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Der Pharma Chemica, 2012, 4 (3): 977-983  
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ISSN 0975-413X  
CODEN (USA): PCHHAX

## Ethylene Derivatives of Liquid Crystalline Properties : Homologous Series : $\alpha$ -4-[-4'-n-Alkoxy Cinnamoyloxy] benzoyl $\beta$ -phenyl ethylenes.

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### ABSTRACT

Homologous series  $\alpha$ -4-[-4'-n-Alkoxy Cinnamoyloxy] benzoyl  $\beta$ -phenyl ethylenes consists of eleven members of the series. Pentyloxy to hexadecyloxy homologues are enantiotropically nematogenic without exhibition of any smectogenic character. Odd-even effect is observed for nematic-isotropic transition curve with alternation of transition temperatures of the homologues as determined using an optical polarizing microscope with heating stage. Methoxy to butyloxy homologues are nonliquid crystals. Analytical data supports the structures of the molecules. Textures of the nematic mesophase is threaded or schlieren type Nematic-isotropic thermal stability of a series is 155.4 °C. Mesomorphic properties of a present series are compared with other structurally similar homologous series.

**Keywords:** Liquid Crystal, Smectic, Nematic, Mesomorphic, Monotropy.

### INTRODUCTION

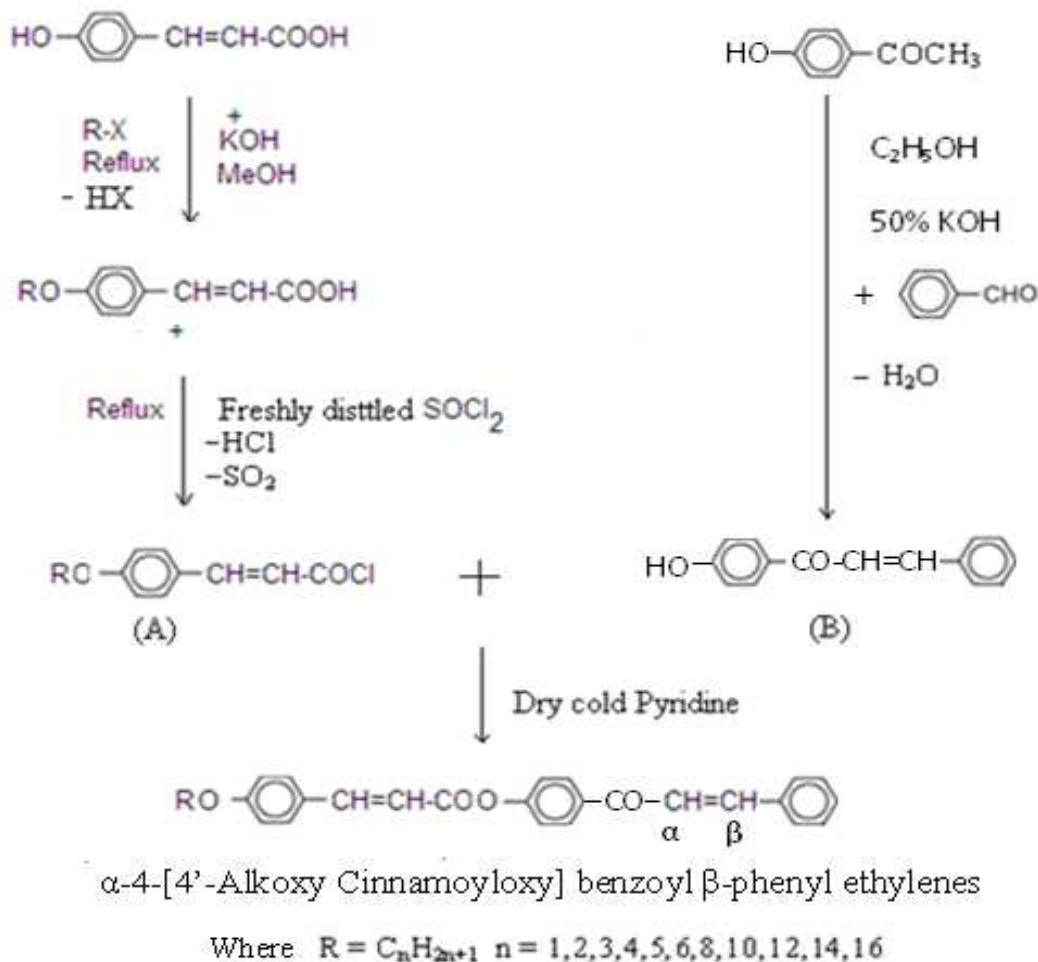
Effect of molecular structure on liquid crystal properties of a substance play an important role in inducing mesogenic characteristics, which has direct relations with resultant molecular rigidity and flexibility. Rigid part of a molecule is due to the phenyl rings and their linking through the central group. Terminal and lateral groups attached at ortho, meta or para positions of phenyl rings act as a flexible part of the series. Present series is planned with a view to understand and establish the relation between molecular structure and liquid crystallinity by constructing a molecular geometry which contains three phenyl rings bridged through vinyl carboxylate and -CO-CH=CH- central groups as a rigid part and n-alkoxy terminal group and -H end groups without any laterally substituted group as a flexible part. Thus, induction of liquid crystallinity to be discussed with reference to molecular structure causing molecular rigidity and flexibility.

