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Synthesis and Study of a Novel Homologous Series of Mesogens with Ethylene link: α -3-[4'-n-Alkoxy Cinnamoyloxy] phenyl- β -3''-nitro benzoyl ethylenes.

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ABSTRACT

Novel homologous series α -3-(4'-n-Alkoxy Cinnamoyloxy) phenyl- β -3''-nitro benzoyl ethylenes consisted of eleven homologues. Methyloxy to butyloxy homologues do not show any mesomorphic behavior, while; the rest of the homologues show mesomorphic behavior. Pentyloxy to tetradecyloxy homologues exhibit smectogenic and nematogenic characteristic, while hexadecyl homologue exhibit only nematogenic characteristics. Transition temperatures of homologues as observed and determined by hot stage polarising microscope are proportional to number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group. Odd-even effect is observed for smectic-nematic and nematic-isotropic transition curves showing phase behavior of a series. Smectic and nematic thermal stabilities are 140.5°C and 164.8°C respectively. Analytical data support the structures of the homologue molecules. A texture of nematic mesophase is threaded or schlieren type and that of a smectic phase is of smectic-A type. Liquid crystal properties of a series are compared with another structurally similar isomeric homologous series. Mesophase lengths vary from 20°C to 55°C with middle ordered melting type.

Keywords: Liquid crystal, mesogen, Smectic, Nematic, Enantiotropy.

INTRODUCTION

Exhibition of an intermediate state of a matter between crystalline solid state and isotropic liquid state in addition to three wellknown states of matter, termed as Liquid Crystal state. The resultant adhering intermolecular forces of attractions based upon molecular structure of a matter has direct relation with molecular rigidity and flexibility caused by rigid core and flexible core of a molecule. The present molecular structure of homologues of a homologous series is constructed by linking three phenyl rings bridged through two central groups viz; -CH=CH-COO- and -CH=CH-CO- as rigid core and n-alkoxy -OR and -NO₂ groups which act as a flexible part of a molecule. Thus, present investigation is planned with a view to understand, establish and discuss a relation between molecular structure and liquid crystallinity of a substance as a consequence of resultant molecular rigidity and flexibility.

