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A synthesis and mesophase behaviour of homologous series: 4-(4'-n-alkoxy benzoyloxy) phenyl azo 4"acetyl benzene

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ABSTRACT

A new homologous series 4-(4'-n-alkoxy benzoyloxy) phenyl azo 4"acetyl-benzene 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

1. INTRODUCTION

The peculiar properties of liquid crystals, which lie halfway between those of liquids and crystals, make them an interesting issue in material science. These substances flow like liquids,

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but they have the structure and order of crystalline solids. Liquid crystal materials, or the science behind them, have attracted a lot of attention due to their special properties that have allowed them to be used in a wide range of applications, including displays and sensors. With respect to LCs, mesogens have a wide range of uses because of their molecular flexibility and polarizability. Liquid crystals are essential for the development of more advanced displays in the future since their underlying chemical interactions and structures have been extensively investigated.[1-5]

The nematic phase is a special state of matter where molecules exhibit long-range order, but it lacks positional symmetry. This phase, which is typically seen in liquid crystals, occurs when the molecules align themselves to either a parallel or perpendicular direction, which is referred to as the director axis. Nematic phases are characterised by a lack of spatial structure, which sets them apart from normal liquids. Nematic fluids are valuable in a wide range of sectors due to their special qualities. Chemical sensors, optical and electro-optical devices, and display technologies are some of these sectors. [6–8] Smectic phase, which occurs in a narrow temperature range and appears orderly in many dimensions, can be advantageous for optical systems and displays. Scholars concentrated on the versatile and auspicious characteristics of smectic and nematic mesogens, which have been extensively utilised in the development of potential display systems. [9–14]

We have generated new homologous series in this work and analysed their liquid crystal properties. Our compounds show both nematic and smectic phases, which could be useful for developing display systems in the future. All of the derivatives were characterised using analytical techniques. The liquid crystalline property was examined using DSC analysis and POM research.

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. ^1H 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)

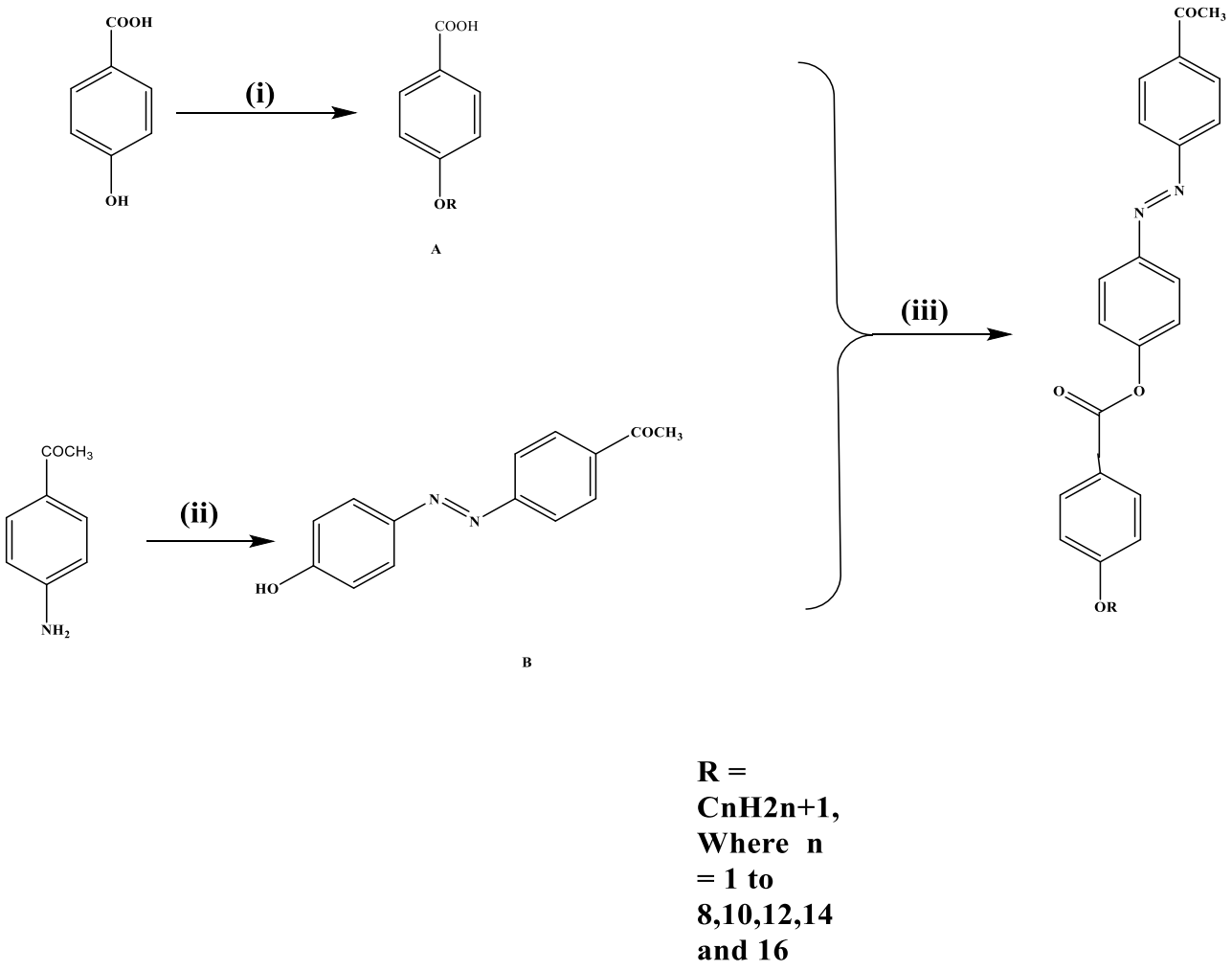
4-*n*-Alkoxybenzoic acid were synthesized by refluxing 4-hydroxybenzoic acid (1 equiv.) with corresponding *n*-alkyl bromides (1 equiv.) in the presence of anhydrous potassium carbonate (1.2 equiv.) using acetone as a solvent.[15] The resulting 4-*n*-alkoxy benzoic acid was purify by crystallization.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