### MATERIALS AND METHODS

#### Synthesis :

4-Hydroxy cinnamic acid was alkylated by suitable alkylating agent and were converted to corresponding 4-n-alkoxy cinnamoyl chloride by a method of Dave and Vora [ ]. [A]  $\alpha$ -4-Hydroxy benzoyl  $\beta$ -phenyl ethylene [B] was prepared from p-hydroxy acetophenone and benzaldehyde by the usual established method [ 5b,10 ]. Component (A)

and (B) were condensed in dry cold pyridine to form the final benzoester compound. Final products were crystallized till constant transition temperatures were obtained. The synthetic route to the series is mentioned below in scheme-1.



Scheme-1 Synthetic route to the series

The constituent components Alkyl halides, thionyl chloride, methanol, KOH, p-Hydroxy acetophenone, benzaldehyde, malonic acid, pyridine and piperidine, ethanol etc., required for the preparation of (A) and (B) and final products were used as received.

#### Characterization :

Some selected members of the series were characterized by elemental analysis (table-1), Infra-Red (IR) and  $^1\text{H}$ NMR spectroscopy. Microanalysis was performed on Perkin Elmer PE2400 CHN analyzer. IR spectra were recorded on Perkin Elmer spectrum and  $^1\text{H}$ NMR spectra were recorded on Bruker spectrometer using  $\text{CDCl}_3$  as solvent. Liquid crystalline properties were investigated on an optical polarizing microscope with heating stage. Texture of the nematic phase was confirmed by the miscibility method on hot stage polarizing microscope. Thermodynamic properties enthalpy ( $\Delta\text{H}$ ) and entropy ( $\Delta\text{S}$ ) are qualitatively discussed instead of DSC scan.

**Analytical data : Elemental analysis for butyloxy and octyloxy derivative :**

Sr. No.	Molecular Formula	Elements % Found ( % Calculated )	
		C	H
1	C <sub>28</sub> H <sub>26</sub> O <sub>4</sub>	78.87(78.84)	6.10(6.09)
2	C <sub>32</sub> H <sub>34</sub> O <sub>4</sub>	79.67(79.70)	7.05(7.07)

**Spectral data for series-1 :**

**NMR in ppm**

**Hexyl derivative :**

0.868 - CH<sub>3</sub> of -OC<sub>6</sub>H<sub>13</sub> ,1.245 (-CH<sub>2</sub>-)<sub>n</sub> of -OC<sub>6</sub>H<sub>13</sub> , 4.08 (Triplet) -OCH<sub>2</sub>-CH<sub>2</sub> of -OC<sub>6</sub>H<sub>13</sub>, 3.840 (Singlet) - O-CH<sub>3</sub>, 6.98 (Broad) - CH=CH-,7.15 & 7.27 -CH=CH-CO-,6.9 to 8.7 p-sub. Phenyl ring NMR Confirm the structure.

