Available online at www.worldscientificnews.com

World Scientific News

An International Scientific Journal

WSN 188 (2024) 186-197 EISSN 2392-2192

A synthesis and mesophase behaviour of homologous series: 4-(4’-n-alkoxy benzoyloxy) 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 benzoyloxy) 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 281.25 °C and the nematogenic mesophase ranges from 42.0 °C to 248.25 °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

(Received 20 November 2023; Accepted 16 December 2023; Date of Publication 18 December 2023)

1. INTRODUCTION

The intriguing topic of liquid crystals in material science is characterised by their unique properties, which fall in between those of liquids and crystals. These materials have the order and structure of crystalline solids, yet they can flow like liquids. Owing to their unique characteristics, which have made them suitable for use in a variety of sectors, such as sensors and displays, liquid crystal research—also referred to as the science of liquid crystal materials—has garnered a lot of attention. Mesogens exhibit a variety of applications in conjunction with LCs due to their molecular flexibility and polarizability. Since liquid crystals' underlying chemical interactions and architectures have been thoroughly studied, they are crucial for the creation of future displays that have better features.[1-5]

Positional symmetry is lacking in the nematic phase, a unique condition of matter where molecules display long-range order. Liquid crystals usually exhibit this phase, when the molecules arrange themselves in a parallel or perpendicular orientation to a certain direction, known as the director axis. Nematic phases differ greatly from conventional liquids in their characteristics due to the absence of any spatial organisationNematic fluids have unique properties that make them useful in many different industries. These industries include chemical sensors, optical and electro-optical devices, and display technologies.[6–8] Smectic phase can be beneficial for displays and optical systems since it forms within a small temperature range and is shown orderly ordered in different dimensions. Researchers focused on the adaptability and promising properties of smectic and nematic mesogens, which have been widely employed to develop possible display systems [9–14]. In this work, we have created novel homologous series and examined their liquid crystal characteristics. The compounds we have created exhibit nematic and smectic phases, which may be helpful in the future development of display systems. Analytical methods were used to characterise each derivative. To investigate the liquid crystalline property, POM research and DSC analysis were done.

2. MATERIALS AND METHODS

4-hydroxybenzaldehyde, piperidine, pyridine, alkyl bromides, anhydrous K_2CO_3, alkyl bromides (R-Br), phenol, *p*-amino benzoic acid, HCl, NaOH, $NaNO_2$, 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) ware purchased from Merck. FT-IR spectra was carried out in KBr pellet method and further analysed in the range of 3800-560 cm^{-1} by Bruker TENSOR 27. ^{1}H and spectra: The spectra were recorded on a Bruker Advance (400 MHz), in $CDCl_3$ 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*-Alkox Benzoic acid (Compound A)

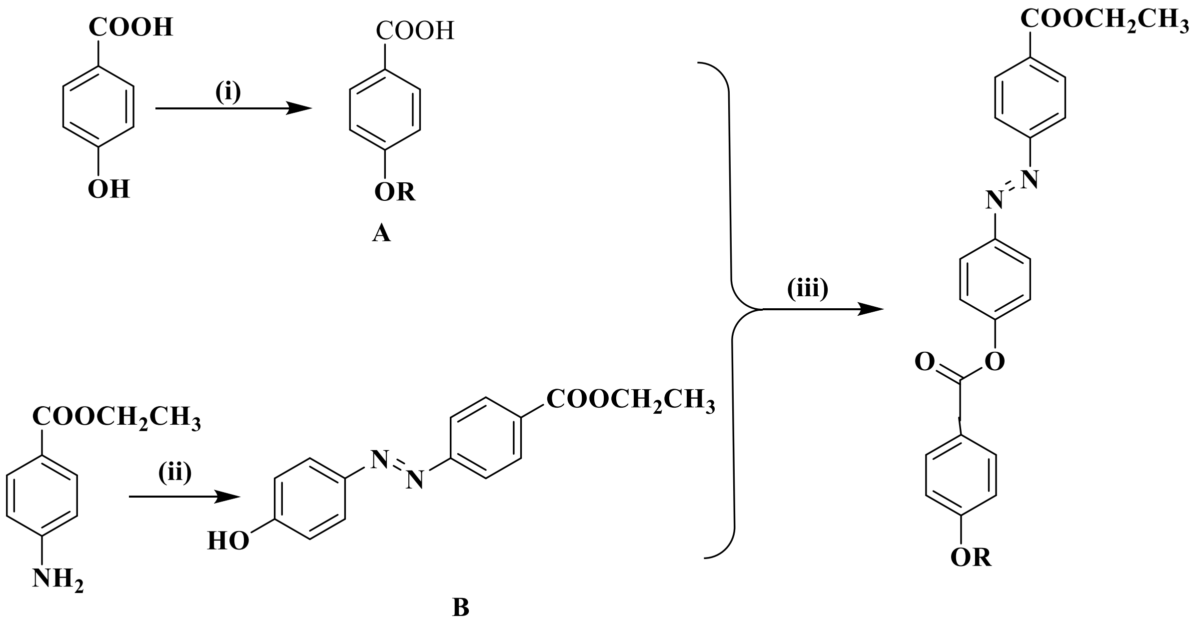
4-*n*-Alkoxybenzoic acid were synthesized by refluxing 4-hydroxybenzoic acid (1 equiv.) with corresponding *n*-alkyl bromides (1 equiv.) in the presence of anhydrous potassium carbonate (1.2 equiv.) using acetone as a solvent.[15] The resulting 4-*n*-alkoxy benzoic acid was purify by crystallization. (A).[16]