3. 2. Synthesis of 4'-hydroxy 4- acetyl azo benzene (Compound B)

4'-hydroxy 4- acetyl azo benzene (B) was prepared by previously established method.[17] The diazotization reaction is performed on 4-amino acetophenone 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"acetyl benzene (Compound AB_1-AB_{12})

4-*n*-alkoxy benzoic acid were directly condensed with the 4'-hydroxy 4- acetyl 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.**



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_1; ^{1}H NMR δ (ppm): 2.67 (S, 3H, -CH_3 of –$COCH_3$) , 3.91 (S, 3H, -OCH_3 of -OCH3), 6.99-7.02 (m, 2H, Ar-H), 7.3-7.4 (s, 4H, Ar-H), 7.97-7.99 (m, 2H, Ar-H), 8.02-8.04 (d, 2H, Ar-H), 7.9-8.1 (m, 2H, Ar-H). **IR in cm^{-1}:** 851 poly(-CH_2-)$_n$ group), 875 (*p*-di substituted benzene ring),, 1119 (-C-H hydrocarbon), 1171 (C-N), 1226 (ether linkage), 1423 (-N=N-), 1498, 1513, (aromatic ring) 1724 (-CO), 2854 (-C-H str).

Compound AB_6; ^{1}H NMR δ (ppm): 0.90 (t, 3H, -CH_3 of –OC_6H_{13}), 1.24 (m, 10H, -CH_2- of – OC_6H_{13}), 2.64 (S, 3H, -CH_3 of –$COCH_3$), 1.48-1.59 (m, 4H, -CH_2- of – OC_6H_{13}), 4.038 (t, 2H, -OCH_2- of -OC_6H_{13}), 7.97-8.099 (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}:** 849 (poly(-CH_2-)$_n$ group), 875 (*p*-di substituted benzene ring), 1122 (-C-H hydrocarbon), 1140 (C-N), 1271 (ether linkage), 1497 (-N=N-), 1412,1497,,1513 (aromatic ring) 1723 (-CO), 2934 (-C-H str).