**Octyl derivative :**

0.881 - CH<sub>3</sub> of -OC<sub>8</sub>H<sub>17</sub> ,1.283 (-CH<sub>2</sub>-)<sub>n</sub> of -OC<sub>8</sub>H<sub>17</sub>, 4.008 (Triplet) -OCH<sub>2</sub>-CH<sub>2</sub> of -OC<sub>8</sub>H<sub>17</sub>, 3.848 (Singlet) - OCH<sub>3</sub>, 7.00 (Broad) - CH=CH-,7.18 -CH=CH-CO-, 6.69 to 8.1 p-sub. Phenyl ring NMR Confirm the structure.

**IR: in cm<sup>-1</sup>**

**Dodecyl derivative :**

1250 & 1610 Confirms -COO- group,1140 Confirms -CO - group,840 Confirms p-sub. Phenyl ring , 690 confirms -(CH<sub>2</sub>)<sub>n</sub> of C<sub>12</sub>H<sub>25</sub>

**Tetradecyl derivative :**

1230,1600 & 1680 Confirms -COO- group,1060 Confirms -CO - group,840 Confirms p-sub. Phenyl ring , 720 confirms -(CH<sub>2</sub>)<sub>n</sub> of C<sub>14</sub>H<sub>29</sub>

**Texture :** By miscibility method : Pentyl, Decyl, Tetradecyl derivatives Threaded/Schlieren type.

## RESULTS AND DISCUSSION

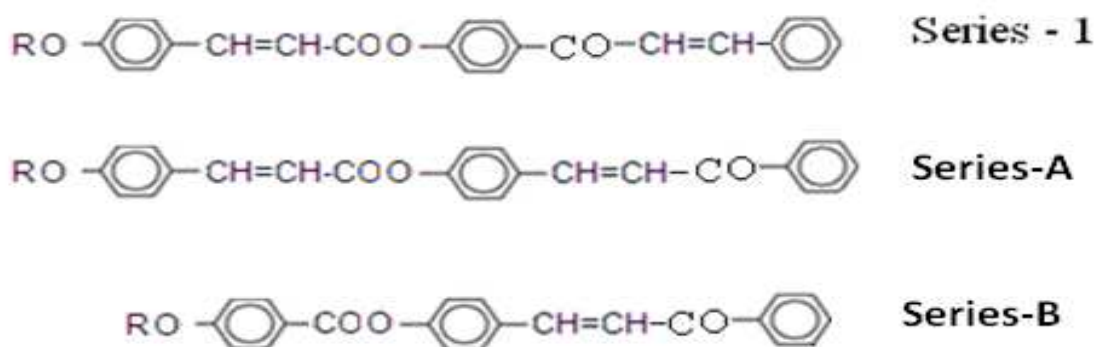
Liquid crystal property induced in presently investigated novel series by linking two nonliquid crystal components viz. cis 4-n-alkoxy cinnamoyloxy acid/ its corresponding acid chloride and  $\alpha$ -4-Hydroxy benzoyl  $\beta$ -phenyl ethylene. Pentyloxy to hexadecyloxy homologues are enantiotropically nematogenic without exhibition of smectogenic property, while the rest of the homologues i.e. methoxy to butyloxy homologues are nonliquid crystals. Transition temperature of the homologues as determined by an optical hot stage polarizing microscope and recorded in table-2 are plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end groups.

**Table-2: Transition Temperatures of series in °C**

Compound no.	n-alkyl group -C <sub>n</sub> H <sub>2n+1</sub> (n)	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	1	-	-	155.0
2	2	-	-	148.0
3	3	-	-	180.0
4	4	-	-	170.0
5	5	-	141.0	169.0
6	6	-	125.0	173.0
7	8	-	123.0	157.0
8	10	-	129.0	152.0
9	12	-	127.0	150.0
10	14	-	132.0	148.0
11	16	-	128.0	139.0

A phase diagram (Figure-1) is obtained by joining like or related points. Phase diagram in figure-1 indicates that, solid-isotropic or Nematic transition curve follows a zigzag path of rising and falling tendency with overall descending tendency with alternating transition temperatures. Nematic-isotropic transition curve adopts descending tendency as series is ascended and behaves in normal expected manner. Odd-even effect observed for nematic-