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.[17] The diazotization reaction is performed on ethyl 4-aminobenzoate with phenol by using $NaNO_2$, 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 Benzoyloxy) azo benzenes 4"ethyl carboxylate (Compound AB$_1$-AB$_{12}$)

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.[18, 19] 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.**



R = CnH2n+1,Where n = 1 to 8,10,12,14 and 16

Scheme 1. Reagent and conditions: (i) R-Br, K_2CO_3, dry Acetone, Reflux, 4-5 h; (ii) Phenol, $NaNO_2$, HCl, NaOH, 0-5 °C; (iii) DCC, DMAP, DCM, 12 hours, rt.

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

Compound AB_8; ^{1}H NMR δ (ppm): 0.87 (t, 3H, $-CH_3$ of $–OC_8H_{17}$), 1.24-1.29 (m, 8H, $-CH_2-$ of $– OC_8H_{17}$), 1.34 (t, 3H, $-CH_3$ of $–OC_2H_5$), 1.41-1.86 (m, 16H, $-CH_2-$ of $– OC_8H_{17}$), 4.03 (t, 2H, $-OCH_2-$ of $-OC_8H_{17}$), 4.39 (t, 2H, $-OCH_2-$ of - OC_2H_5), 6.96-7.0 (m, 2H, Ar-H), 7.3-7.4 (s, 4H, Ar-H), 7.94-7.96 (m, 2H, Ar-H), 8.02-8.04 (d, 2H, Ar-H), 8.17-8.21 (m, 2H, Ar-H). **IR in cm^{-1}:** 845 poly($-CH_2-$)$_n$ group), 878 (*p*-di substituted benzene ring),, 1123 (-C-H hydrocarbon), 1175 (C-N), 1222 (ether linkage), 1417 (-N=N-), 1487, 1494, 1510 (aromatic ring) 1732 (-COO), 2854 (-C-H str).

Compound AB_{10}; ^{1}H NMR δ (ppm): 0.86 (t, 3H, $-CH_3$ of $–OC_{10}H_{21}$), 1.24-1.27 (m, 24H, $-CH_2-$ of $– OC_{10}H_{21}$), 1.30 (t, 3H, $-CH_3$ of $–OC_2H_5$), 1.80-1.82 (m, 4H, $-CH_2-$ of $– OC_{10}H_{21}$), 4.03 (t, 2H, $-OCH_2-$ of $-OC_{10}H_{21}$), 4.39 (t, 2H, $-OCH_2-$ of - OC_2H_5), 6.97-6.99 (m, 2H, Ar-H), 7.38-7.40 (s, 4H, Ar-H), 7.94-7.96 (m, 2H, Ar-H), 8.02-8.05 (d, 2H, Ar-H), 8.15-8.17 (m, 2H, Ar-H). **IR in cm^{-1}:** 844 (poly($-CH_2-$)$_n$ group), 880 (*p*-di substituted benzene ring), 1109 (-C-H hydrocarbon), 1144 (C-N), 1276 (ether linkage), 1467 (-N=N-), 1510, 1577, 1606 (aromatic ring) 1724 (-COO), 2953 (-C-H str).

