



# World Scientific News

An International Scientific Journal

WSN 181 (2023) 164-175

EISSN 2392-2192

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## **A synthesis and mesophase behaviour of homologous series: 4-(4'-n-alkoxy cinnamoyloxy) azo benzenes 4''ethyl carboxylate with terminal ester group as a ethyl carboxylate**

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### **ABSTRACT**

A new homologous series 4-(4'-n-alkoxy cinnamoyloxy) azo benzenes 4''ethyl carboxylate is synthesized with a view to understand and establish the relation between mesogenic properties and structure of molecules. Ethyl to hexadecyl all twelve homologues are enantiotropically nematogenic. None of the homologues exhibit a smectogenic mesophase. An odd-even effect is observed in the transition curve. The average thermal stability is 280 °C and the nematogenic mesophase ranges from 10.0 °C to 130.0 °C. Thus, the series is of a middle ordered melting type with moderate nematogenic range. Analytical data confirm the structure of the compounds, and the mesomorphism was identified by optical microscopy. The mesogenic properties are compared with structurally similar compounds.

**Keywords:** Liquid crystal, smectogenic phase, nematic phase, mesophase

## 1. INTRODUCTION

Liquid crystals are an attractive field of material science, that exhibit peculiar properties that deal with the intermediate between those of liquids and crystals. These materials can flow like liquids while also displaying the structure and order of crystalline solids. Because of the special properties that have enabled for applications in a range of industries, including displays, sensors, and liquid crystal research, also known as the science of liquid crystal materials, has attracted a lot of interest. Mesogens have a flexibility and polarizability in molecules so its show a various applications along with LCs. Liquid crystals inherent molecular interactions and structures have also undergone extensive study, which makes them essential for the development of potential displays with superior qualities<sup>[1-5]</sup>. The nematic phase is a special state of matter in which positional symmetry is absent yet the molecules exhibit long-range order. This phase, where the molecules organize themselves in a parallel or perpendicular orientation to a certain direction, known as the director axis, is frequently seen in liquid crystals.

The lack of any spatial order in the nematic phase produces properties that are very different from those of traditional liquids. Nematic fluids offer a wide range of uses in a variety of industries because of their special features, including display technologies, optical and electro-optical devices, and chemical sensors.<sup>[6-8]</sup> Smectic phase formed within a narrow temperature range, display orderly arranged in various dimensions it can be useful for displays, and optical devices. Researchers paid close attention to promising qualities and adaptability of smectic and nematic mesogens, which has widely used to creation of potential display devices.<sup>[9-14]</sup> In the present study, we have synthesized new homologous series and studied for liquid crystal properties our synthesized compound show nematic and smectic phase, which may be useful for development of display devices. All the derivatives was characterized by analytical techniques. POM investigation and DSC analysis was carried out for studied of liquid crystalline property.

## 2. MATERIALS AND METHODS

4-hydroxybenzaldehyde, piperidine, pyridine, alkyl bromides, anhydrous K<sub>2</sub>CO<sub>3</sub>, alkyl bromides (R-Br), phenol, *p*-amino benzoic acid, HCl, NaOH, NaNO<sub>2</sub>, DCC, DMAP and 4-hydroxy-3-methoxybenzaldehyde (vanillin) were purchased from Avra Chemical, India. Acetone and MDC solvents were purchased from Finar and further purified by usual established method. TLC plates (silica gel 60 F254 silica-aluminum plates) were purchased from Merck. FT-IR spectra was carried out in KBr pellet method and further analysed in the range of 3800-560 cm<sup>-1</sup> by Bruker TENSOR 27. <sup>1</sup>H and spectra: The spectra were recorded on a Bruker Advance (400 MHz), in CDCl<sub>3</sub> Solvents where TMS is internal standard. The mesophase is identified by Polarizing Optical Microscope (Nikon Eclipse LV-100 POL) with temperature controlled heating stage.