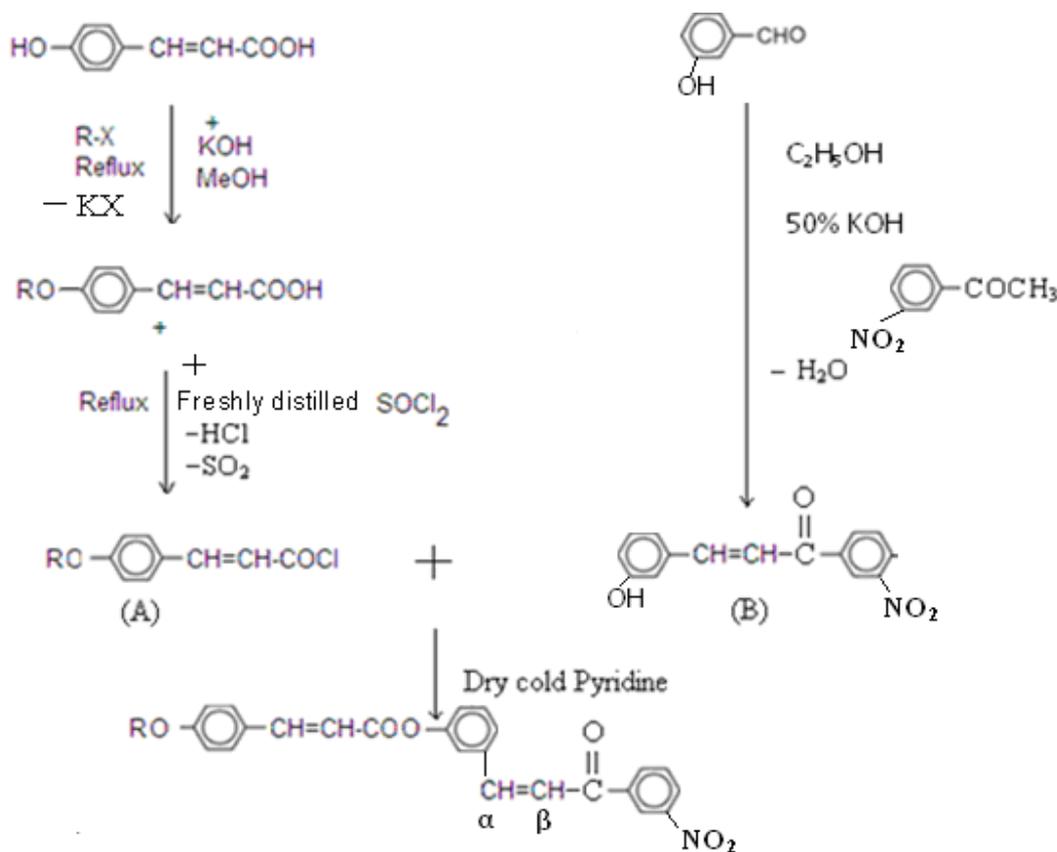
MATERIALS AND METHODS

Characterization:

Representative homologues of a titled novel series were characterized by infra red [IR], ^1H NMR technique and elemental analysis. IR spectra were recorded on Perkin Elmer spectrum GX and ^1H NMR spectra were recorded using CDCl_3 as solvent. Microanalysis was performed on Perkin- Elmer PE 2400 CHN analyzer as shown in Table-1. Liquid Crystal properties i.e. transition and melting temperatures of homologues were investigated by an optical polarizing microscopy with heating stage. Textures of the mesophases were determined by miscibility method. Thermodynamic quantities enthalpy ΔH and entropy ΔS are qualitatively discussed.

Synthesis:

P-Hydroxy cinnamic acid was alkylated by suitable alkylating agents. 4-n-Alkoxy cinnamic acids and their corresponding acid chlorids [A] were prepared by the method of Dave and Vora [4.] using anhydrous SOCl_2 . α -3-Hydroxy phenyl β -3'-nitro benzoyl ethylene [B] was prepared by usual established method [7,4], Component [A] acid chloride and [B] ethylene derivative were condensed in dry cold pyridine [6,7]. Final products were purified and recrystallised from alcohol till constant transition temperatures were obtained. 4-hydroxy benzaldehyde, malonic acid, pyridine, piperidine, MeOH, KOH, ethanol, thionyl chloride, Alkyl halides, 3-hydroxy benzaldehyde, 3-nitro acetophenon etc., required for synthesis were used as received. Synthetic route to the series is outlined as below in scheme-1.



α -3-[4'-n-Alkoxy Cinnamoyloxy] phenyl- β -3'-nitro benzoyl ethylenes

$\text{R} = \text{C}_n\text{H}_{2n+1}$ $n = 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16$.

Scheme – 1 Synthetic route to the series

Table-1 Elemental analysis for Butyloxy ,pentyloxy , dodecyloxy and hexadecyloxy derivatives.

Molecular formula	Element % found (% calculated)		
	C	H	N
C ₂₈ H ₂₅ NO ₆	71.31 (71.34)	5.36 (5.31)	3.02 (2.97)
C ₂₉ H ₂₇ NO ₆	71.79 (71.75)	5.63 (5.57)	2.91 (2.89)
C ₃₆ H ₄₁ NO ₆	74.05 (74.10)	6.98 (7.03)	2.38 (2.40)
C ₄₀ H ₄₉ NO ₆	75.14 (75.12)	7.69 (7.67)	2.23 (2.19)

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

0.872 (-CH₃ of -OC₁₀H₂₁), 1.2655(-CH₂- of -O C₁₀H₂₁), 4.011(Triplet) (-OCH₂-CH₂) of -OC₁₀H₂₁), 6.9 (broad) -CH=CH, 6.909 to 6.931(-CH=CH-CO-), 6.9 to 8.1 (m-p sub.Phenyl ring) NMR confirms the structure.