Table 1. Elemental analysis for compound AB_{11} and AB_{12}

Sr. No.	Molecular Formula	Elements % Found (% Calculated)		
		C	H	N
1.	$C_{23}H_{20}N_2O_5$	68.31% (68.48%)	4.98% (5.90%)	6.93% (6.97 %)
2.	$C_{24}H_{22}N_2O_5$	68.89% (69.97%)	5.30% (6.18%)	6.69% (7.37 %)

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 (ΔH), entropy change (ΔS) concept discussed qualitatively due to inadequate facility available to the source, otherwise quantitatively ΔH and ΔS values would have been determined from the peak value temperature of DSC scan.[20-26] In this series most compound showing two type of phases. First compound converts solid to nematic phase than after nematic convert into sematic and lastly compound goes in isotropic phase. The phase behaviour texture of AB_9 (decyloxy) captured during POM investigation was showed in **Figure 1**. In the DSC analysis, two compounds AB_6 and AB_{12} 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_6 showed peak at 90 °C for the conversion of crystal to smectic phase and no other peak observe at other tempreture indicate the smectic to nematic phase is not present **(Figure 2)**. Compound AB_{12} showed peak at 116 °C for the conversion of crystal to smectic phase and peak at 243 °C indicate the smectic to isotropic phase **(Figure 3)**.

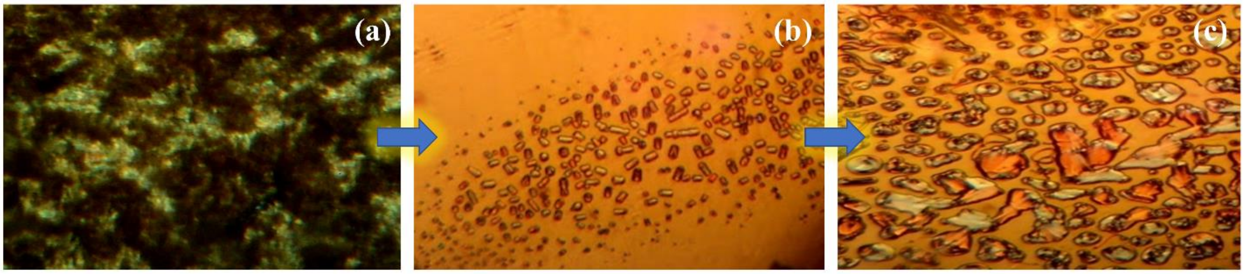
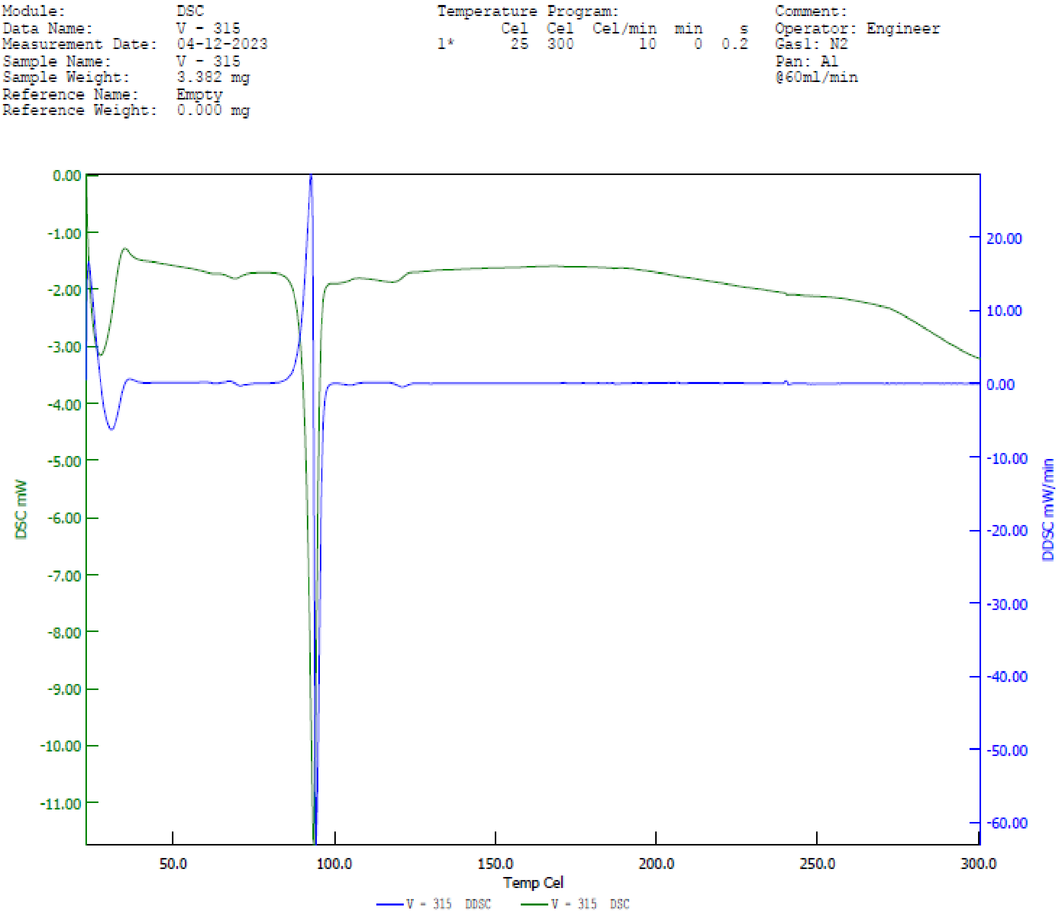