## 3. RESULT AND DISCUSSIONS

### 3. 1. Synthesis of 4-*n*-Alkoxy Cinnamic acid (Compound A)

4-*n*-Alkoxybenzaldehyde were synthesized by refluxing 4-hydroxybenzaldehyde (1 equiv.) with corresponding *n*-alkyl bromides (1 equiv.) in the presence of anhydrous potassium

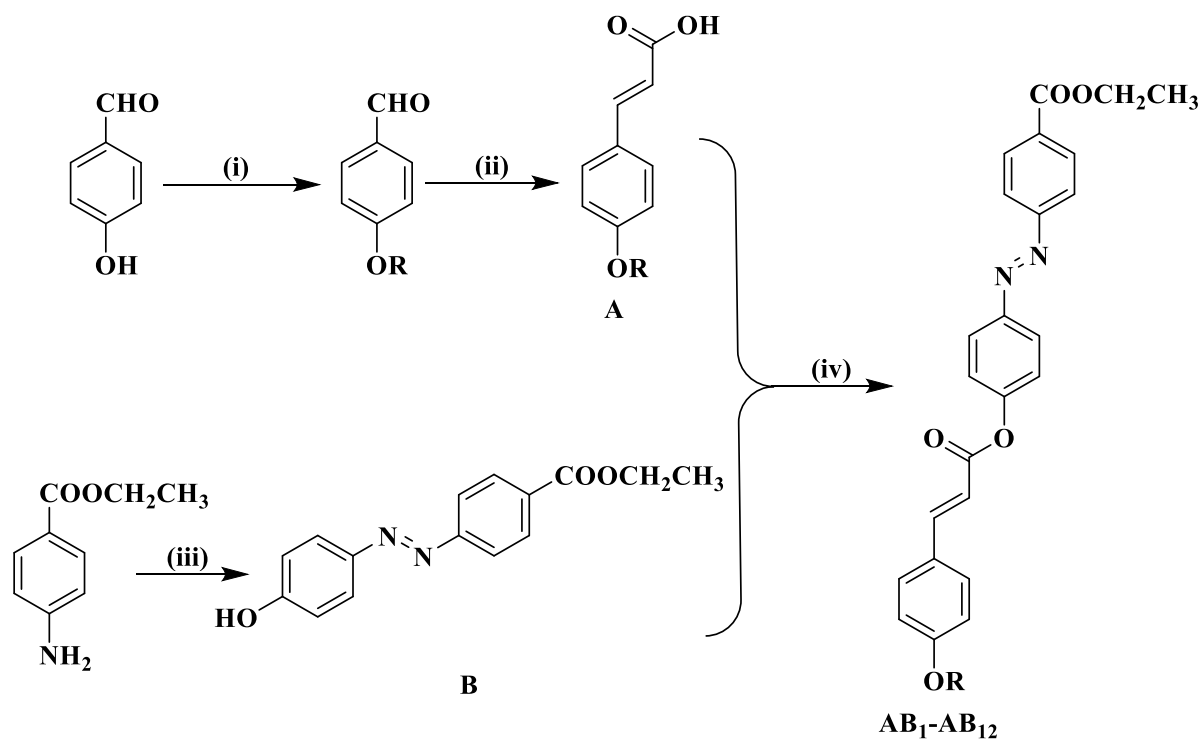
carbonate (1.2 equiv.) using acetone as a solvent.<sup>[15]</sup> The resulting 4-*n*-alkoxy benzaldehyde were reacted with malonic acid (1.2 equiv.) in the presence of 1–2 drops piperidine as catalyst and pyridine as solvent to yield corresponding trans-*p*-*n*-alkoxy Cinnamic acids (A).<sup>[16]</sup>

### 3. 2. Synthesis of 4'-hydroxy 4- ethyl carboxylate azo benzene (Compound B)

4'-hydroxy 4-ethyl carboxylate azo benzene (B) was prepared by previously established method.<sup>[17]</sup> The diazotization reaction is performed on ethyl 4-aminobenzoate with phenol by using NaNO<sub>2</sub>, HCl, and NaOH in an ice bath. The mass volume of the reaction was vigorously mixed for 2 hours. At that point, the azo dye product (B) conformed by using starch iodide and congo red paper, showing the positive test by turning to blue.

### 3. 3. Synthesis-(4'-*n*-alkoxy cinnamoyloxy) azo benzenes 4''ethyl carboxylate (Compound AB<sub>1</sub>-AB<sub>12</sub>)

4-*n*-alkoxy cinnamic acid were directly condensed with the 4'-hydroxy-4-ethyl carboxylate azo benzene by the reported method using DCC reagent and DMAP as catalyst in MDC solvent. The reaction was than stirred at room temperature for 12 hours.<sup>[18, 19]</sup> The reaction compilation was confirmed by using thin layer chromatography. Further, the product was purified The synthetic route to the series is mentioned below in **Scheme 1**.