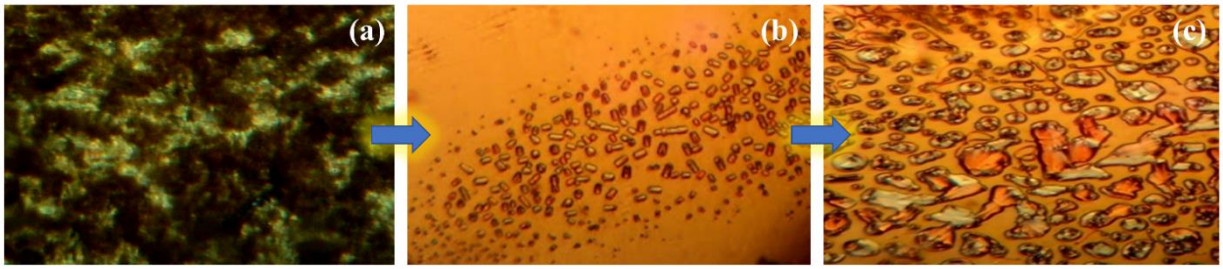
Table 1. Elemental analysis for compound AB_1 and AB_2

Sr. No.	Molecular Formula	Elements % Found (% Calculated)		
		C	H	N
1.	$C_{22}H_{18}N_2O_4$	70.58% (70.88%)	4.85% (4.90%)	7.48% (7.97 %)
2.	$C_{23}H_{20}N_2O_4$	71.12% (71.97%)	5.19% (5.78%)	7.21% (7.37 %)