NMR in PPM for tetradecyloxy derivative:

0.88 (-CH₃ of -OC₁₄H₂₉), 1.249(-CH₂- of -OC₁₄H₂₉), 4.008(Triplet) (-OCH₂-CH₂) of -OC₁₄H₂₉), 6.92 (broad) -CH=CH, 6.9 to 7.9 (-CH=CH-CO-), 6.9 to 8.1 (m-p sub.Phenyl ring) NMR confirms the structure.

IR in Cm⁻¹ for Hexyloxy derivative:

720 (polyethylene of -OC₆H₁₃), 650&760 (m-sub. Phenyl ring) ,840 (p-sub. Phenyl ring), 950 (-CH = CH-), 1160-C-O of -OC₆H₁₃ ,1260, 1610 & 1680 (-COO group), 1430 & 1390 (-NO₂ group), IR confirms the structure.

IR in Cm⁻¹ for Octyloxy derivative:

650 & 770 (m-sub. Phenyl ring), 850 (p-sub. Phenyl ring), 1165 (C-O of -OC₈H₁₇), 1260 , 1610 & 1700 (-COO group), 1475&1520 (-NO₂ group) IR confirms the structure.

Texture by miscibility method

- | | |
|--------------------------|------------------|
| • Hexadecyloxy homologue | Threaded nematic |
| • Octyloxy homologue | Schlieren |
| • Pentyloxy homologue | Smectic- A |

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	-	-	191.0
2	2	-	-	195.0
3	3	-	-	210.0
4	4	-	-	214.0
5	5	130.0	135.0	150.0
6	6	116.0	138.0	171.0
7	8	109.0	145.0	158.5
8	10	110.0	143.0	160.0
9	12	120.0	140.0	160.0
10	14	112.0	142.0	165.0
11	16	-	170.0	190.0

Sm- Smectic Nm-Nematic

RESULTS AND DISCUSSION

Cis 4-n-Alkoxy cinnamoyl chloride and α -3-hydroxy phenyl β -3'-nitrobenzoyl ethylene are nonliquid crystal substances and melt sharply at their melting point. However, smectic and/or nematic mesophases are induced in a homologous series synthesized from these two components. Methoxy to butyloxy homologues are nonmesomorphic, Pentyloxy to tetradecyloxy homologues exhibit smectiogenic property in addition to nematogenic mesophase. Hexadecyloxy homologue is an enantiotropically nematogenic without exhibition of any smectogenic character. A phase diagram [Figure-1] is plotted for number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group versus the transition temperatures of homologues as observed and determined using an optical polarizing microscope equipped with a heating stage, as recorded in table-2. Solid-isotropic or mesomorphic transition curve partly follows a zigzag path of rising and falling as series is ascended with overall descending tendency except its