**Scheme 1.** Reagent and conditions: (i) R-Br, K<sub>2</sub>CO<sub>3</sub>, dry Acetone, Reflux, 4-5 h; (ii) malonic acid, piperidine, pyridine, reflux, 3-4 h; (iii) Phenol, NaNO<sub>2</sub>, HCl, NaOH, 0-5 °C; (iv) DCC, DMAP, DCM, 12 hours, rt.

**Spectral Data:** Analytical data of some selected representative homologues viz; elemental analysis (Table 1), IR and  $^1\text{H NMR}$  data support the structure of molecules.

**Compound AB<sub>11</sub>;  $^1\text{H NMR } \delta$  (ppm):** 0.88 (t, 3H,  $-\text{CH}_3$  of  $-\text{OC}_{14}\text{H}_{29}$ ), 1.22-1.31 (m, 8H,  $-\text{CH}_2-$  of  $-\text{OC}_{14}\text{H}_{29}$ ), 1.34 (t, 3H,  $-\text{CH}_3$  of  $-\text{OC}_2\text{H}_5$ ), 1.46-1.83 (m, 16H,  $-\text{CH}_2-$  of  $-\text{OC}_{14}\text{H}_{29}$ ), 3.78 (t, 2H,  $-\text{OCH}_2-$  of  $-\text{OC}_{14}\text{H}_{29}$ ), 4.36 (t, 2H,  $-\text{OCH}_2-$  of  $-\text{OC}_2\text{H}_5$ ), 6.50 (d, 1H,  $J=16$  Hz, *trans* -CH=CH-), 6.79 (d, 1H,  $J=15.4$  Hz, *trans* -CH=CH-), 6.96-7.04 (m, 2H, Ar-H), 7.46-7.51 (s, 4H, Ar-H), 7.80-7.99 (m, 2H, Ar-H), 8.01-8.04 (d, 2H, Ar-H), 8.17-8.19 (m, 2H, Ar-H). **IR in  $\text{cm}^{-1}$ :** 829 (poly( $-\text{CH}_2-$ )<sub>n</sub> group), 871 (*p*-di substituted benzene ring), 987 (*trans* -CH=CH-group), 1123 ( $-\text{C}-\text{H}$  hydrocarbon), 1176 (C-N), 1228 (ether linkage), 1451 ( $-\text{N}=\text{N}-$ ), 1451, 1512, 1591 (aromatic ring) 1708 ( $-\text{COO}$ ), 2853 ( $-\text{C}-\text{H}$  str).

**Compound AB<sub>12</sub>;  $^1\text{H NMR } \delta$  (ppm):** 0.87 (t, 3H,  $-\text{CH}_3$  of  $-\text{OC}_{14}\text{H}_{29}$ ), 1.29-1.37 (m, 24H,  $-\text{CH}_2-$  of  $-\text{OC}_{14}\text{H}_{29}$ ), 1.36 (t, 3H,  $-\text{CH}_3$  of  $-\text{OC}_2\text{H}_5$ ), 1.70-1.80 (m, 4H,  $-\text{CH}_2-$  of  $-\text{OC}_{14}\text{H}_{29}$ ), 4.01 (t, 2H,  $-\text{OCH}_2-$  of  $-\text{OC}_{14}\text{H}_{29}$ ), 4.36 (t, 2H,  $-\text{OCH}_2-$  of  $-\text{OC}_2\text{H}_5$ ), 6.74 (d, 1H,  $J=16$  Hz, *trans* -CH=CH-), 6.97 (d, 1H,  $J=15.4$  Hz, *trans* -CH=CH-), 7.01-7.15 (m, 2H, Ar-H), 7.71-7.76 (s, 4H, Ar-H), 7.79-7.99 (m, 2H, Ar-H), 8.02-8.19 (d, 2H, Ar-H), 8.17-8.19 (m, 2H, Ar-H). **IR in  $\text{cm}^{-1}$ :** 823 (poly( $-\text{CH}_2-$ )<sub>n</sub> group), 866 (*p*-di substituted benzene ring), 990 (*trans* -CH=CH-group), 1106 ( $-\text{C}-\text{H}$  hydrocarbon), 1138 (C-N), 1254 (ether linkage), 1471 ( $-\text{N}=\text{N}-$ ), 1492, 1514, 1574, 1604 (aromatic ring) 1771 ( $-\text{COO}$ ), 2922 ( $-\text{C}-\text{H}$  str).

