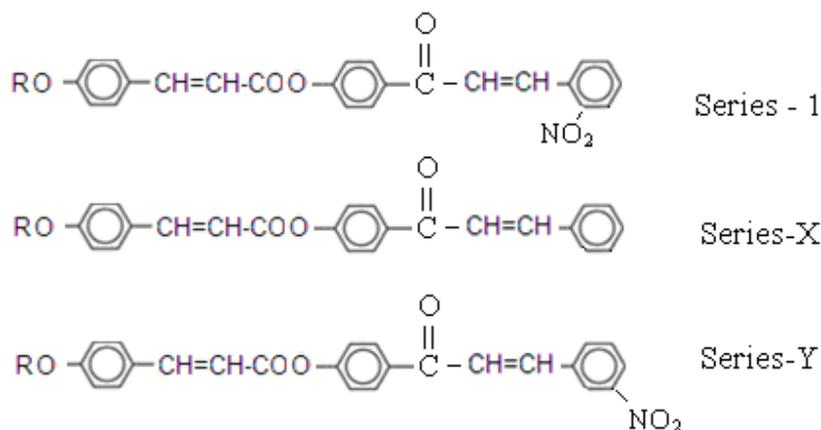


Figure-2 Structurally similar / isomeric series

Homologous series 1 ,X [9]and Y[10] contains three phenyl rings bridged through $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ central groups as identical features of rigid core and varying left n-alkoxy terminal end group as well as laterally substituted Nitro group at ortho or meta positions of fixed polarity as flexible core of linearly shaped molecules of series under comparison. Therefore the liquid crystal properties and the degree of liquid crystallinity will vary according to variations observed in series 1, X and Y.

Average thermal stability and the commencement of mesophase formation of the series under comparison are given in table-3 as under.

Table 3 : Average Thermal Stability in $^\circ\text{C}$

Series	Average transition temperatures in $^\circ\text{C}$		
	Series (1)	Series(X)	Series(Y)
Smectic-Nematic or smectic-isotropic			141.0 (C_5-C_{10})
Commencement of smecticphase	-	-	C_5
Nematic-isotropic	171.5 (C_5-C_{10})	155.4 (C_5-C_{16})	156.0 (C_5-C_{16})
Commencement of Nematic mesophase	C_5	C_5	C_5

Table-3 indicates that, the nematic-isotropic average thermal stability of present series 1 is the highest among the series under comparison. Thermal stability of nematic mesophase of series X and Y are almost equal or equivalent which are differing negligibly 0.6 unit. Thus ortho substituted $-\text{NO}_2$ group of presently investigated series shows stronger intermolecular end to end attractions than a meta substituted $-\text{NO}_2$ group. Hence ortho substituted $-\text{NO}_2$ group must be activated more than the meta substituted $-\text{NO}_2$ in the neighbourhood of $-\text{CO}-\text{CH}=\text{CH}-$ central group i.e. inductive effect of same $-\text{NO}_2$ group varies with the distance from the central group surpassing the effect due to steric hindrance caused by $-\text{NO}_2$ group. Smectogenic behavior though Nil in case of series 1 and X but their nematic thermal stability enhance at the cost of smectic property. The smectic thermal stability of series Y is 141.0 but of other two series 1 and X show Nil value for the same. This indicates that, lower value of inductive and steric effect is favourable to induce (meta substituted $-\text{NO}_2$) lamellar packing of molecules in crystal lattices of a substance. The commencement of mesophase either nematic or/and smectic takes place from fifth homologue of series 1,X,Y. i.e. series 1, X and Y are equicoplaner but mesophase stabilizes from pentyl to decyl derivative of series 1 and it discontinues to prolong up to hexadecyl derivative. In case of series X and Y it prolongs upto hexadecyl derivative. This difference of prolongation of mesophase stabilization can be linked to extent of inductive and steric effect caused by $-\text{NO}_2$ group. The variation in mesomorphic behavior from series to series for the same homologue is due to varying terminal or lateral groups of fixed polarity or varying position of same substituted group like $-\text{NO}_2$. The odd-even effect and variation in liquid crystal properties from homologue to homologue in the same series is attributed to the sequentially added methylene unit in n-alkyl chain of n-alkoxy group[5].

CONCLUSION

- (1) Group efficiency order derived for smectic and nematic on the basis of thermal stability are as under.
Nematic : ortho $-\text{NO}_2 > -\text{H} \approx$ meta $-\text{NO}_2$
Smectic : meta $-\text{NO}_2 > -\text{H}$ and ortho $-\text{NO}_2$
- (2) Molecular flexibility variation by varying position of the same functional group from meta to ortho increases thermal stability for nematic mesophase formation.
- (3) Shifting of $-\text{NO}_2$ group away from $>\text{C}=\text{O}$ group induces smectogenic property.
- (4) Present series is predominantly nonmesogenic and partly nematogenic.

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