Figure 1. POM images of compound AB_9: solid (a); Nematic phase (b); sematic phase (c).



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Module:            DSC                 Temperature Program:               Comment:
Data Name:         V - 315                   Cel  Cel  Cel/min  min    s  Operator: Engineer
Measurement Date:  04-12-2023          1*     25  300       10    0  0.2  Gas1: N2
Sample Name:       V - 315                                                Pan: Al
Sample Weight:     3.382 mg                                               @60ml/min
Reference Name:    Empty
Reference Weight:  0.000 mg
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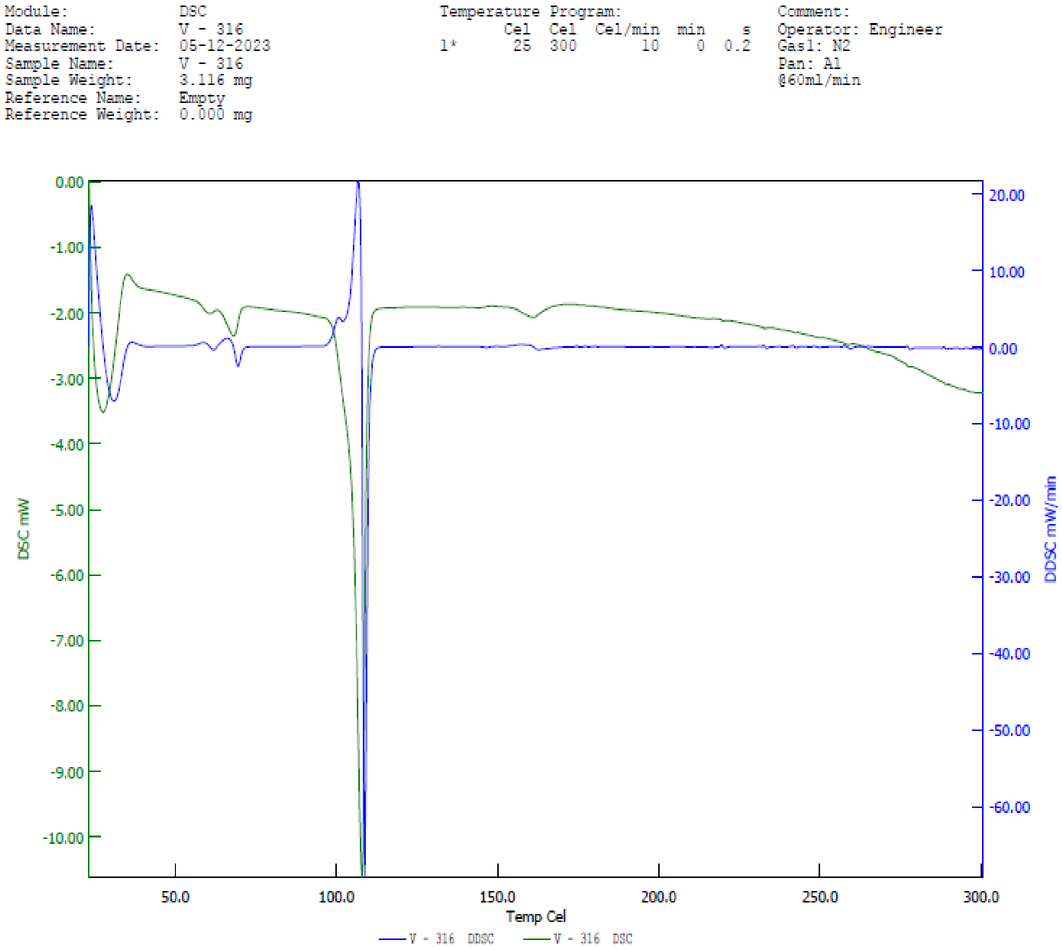
Figure 2. DSC data of compound AB_6 **(**Hexcyloxy**)**