**Table 1.** Elemental analysis for compound AB<sub>11</sub> and AB<sub>12</sub>

Sr. No.	Molecular Formula	Elements % Found (% Calculated)		
		C	H	N
1.	C <sub>38</sub> H <sub>48</sub> N <sub>2</sub> O <sub>5</sub>	74.40% (74.48%)	7.82% (7.90%)	4.48% (4.57 %)
2.	C <sub>40</sub> H <sub>52</sub> N <sub>2</sub> O <sub>5</sub>	74.89% (74.97%)	7.04% (8.18%)	4.29% (4.37 %)

### 3. 4. POM and DSC investigation

Transition temperatures are observed through a polarizing microscope with heating stage as recorded in **Table 2**. Textures of homologues are confirmed by miscibility method. The enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) concept discussed qualitatively due to inadequate facility available to the source, otherwise quantitatively  $\Delta H$  and  $\Delta S$  values would have been determined from the peak value temperature of DSC scan.<sup>[20-26]</sup> In this series most compound showing two type of phases.

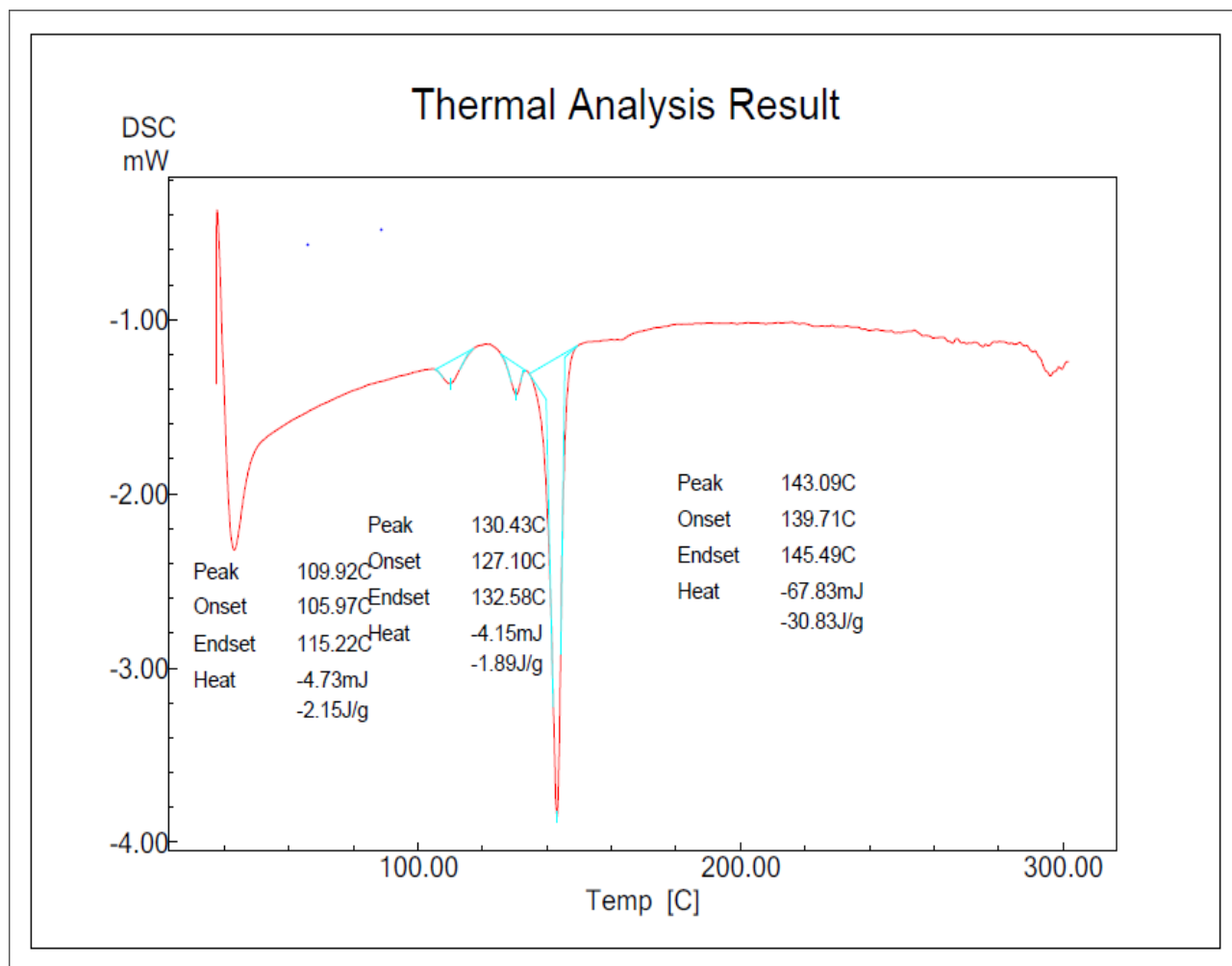
First compound converts solid to nematic phase than after nematic convert into smectic and lastly compound goes in isotropic phase. The phase behaviour texture of AB<sub>9</sub> (decyloxy) captured during POM investigation was showed in **Figure 1**.