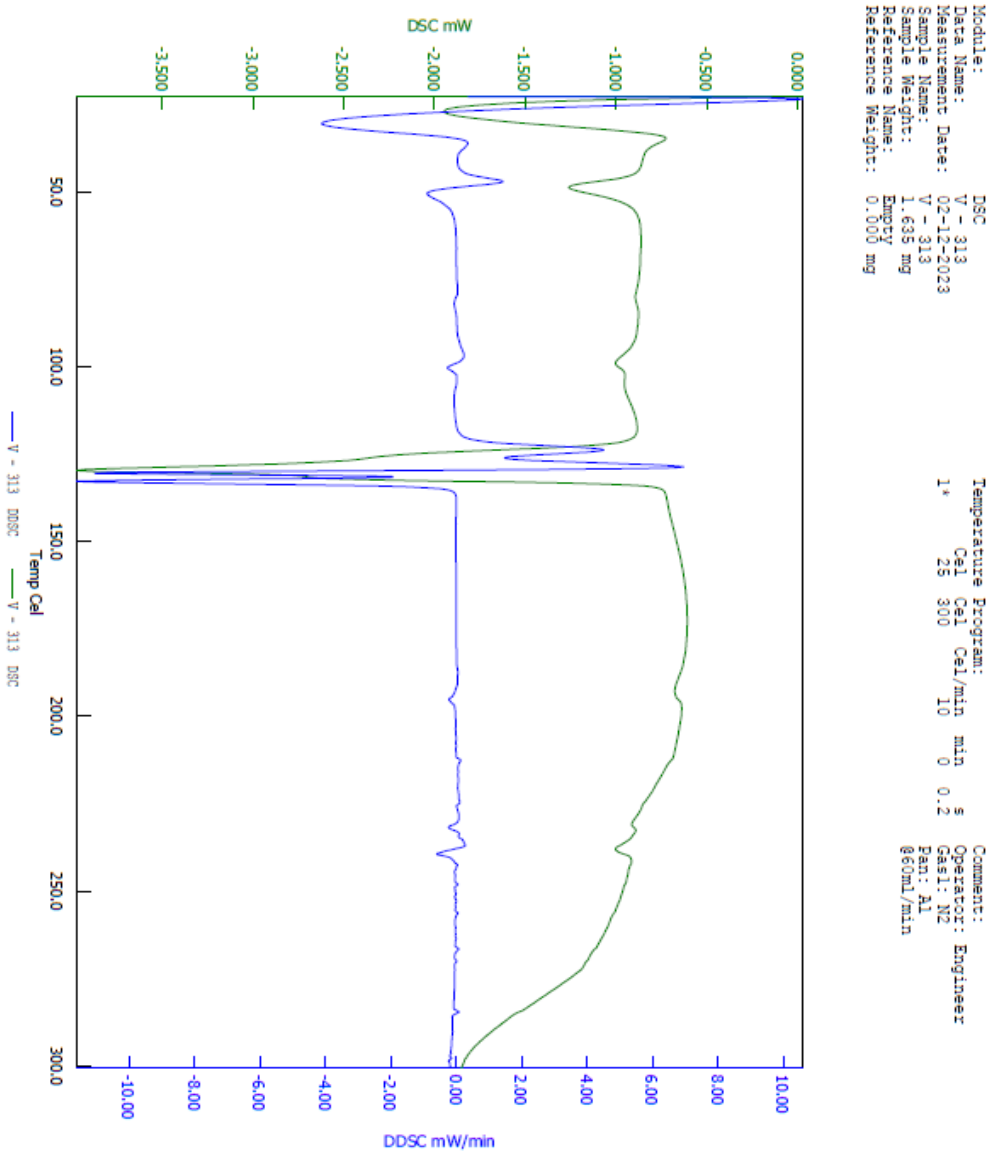
3. 4. POM and DSC investigation

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.

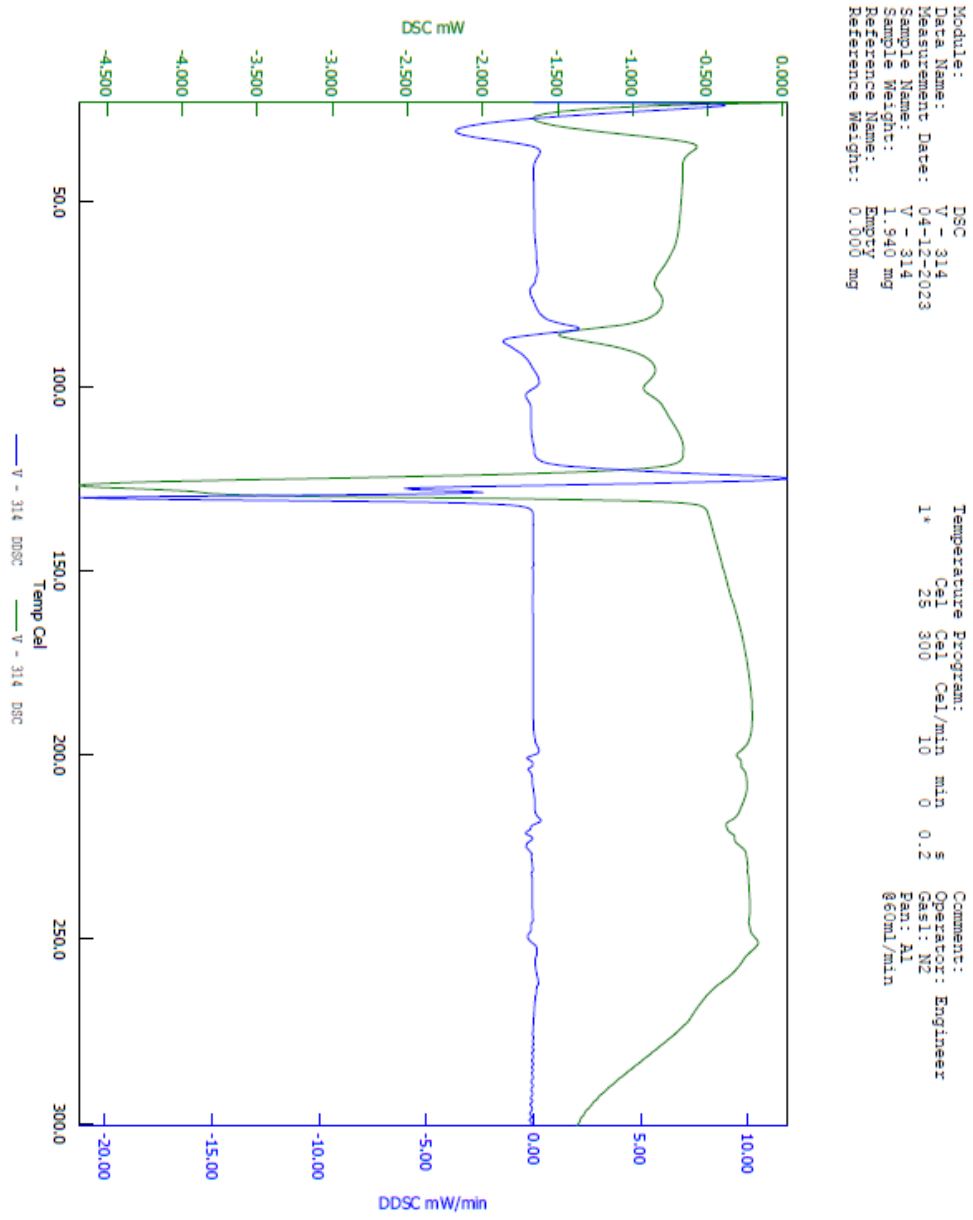
First compound converts solid to nematic phase than after nematic convert into sematic and lastly compound goes in isotropic phase. The phase behaviour texture of AB_9 (decyloxy) captured during POM investigation was showed in **Figure 1**. In the DSC analysis, two compounds AB_8 and AB_{10} was selected for spectral analysis. DSC spectra showed two peaks which indicates one peaks for nematic phase and secound for isotropic conversion mesophase present in molecules. Compound AB_8 showed peak at 148 °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_{10} showed peak at 140 °C for the conversion of crystal to nematic phase and other peak indicate the nematic to isotropic phase **(Figure 3)**.