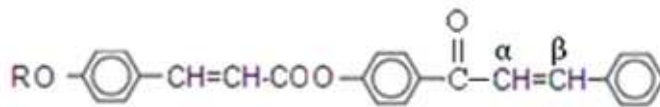
isotropic transition curve. Mesomorphic phaselength vary between 11 °C to 48 °C at hexadecyloxy and hexyloxy homologues respectively. Thus series under discussion is entirely nematogenic with absence of smectogenic character. Nonmesomorphic tendency of methoxy to butyloxy derivatives observed is due to their high crystallizing tendency arising from their resultant molecular rigidity and flexibility [1,2,3] related to intermolecular end to end attractions and stabilization energy stored ( $\Delta H$ ) at room temperature at constant pressure. The molecules of nonliquid crystal homologues are unable to resist thermal vibrations exposed upon them, and intermolecular binding forces are weakened to such an extent that, sample substance under examination sharply transforms from crystalline solid state to isotropic liquid state without passing through an intermediate state of existence, called liquid crystal state or mesomorphic state. The molecule of pentyloxy to hexadecyloxy homologues are capable of withstanding thermal vibrations exposed upon them as a consequence of their favorable resultant molecular rigidity and flexibility. Under such situation molecules of sample substances under microscopic examination disalign at an angle less than ninety degree on the plane of the surface at particular temperature  $T_1$  and continue to resist exposed vibrations upto higher temperature  $T_2$  with maintenance of molecules in floating condition. Thus, molecules show nematogenic mesophase between  $T_1$  and  $T_2$ . Nematic mesophase disappears beyond  $T_2$  because molecules lie on the plane of floating surface at higher temperature above  $T_2$  reversibly. The magnitudes of anisotropic forces of intermolecular forces of attractions between  $T_1$  and  $T_2$  become favourable to form nematic mesophase. However molecules acquire exposed heat energy to adopt high order of disorder or randomness or entropy ( $\Delta S$ ) beyond  $T_2$  and exhibit isotropic state. The range of temperature between  $T_1$  and  $T_2$  is called the range of liquidcrystallinity or phaselength of a mesophase, which ranges minimum of eleven degree at hexadecyloxy homologue to a maximum of forty eight degree centigrade at the hexyloxy homologue. Absence of smectic property of nematogenic homologues of presently investigated series 1 is attributed to the absence of lamellar packing of molecules in the crystal lattices of respective homologues of series under discussion. Odd-even effect observed for nematic-isotropic transition curve and variation in mesomorphic properties from homologue to homologue in the same series is attributed to the sequentially added methylene unit. The mesomorphic properties of the present series 1 including its thermal stability (Table-3) etc. compared with structurally similar other homologous series A [10] and B [9] as shown below in figure-2.



**Figure-2 : Structurally similar series**

Presently investigated homologous series 1 and A are isomeric with each other but they differ in their position of  $>CO$  group linked directly with middle phenyl ring in series-1 while it is linked directly with third phenyl ring in series A, Otherwise everything identical i.e. three phenyl rings, left and right flexible end groups  $-OR$  and  $-H$  and central group  $-CH=CH-COO-$ . Homologous series 1 and B differ with respect to their central groups i.e.  $-CH=CH-COO-$  replaced by  $-COO-$  and  $-CO-CH=CH-$  replaced by isomeric group  $-CH=CH-CO-$ , otherwise three phenyl rings and flexible end groups  $-OR$  and  $-H$  are identical. Series A and B differs only by central group Viz,  $-CH=CH-COO-$  in place of  $-COO-$ . Differences mentioned in the molecular structures among series 1, A and B are responsible for the variations of mesomorphic properties and the degree of mesomorphism including thermal stabilities of the structurally similar homologous series. Table-3 represents average thermal stabilities of series 1, A and B.

Homologous Series :



$\alpha$ -4-[-4'-n-Alkoxy Cinnamoyloxy] benzoyl  $\beta$ -phenyl ethylenes.