In the DSC analysis, two compounds AB<sub>7</sub> and AB<sub>8</sub> was selected for spectral analysis. DSC spectra showed three peaks which indicates tow peaks for nematic and smectic phase and third for isotropic conversion mesophase present in molecules.

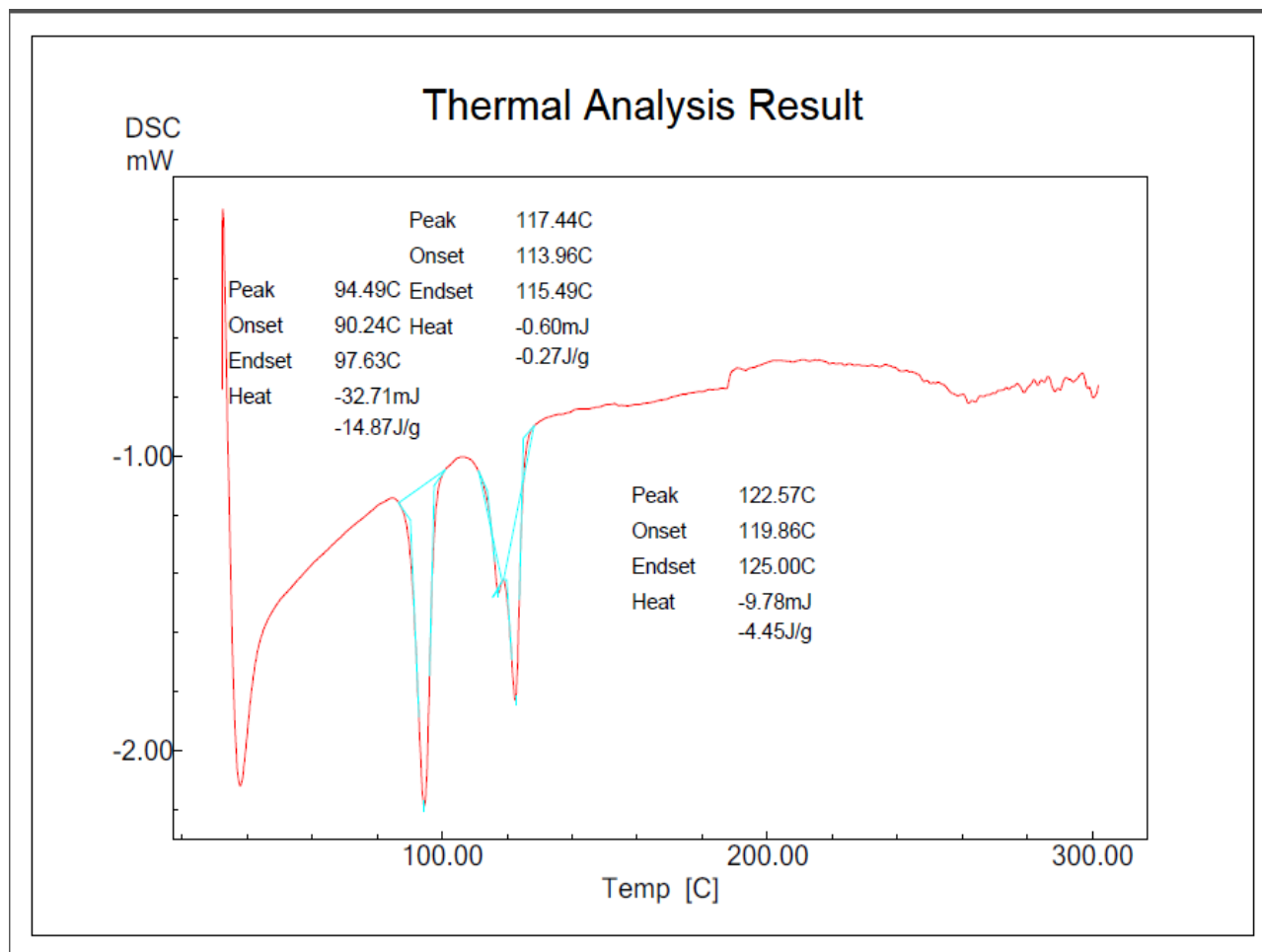
Compound AB<sub>7</sub> showed peak at 109 °C for the conversion of crystal to smectic phase and peak at 130 °C indicate the smectic to nematic phase (Figure 2). Compound AB<sub>8</sub> showed peak at 94 °C for the conversion of crystal to smectic phase and peak at 117 °C indicate the smectic to nematic phase (Figure 3).