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



Figures 2. DSC data of compound AB_8 **(**Octcyloxy**)**



Figures 3. DSC data of compound AB_{10} (decyloxy)

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**. Smooth curves are drawn through like or related

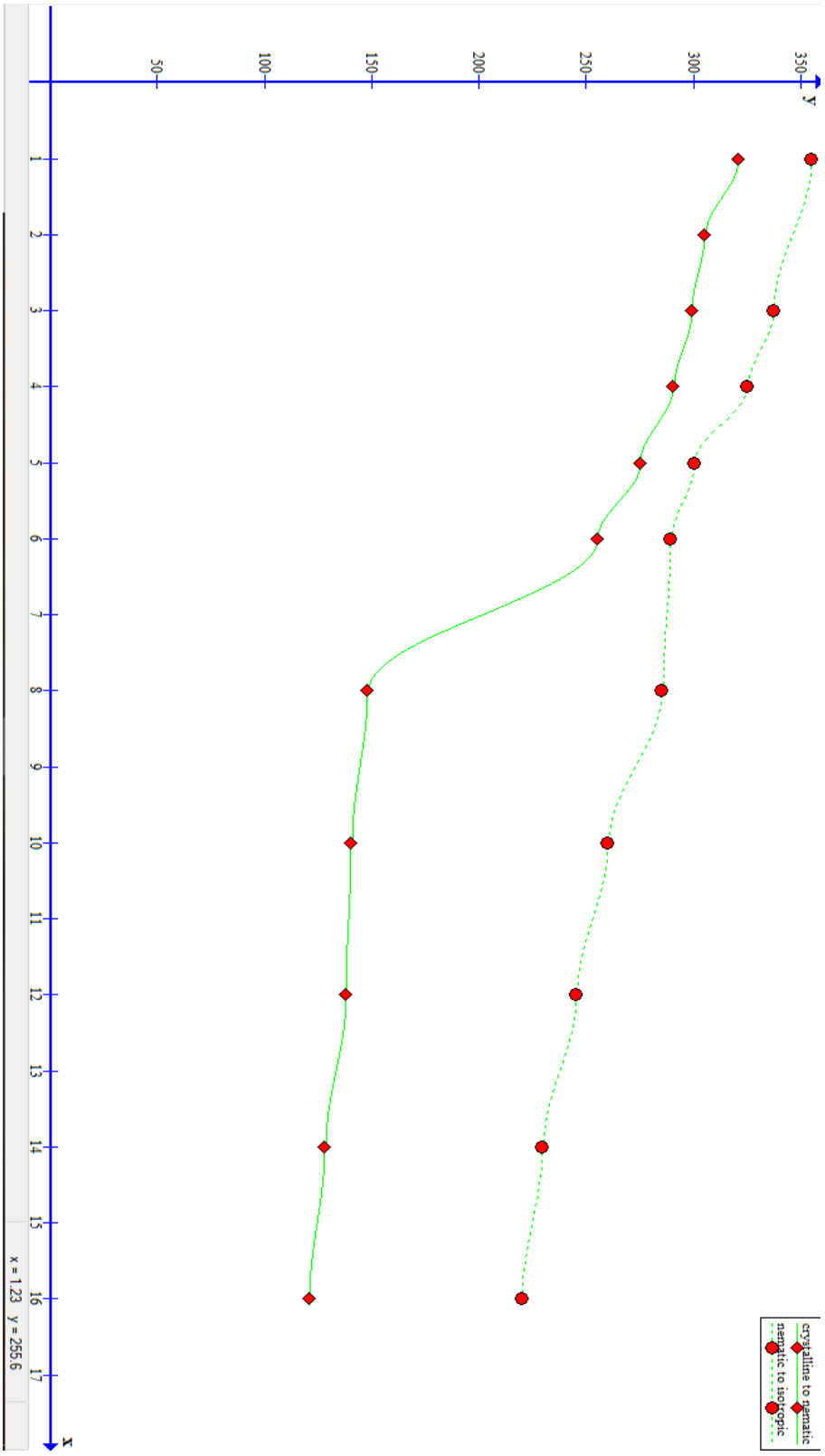
points. The solid-mesomorphic transition curve follows a parallel path of rising and falling nature. The nematic –isotropic transition curve exhibits first rises and falling tendency as the series is ascended except at the decyl homologue of the series in which nematic-isotropic transition curve abnormally 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.