rise in hexadecyloxy homologue of the series. Smectic nematic transition curve initially rises, passes through maxima and then adopt a descending tendency as series is ascended. Negligible rise of 2°C temperatures as observed for tetradecyloxy homologue. Nematic-isotropic transition curve initially showed descending tendency and then ascending tendency from and beyond dodecyloxy derivative. Thus it behaves partly in abnormal manner from dodecyloxy to hexadecyloxy derivative. Both curves viz; Smectic-nematic and nematic-isotropic transition curves showed odd-even effect and curves for odd and even homologues merges into each other at the Octyloxy derivative of the series. Nematic isotropic transition curve is extrapolated to nonmesomorphic butyloxy homologue from mesomorphic hexyloxy homologue; taking care to follow trend of a curve. The nematic-isotropic temperature of butyloxy derivative and its solid-isotropic transition temperature coincided on extrapolation. Thus, this point of coincidence, indicate that, nematic phase length of butyloxy homologue should be zero, proving that, butyl homologue should be nonliquid crystal and practically also it is nonliquid crystal. Similarly smectic-nematic transition curve is extrapolated for hexadecyloxy derivative, which showed a probable, latent transition temperature for smectic 154°C. Which is not practically realizable. The mesomorphic properties are varying from homologue to homologue in same series because of sequentially added methylene unit in n-alkyl-chain of left n-alkoxy terminal. Odd-even effect observed for smectic-nematic and nematic-isotropic transition curve is attributed to the progressively added methylene unit at the left n-alkoxy end group, but such effect diminishes as series is ascended beyond octyloxy derivative, because, longer n-alkyl chain beyond octyloxy homologue may coil, or flex or couple to lie in the line with major axis these of core [5,8] and bend in such a manner that, end to end contact would then ultimately be the same for odd and even homologues. Thus, higher homologues may not contribute to the odd-even effect. Therefore odd numbered homologues are avoided to synthesized in the series and not included in the phase diagram. Induced liquid crystal property in the homologues from pentyloxy to hexadecyloxy synthesized from two nonliquid crystal components [A] and [B] is attributed to the added phenyl ring which increases the number of phenyl ring linked through -CH=CH-CO- central group and in presence of highly polar -NO₂ group substituted at meta position to central bridge, because the molecular aromaticity, polarity and polarizability, rigidity and flexibility raises controlling the suitable magnitude of anisotropic forces of intermolecular attractions to induce mesomorphism in A-B products. Pentyloxy to hexadecyloxy homologues could resist the thermal vibrations exposed upon them and showed smectogenic behavior in addition to nematogenic behavior except hexadecyloxy derivative which arranges and maintains its molecules as statically parallel orientational order only with absence of lamellar packing in its crystal lattice which did not allow to float with sliding layered arrangement of molecules to emerge smectogenic mesophase under the influence of heat energy. Thus, hexadecyloxy derivative of the series is only nematogenic without exhibition of any smectogenic character. Methoxy to butyloxy derivatives of the series are unable to resist thermal vibrations exposed upon them due to high crystallizing tendency and smoothly and sharply passes from solid to isotropic state at their melting point. This happens because, the resultant molecular rigidity and flexibility causes unsuitable magnitudes of anisotropic forces of intermolecular attractions and molecules are randomly oriented in all possible directions with high order of disorder or entropy [ΔS] at their transition temperature. Smectogenic phase length vary between 5°C to 36°C and nematogenic phase length vary between 13.5°C to 33°C. Overall mesophase length vary minimum of 20°C at the pentyloxy homologue to a maximum of 55°C at the hexyloxy homologue. Thus seven members of the series are nematogenic and six members of the series are smectogenic with middle ordered melting type. Smectic and nematic mesophase formation commences from pentyloxy derivative of the series. Abnormal rise of nematogenic character at the hexadecyl homologue is attributed to the irregular coiling or bending or flexing of hexadecyl n-alkyl chain which has direct impact on molecular rigidity and flexibility [1,2,3]; responsible for intermolecular adhesion.

Average thermal stability [table=3] and other liquid crystal properties of the titled homologous series-1 is compared with structurally similar isomeric series-y [9] as shown below in figure-2.