Figures 1. POM images of compound AB<sub>9</sub>: solid (a); Nematic phase (b); smectic phase (c).



Figures 2. DSC data of compound AB<sub>7</sub> (Heptyloxy)



**Figures 3.** DSC data of compound AB<sub>8</sub> (Octyloxy)

Homologous series 4-(4'-n-alkoxy cinnamoyloxy) azo benzenes 4''ethyl carboxylate is entirely mesomorphic in character. All the members of the series display mesomorphism in enantiotropic manner with enough range of liquid crystallinity. All the homologues display mesomorphism of nematic type with exhibition of smectic mesophase (**Figure 3**). Transition temperatures of the homologues are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal as given in **Figure 4**. Smooth curves are drawn through like or related points. The solid-mesomorphic transition curve follows a zig-zag path of rising and falling nature. The nematic –isotropic transition curve exhibits first rises and falling tendency as the series is ascended except at the decyl homologue of the series in which nematic-isotropic transition curve abnormally behaves otherwise nematic isotropic transition curve behaves in a normal manner. Well known odd-even effect is observed in the nematic-isotropic transition curve with alternation of transition temperatures and merges into each other at the ninth homologue.

The texture of nematic mesophase is threaded and drop late type as clearly judged from the field of view of hot stage polarizing microscope while observing the samples. The mesomorphic-isotropic transitions are between 220.0 °C and 340.0 °C with mesomorphic range