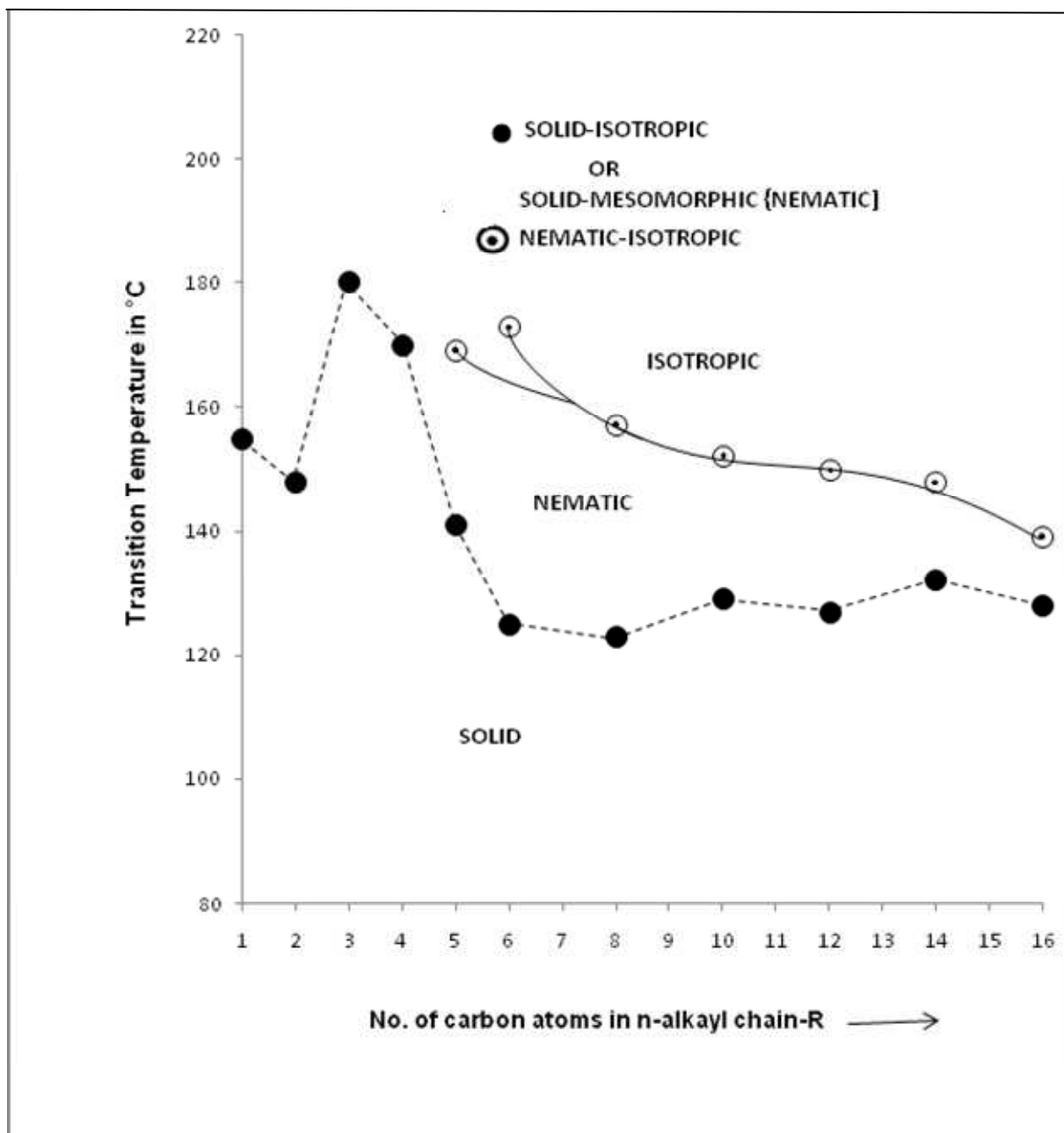


Figure : 1 Phase Behavior of Series

Table-3 : Average Thermal stabilities in °C

Series	Average transition temperatures in °C		
	Series (I)	Series(A)	Series(B)
Smectic-Nematic or isotropic	-	-	106.66 (C <sub>10</sub> -C <sub>14</sub> )
Commencement of smectic phase			C <sub>10</sub>
Nematic-isotropic	155.4 (C <sub>5</sub> -C <sub>16</sub> )	144.5 (C <sub>6</sub> -C <sub>16</sub> )	119.8 (C <sub>8</sub> -C <sub>16</sub> )
Commencement of Nematic mphase	C <sub>5</sub>	C <sub>6</sub>	C <sub>8</sub>