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] 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.

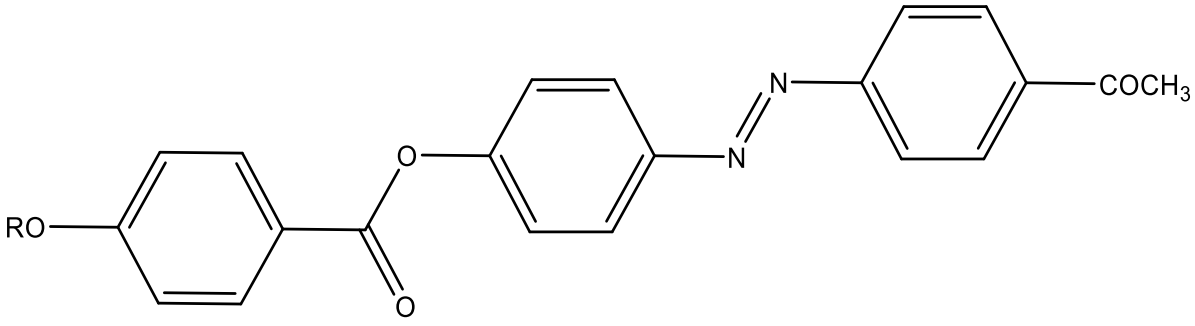


Figures 4. Phase behaviour of compound AB_1-AB_{12}: No of carbon in alkyl chain vs Temperature

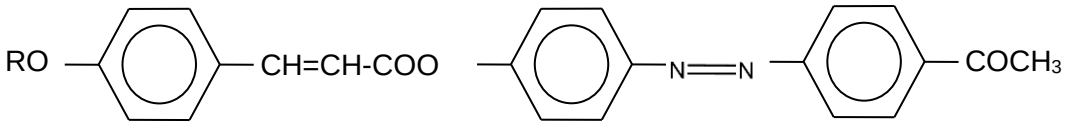
Table 2. Transition temperatures

Sr. No.	*n*-Alkyl Group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	321	355
2	Ethyl	-	305	345
3	Propyl	-	299	337
4	Butyl	-	290	325
5	Pentyl	-	275	300
6	Hexyl	-	255	289
7	Heptyl	-	-	-
8	Octyl	-	148	285
9	Decyl	-	140	260
10	Dodecyl	-	138	245
11	Tetradecyl	-	128	229
12	Hexadecyl	-	121	220

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.



Series – 1



Series – A

Table 3. Average thermal stability

Series	Series – 1	Series – A
Nematic -isotropic Commencement of nematic Phase	290.0 °C (C_1 - C_{16}) C_1	136.83 °C (C_1 - C_{16}) C_1
Total mesophase length in °C (Nm-Iso) Cn_1 Cn_2	25 °C – 138 °C C_{16} - C_1	25 °C – 120 °C 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.

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