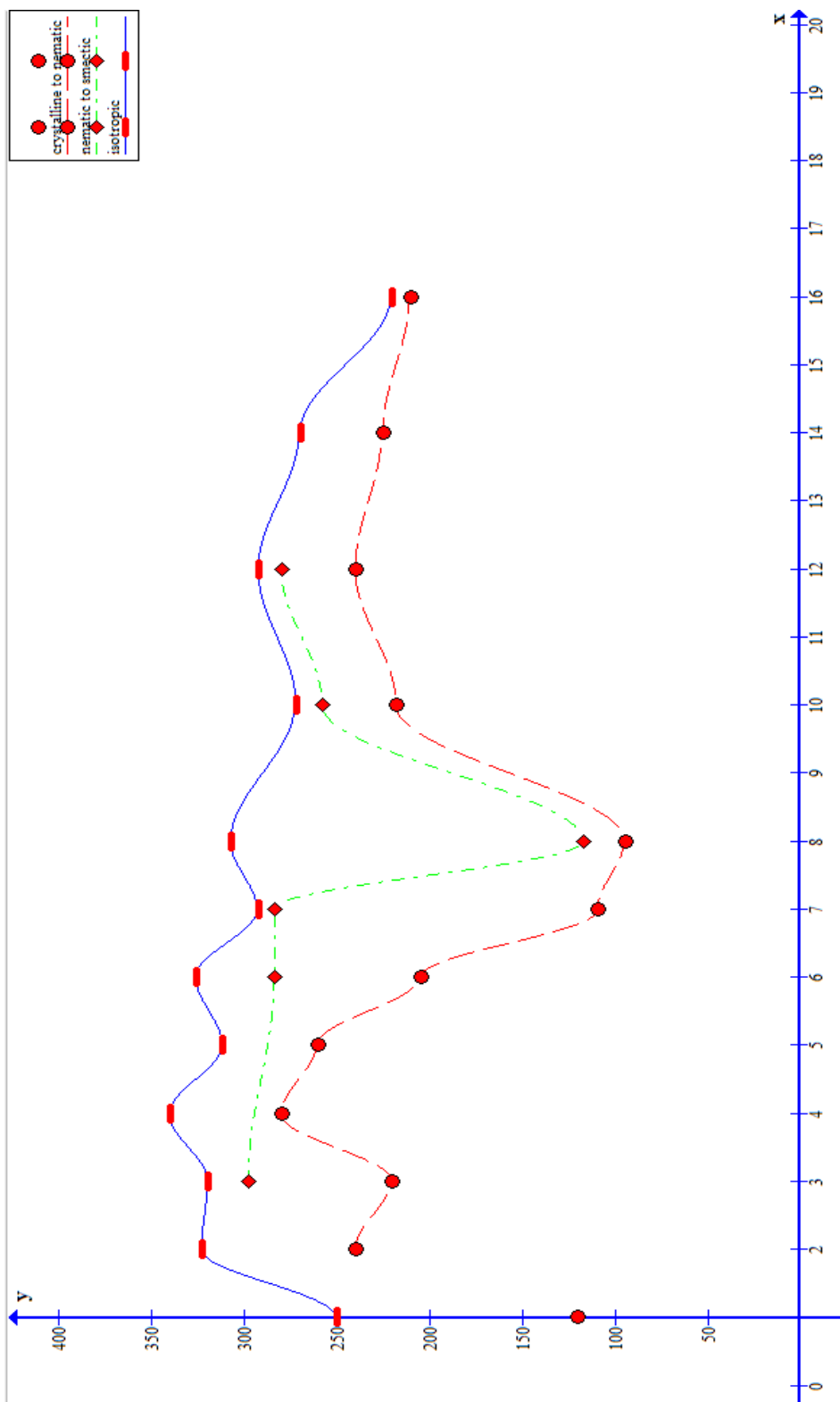
varying from 10.0 °C at the hexadecyl homologue to a maximum of 130.0 °C at the methyl homologue of the series. Thus, the present homologues series is considered as middle ordered melting type with wide range of liquid crystallinity. Display of nematic mesophase with exhibition of smectic character is attributed to the only statistically parallel orientations of molecules with maintenance of two-dimensional arrays of molecules in the floating condition. Formation of sliding layered arrangement of molecules does not occur in crystal structure for all compounds which resulted in absence of smectic mesophase for some of the homologue. Terminal –COOC<sub>2</sub>H<sub>5</sub> is less polar group which contributes to the weaker intermolecular end to end attractions.

Thus, all the members of the series are enantiotropic nematic in character. Ester group is generally nematogenic and present homologous series is also entirely nematogenic. Solid to nematic transition curve rises and falls in zigzag manner. However, rise and fall does not take place from homologue to homologue in regular manner due to presence of polar –COOC<sub>2</sub>H<sub>5</sub> end group. Emergence of odd-even effect in nematic-isotropic transition curve is observed due to presence of methylene units linked through oxygen atom as alkoxy group. This effect diminishes and disappears from tenth homologue and onwards because longer n-alkyl chain bends and coils as series is ascended. Thus, presence of odd or even number of methylene units does not contribute to odd-even effect beyond tenth homologue as series is ascended.