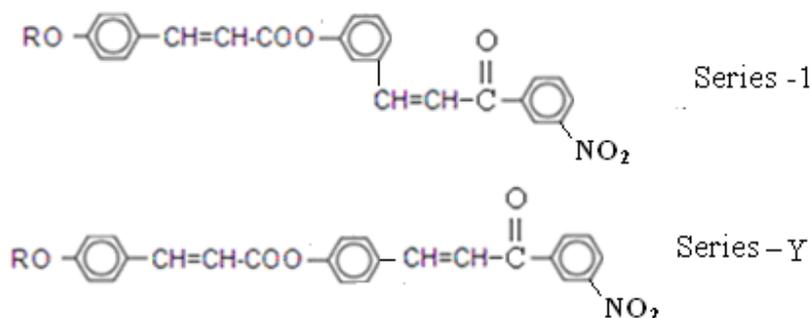


Figure-2 structurally similar isomeric series

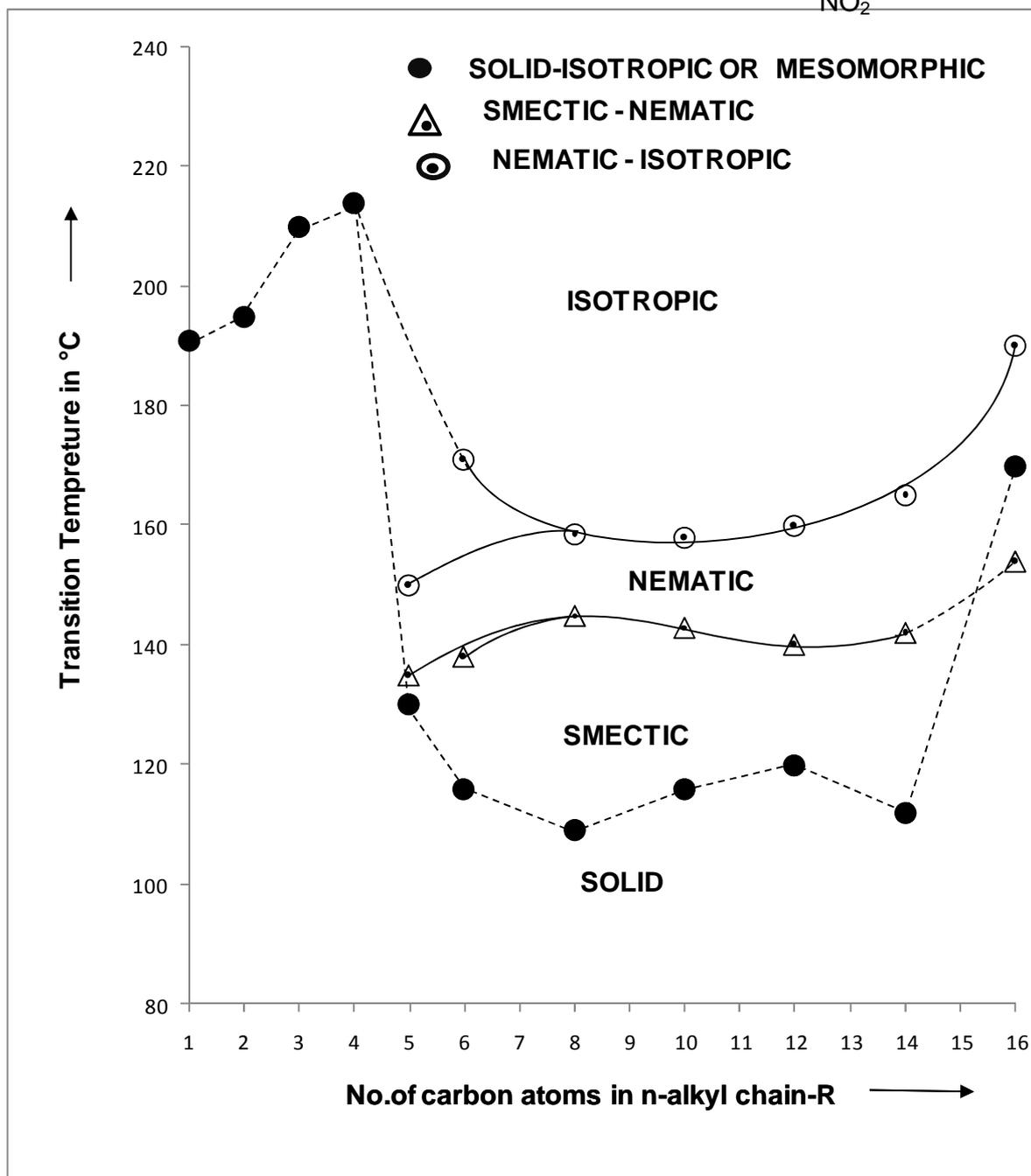
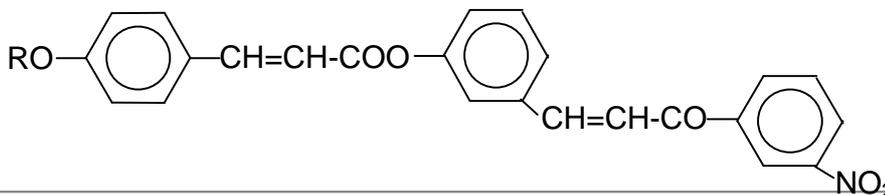
Homologous series (1) and (y) consist of three phenyl rings bridged through identical central bridged viz; -CH=CH-COO- and -CH=CH-CO- and identical flexible groups -OR and -NO₂ substituted at the identical positions at the first and third phenyl rings respectively. But they differ in the position of linking -CH=CH-CO- central group which links middle and third phenyl rings. Therefore observed difference in thermal stability and other liquid crystal properties can be linked to the positional difference of central bridge -CH=CH-CO- linking middle and third phenyl rings. Table-3 depicts average thermal stability for smectic and nematic mesophases and commencement of mesophases as under.