All the homologous series 1,A, B contains three phenyl rings, and end groups –OR and –H as common identical features but differences lie in their central bridges. Therefore though molecular flexibilities due to –OR and –H remains unaltered but molecular rigidity is predominantly altered and played main role in alteration of molecular rigidity[1,2,3]. Table-3 shows that nematic-isotropic thermal stability gradually decreases from series 1 to A to B. Smectic thermal stability of series 1 and A are Nil, while it is 106.66 of series B. The absence of smectic character in series 1 and A suggests that, lamellar packing in the crystal lattices of respective molecules belonging to series 1 and A is hindered by –CH=CH-COO- central group. While, the same is not hindered by –COO- central group occupying at an identical position bridging first and middle phenyl rings. The descending order of nematic mesophase thermal stability from series 1<A<B; can be attributed to the positional difference of >CO group i.e. placing of -CO group attached directly to the middle phenyl ring which strengthens intermolecular polarity which comfortably and favourably allows to form statistically parallel orientational order of molecules causing end to end attractions in floating condition[11]. Thus, nematic mesophase commences from fifth homologue of the series 1 while it commences from sixth and eighth homologues of the series A and B respectively. Thus, as –CO group occupies its position away from middle phenyl ring ( nearer to third phenyl ring ) reduced nematic thermal stability and later commencement of nematic mesophase. The commencement of smectic mesophase takes place from tenth homologue of the series B while it does not occur till the last hexadecyloxy homologue of the series 1 and A. Homologous series 1 and A bridges first and middle phenyl rings by –CH=CH-COO- central group while, in case of series B, the first and middle phenyl rings are bridged through –COO- central group. Vinyl carboxy group is relatively longer than a carboxy group ( series B) by –CH=CH- unit. This longness causes difference in molecular length to breadth ratio and molecular polarity, polarizability, molecular rigidity and extent of noncoplanarity caused by respective molecules [6,7]. Thus additional –CH=CH- unit of series 1 and A causes relatively more noncoplanarity than only –COO-group ( with absence of –CH=CH- unit ) due to a twist obtained, as the oxygen atoms of the –CH=CH-COO- group bump into the nonbonded adjacent hydrogen atoms of aromatic phenyl ring. On account of this difference, the extent of molecular noncoplanarity induced by –CH=CH-COO- central group is relatively (in series 1 and A ) more than the similar effect caused by a shorter central bridge –COO- (in series B). On account of this difference[4,6,7] of extent of noncoplanarity a smectic mesophase (formation of sliding layered arrangement of molecules from lamellar packing ) commences earlier from decyloxy homologue in series B but it does not commence till the last hexadecyl derivative of the series 1 and A. Thus smectic phase occur at the cost of nematic phase in series B. Hence, nematic-isotropic thermal stability of series B is relatively lower than the series 1 and A as realized from present investigation. The variation of mesomorphic properties for the same homologue from series to series is attributed to the right terminal end group of fixed polarity, But the right terminal of fixed polarity for all the homologous series 1, A and B under present comparison is identically same i.e. -H. Therefore, such variation of mesomorphic properties for the same homologue from series to series is attributed to the varying central groups –CH=CH-COO- and –COO- only.

### CONCLUSION

Presently investigated homologous novel series is :

- (1) Entirely nematogenic without exhibition of smectogenic character.
- (2) Vinyl carboxy group is favorably nematogenic whereas carboxy group is favorably smectogenic.
- (3) A molecule consisted of three phenyl rings, the presence of –CO- group directly linked to last phenyl ring i.e. –CH=CH-CO gives rise to a nematogenic homologues of low thermal stability and thermal stability increases on shifting of –CO- group from third phenyl ring ( right to left ) to middle phenyl ring i.e. –CO-CH=CH- central group, i.e. Nematogenic group efficiency order on the basis of thermal stability is –CO-CH=CH- > -CH=CH-CO-.
- (4) Shifting of >CO group causes variation of molecular rigidity and flexibility which affects to the physical properties of a substance.

**Acknowledgement**

Authors acknowledge the thanks to the all members of the management of Bai Jivkor Lallubhai trust, Principal Dr. R.R.Shah and Head, Chemistry department Dr.R.B.Patel of K.K.Shah Jarodwala Maninagar science college for their kind and valued co-operation in the present investigation. Also thanks are due to the vaibhav laboratory for analytical services and to the chemistry department, Arts and Science college, Godhara.

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