**Table 2.** Transition temperatures

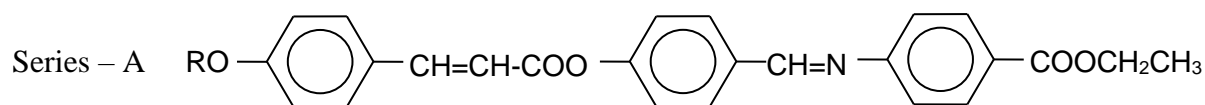
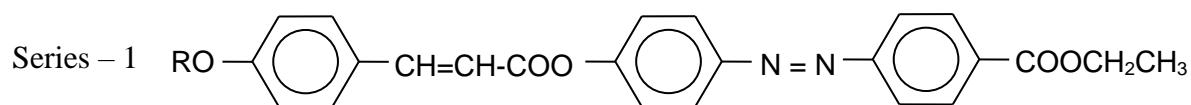
Sr. No.	<i>n</i> -Alkyl Group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	120	250
2	Ethyl	-	240	323
3	Propyl	220	298	320
4	Butyl	-	280	340
5	Pentyl	-	260	312
6	Hexyl	205	284	326
7	Heptyl	109	130	292
8	Octyl	94	117	307
9	Decyl	218	258	272
10	Dodecyl	240	280	292
11	Tetradecyl	-	225	270
12	Hexadecyl	-	210	220





**Figures 4.** Phase behaviour of compound AB<sub>1</sub>-AB<sub>12</sub>: No of carbon in alkyl chain vs Temperature





Average thermal stability and stage of commencement of mesophase formation are recorded in **Table 3** as under.

The present homologues series (1) is compared with structurally similar other homologous series (A).<sup>[27]</sup> For molecular characteristics and thermal stabilities which are shown in **Table 3**. The above homologous series (1) and (A) under discussion have the basic length due to three phenyl rings linked through central linking units –CH=CH-COO- and –N=N-, –CH=N- left n-alkoxy group and right terminal –COOC<sub>2</sub>H<sub>5</sub> functional group at para position. Hence, display of mesomorphic properties due to the molecular forces arising on account of these remains the same.

The homologous series (1) and (A) differ only at middle part of the molecules. Middle part is –N=N- bridge for series (1) while respect to –CH=N- bridge for series (A). Hence, the variation in mesomorphic characteristics has direct relation with central bridges.

The length to breadth ratio is diminished for series (1) as compared to series (A). Broadening of molecules increases intermolecular distance and hence it nearly the intermolecular forces of attractions on one hand while broadening of molecule increases polarizability of molecules and hence results in increase of intermolecular forces of attractions.

However, the net effective resultant forces of intermolecular attractions are capable to resist thermal vibrations and maintain only statistically parallel orientations of molecules in floating condition displaying nematogenic character with exhibition of smectic character.

Thus, forces of attractions are weakening due to broadening a molecule. Thus, in case of series (1) as compared to series (A) melting and transition temperatures of titled homologous series (1) are relatively nearly same than series (A).

**Table 3.** Average thermal stability

Series	Series - 1	Series - A
Nematic -isotropic	293.66 °C (C <sub>1</sub> - C <sub>16</sub> )	262.5 °C (C <sub>1</sub> - C <sub>16</sub> )
Commencement of nematic Phase	C <sub>1</sub>	C <sub>1</sub>
Total mesophase length in °C (Nm-Iso)	10 °C – 130 °C	8.0 °C - 75.0 °C.
C <sub>n1</sub> C <sub>n2</sub>	C <sub>16</sub> - C <sub>1</sub>	C <sub>14</sub> - C <sub>7</sub>

This is also reflected in relative thermal stability of series (1) and (A). Therefore, nematic-isotropic thermal stability for series (1) is nearly same than series (A). Thus, nematic group efficiency order with respect to type of linking central bridges i.e. middle part positional substitution is as under on the basis of average thermal stability.

#### **4. CONCLUSION**

In summary, we have synthesized azo ester based homologous series (AB<sub>1</sub>-AB<sub>12</sub>) by veering twelve alkyl chains on terminal of moieties. All compound were prepared with good yield by esterification in final step. All derivative were confirmed by FTIR and NMR analysis. Liquid crystalline behaviour of compounds was examined by POM and confirmed by DSC analysis. Titled homologous series is entirely nematogenic with short range of liquid crystallinity exhibition of smectic phase. Present investigation support the earlier view and raises credibility to the established views derived earlier. Study suggested that this mesogens could be useful for further investigation and fabrication of LCs.

#### **Acknowledgement**

Authors acknowledge thanks to the S.P.T. Science College, Godhra for research facilities services as and when needed. Authors obliged to Dr. M. B. Patel, Principal, S.P.T arts & Science College, Godhra for their valuable helping in laboratory facility. Authors acknowledge thanks to Dept. of chemistry, Saurashtra University, Rajkot for analytical and spectral services.

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