Homologous series 4-(4'-n-alkoxy benzoyloxy) 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**.



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Module:            DSC                    Temperature Program:                 Comment:
Data Name:         V - 316                         Cel  Cel  Cel/min  min   s  Operator: Engineer
Measurement Date:  05-12-2023             1*        25  300       10    0 0.2  Gas1: N2
Sample Name:       V - 316                                                     Pan: Al
Sample Weight:     3.116 mg                                                    @60ml/min
Reference Name:    Empty
Reference Weight:  0.000 mg
```

Figure 3. DSC data of compound AB_{12} (Dodecyloxy)

Smooth curves are drawn through like or related points. The solid-mesomorphic transition curve follows a parallel 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 nineth 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 90.0 °C and 338.0 °C with mesomorphic range varying from 10.0 °C at the hexadecyl homologue to a maximum of 28.0 °C at the hexyl 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 –$COOC_2H_5$ 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 –$COOC_2H_5$ end group. Emergence of parallel 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 parallel effect beyond tenth homologue as series is ascended.

Table 2. Transition temperatures

Sr. No.	***n*-Alkyl Group**	**Transition temperatures in °C**		
		Smectic	**Nematic**	**Isotropic**
1	Methyl	90	309	338
2	Ethyl	99	292	326
3	Propyl	-	-	-
4	Butyl	114	264	300
5	Pentyl	-	-	-
6	Hexyl	90	-	287
7	Heptyl	-	-	-
8	Octyl	162	255	267
9	Decyl	181	235	252
10	Dodecyl	116	-	243
11	Tetradecyl	-	-	-
12	Hexadecyl	195	219	237

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). [27]

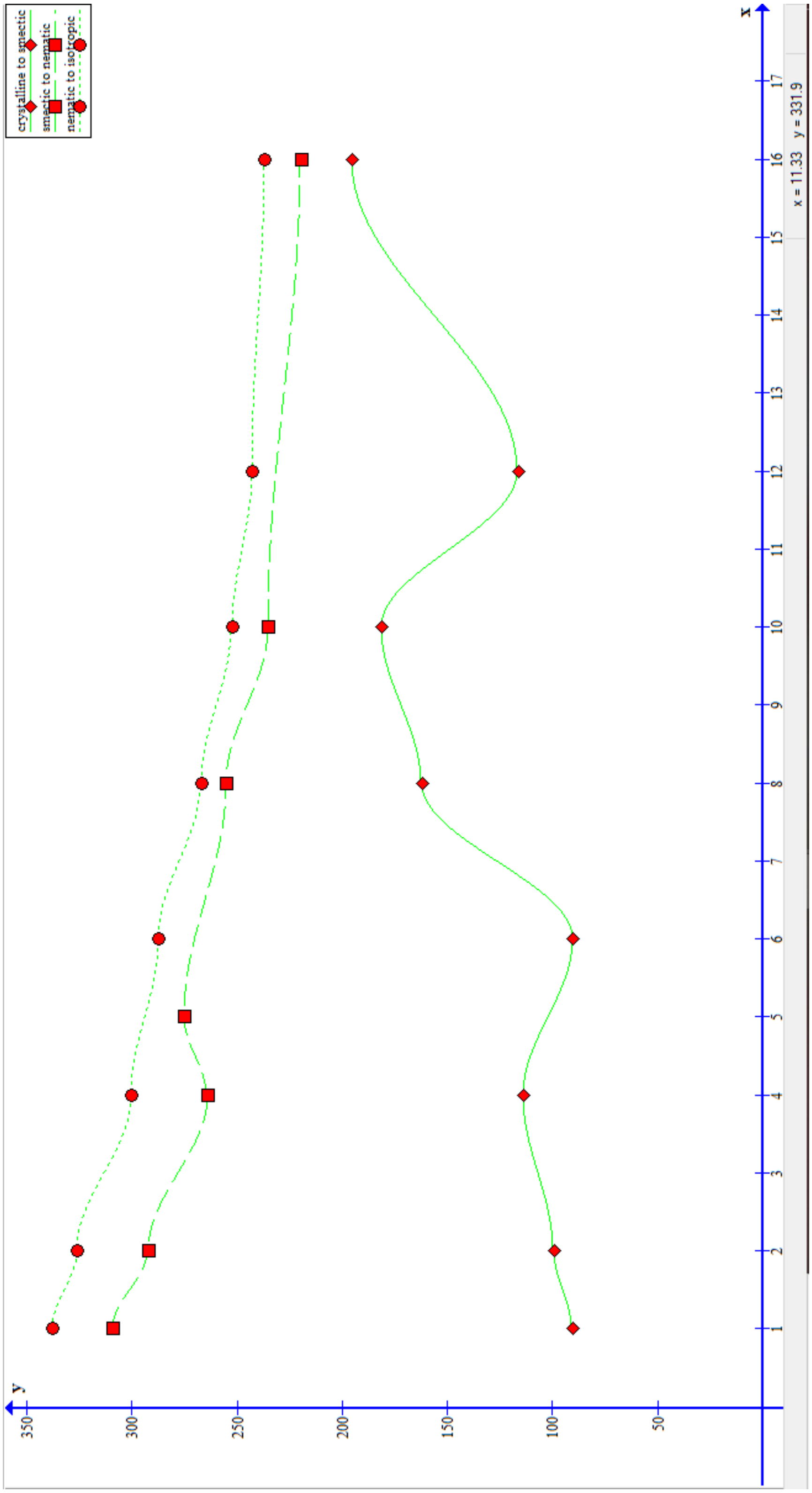
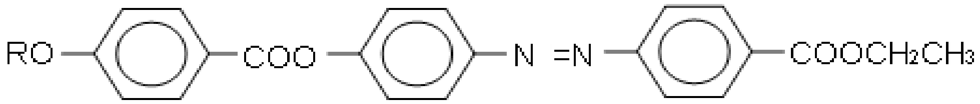
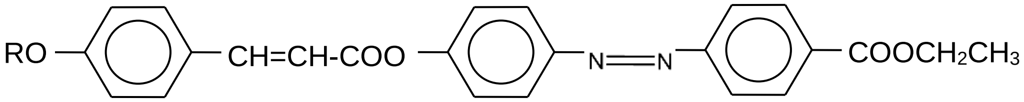


Figure 4. Phase behaviour of compound AB$_1$-AB$_{12}$: No of carbon in alkyl chain vs Temperature



Series – 1



Series – A

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 –COO- and –N=N-, –N=N- left n-alkoxy group and right terminal $–COOC_2H_5$ 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 –N=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). 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.

Table 3. Average thermal stability.

Series	**Series - 1**	**Series – A**
Nematic -isotropic	281.25 °C (C_1 - C_{16})	293.66 °C (C_1 - C_{16})
Commencement of nematic Phase	C_1	C_1

Total mesophase length in °C (Nm-Iso)	42 °C – 248°C	10 °C – 130°C
Cn_1 Cn_2	C_{16} - C_1	C_{16} - C_1

4. CONCLUSION

In summary, we have synthesized azo ester based homologous series (AB_1-AB_{12}) 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, Saurastra University, Rajkot for analytical and spectral services.

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