Table-3: Average thermal stability in C^o

Series	Average transition temperatures in °C	
	Series (1)	Series(Y)
Smectic-Nematic or isotropic	140.5 (C ₅ -C ₁₄)	154.6 (C ₅ -C ₈)
Commencement of smectic phase	C ₅	C ₅
Nematic-isotropic	164.8 (C ₅ -C ₁₆)	163.8 (C ₅ -C ₁₆)
Commencement of Nematic mesophase	C ₅	C ₅

Table-3 indicates that nematic -isotropic average thermal stabilities and the commencement of nematic mesophase are almost equivalent or nearly equal but smectic-nematic average thermal stability differ by 14.1^oC with identical commencement of smectogenic mesophase. This difference can be linked with intermolecular forces of attractions arising from widening of molecule of series-1 as compared to the intermolecular closeness of the linearly shaped molecule of series-y. Molecule of series-1 being broader than a molecule of series-y causes increase in the intermolecular distance. As a result of this, two opposing effects viz;(1) molecular widening decreases the intermolecular attractions of series-1 as compared to series-y. and (2) broadening of molecule increases the intermolecular attractions due to increased polarizability of series-1 as compare to series-y. The resultant intermolecular attractions may be due to the combine effects (i) and (ii) or a phenomenon may be operated by predominancy of any one of the individual effects. Thus, two opposing effects are operating at a time. But looking to the values of average thermal stabilities of present investigated homologous series-1 and a series under comparison y, the effect (i) due to intermolecular distance predominates in case of smectic -nematic thermal stability as compared effect (ii) Increased polarizability of series-1 facilitates favourably to strengthen lamellar packing of molecules and exhibition of prolonged smectogenic character in series-1. i.e. from pentyloxy to tetradecyloxy homologues in floating condition; while, the lamellar packing in the crystal lattice of molecules in series-y facilitated from pentyloxy to octyloxy homologue only. Thus, lamellar packing in crystal lattice can favourably be affected by a broader molecule more than a linear rod like molecule. Hence, molecular shape has an important contribution to the molecular rigidity and flexibility[1,2,3] in forming lamellar packing of a molecule in crystal lattices. The nematogenic mesophase formation remains ineffective irrespective of its molecular shape in isomeric homologous series. The commencement of smectic mesophase takes place from pentyloxy homologue which indicates that extent of noncoplanarity are in series-1 and y are equal or the molecules of series-1 and of series-y are equicoplaner, However smectogenic behavior prolong to tetradecyloxy homologue in series-1 while it prolongs upto octyloxy homologue in series-y. Thus, the variation in mesomorphic properties from series to series for same homologue in isomeric series is attributed to the positional difference of central group or / and substituent groups affecting molecular rigidity and /or flexibility.

Homologous Series: α -3-[4'-n-Alkoxy Cinnamoyloxy] phenyl- β -3''- Nitrobenzoyl- ethylenes



CONCLUSION

- (1) Molecular rigidity and flexibility can be affected by the shape of a molecule.
- (2) Lamellar packing of a molecule favorably enhanced by broadening of a molecule.
- (3) Smectogenic character can be affected more than a nematogenic character by broadening of a molecule.
- (4) Nematogenic mesophase formation is not affected by the positional displacement of group or groups.
- (5) Molecular rigidity and flexibility can affect thermal stabilities and other LC properties of a molecule.

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