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A Synthesis and Mesophase behaviour of Homologous Series: (4’-n-alkoxy Benzoyloxy) 1-(4-(4-hydroxy 3- methoxy benzylidene) amino) phenyl) ehane-1-one

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ABSTRACT

A new homologous series (4’-n-alkoxy Benzoyloxy) 1-(4-(4-hydroxy 3- methoxy benzylidene) amino) phenyl) ehane-1-one 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.

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1. INTRODUCTION

The liquid crystal compound behaves special molecule behaviour, it totally different from organic molecules, because other organic compound possesses only one transition during melting process, while liquid crystal compound shows multiple transition during melting process. The general organic compound shows on solid-liquid transition, while liquid crystal compound shows solid-mesophase transition. In liquid crystal compound during heating, a molecule passed through special and spatial arrangement. This special spatial arrangement gives uniqueness of compound. Based on this arrangement, the liquid crystal shows specific mesophase such as a smectic mesophase, nematic mesophase, climatic mesophase, etc. The building block of liquid crystal compound is specific. The major target of present work is investigating liquid crystal properties depends on structure [1-7].

The specific transition occurs a specific temperature, it known as a transition temperature and depends on structural arrangement of molecule. The all mesophase available for specific temperature range is called mesophase length; it also influence by design of structure. The structural feature such a number of rigid core, position of group, number of groups, types of groups, these all factor affecting on mesogenic behaviour of compounds. The present investigated research included structural similar series differentiate by right terminal group [8-11].

All binding connectivity of structure are same, molecular length of structure of both series are same, position of group same, only distinguish by right terminal group based on their polarity. The structural confirmation carried out by different spectroscopic method such ^{1}H-NMR and IR. The percentage of element present in compound is carried out by elementary analysis. The mesophase behaviour and liquid crystal confirmation carried out by DSC [12] and POM [13-14] method. The polarities of group is positive factor for liquid crystal behaviour.

2. MATERIALS AND METHODS

4-hydroxybenzoic acid, acetone, methanol, n-hexane, ethyl acetate, alkyl bromides, anhydrous K_2CO_3, alkyl bromides (R-Br), phenol, *p*-amino acetophenone, HCl, NaOH, DCC, DMAP and 4-hydroxy-3 methoxy benzaldehyde.

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 analyzed 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]

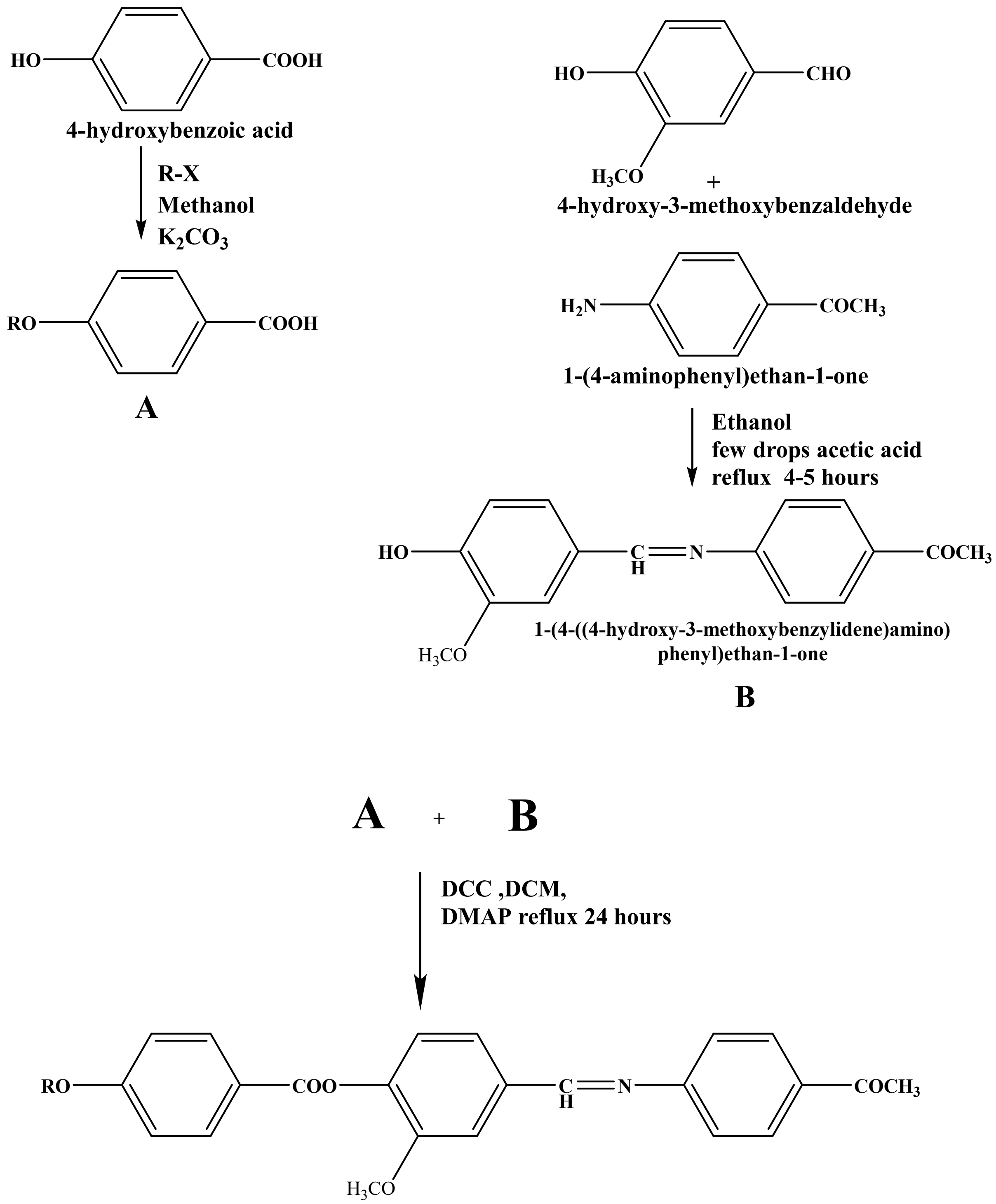
3.2. Synthesis of 1-(4-(4-hydroxy 3- methoxy benzylidene) amino) phenyl) ehane-1-one (Compound B)

1-(4-(4-hydroxy 3- methoxy benzylidene) amino) phenyl) ehane-1-one (B)

Was prepared by previously established method.[17] The Schiff base reaction is performed on 4-amino acetophenone with vanillin by using few drop of HCl and heat at 70 degree in an oil bath. The mass volume of the reaction was vigorously mixed for 2 hours. At that point, the Schiff base product (B) conformed by using TLC.

3.3. Synthesis-(4'-n-alkoxy Benzoyloxy) 1-(4-(4-hydroxy 3- methoxy benzylidene) amino) phenyl) ehane-1-one (Compound AB_1-AB_{12})

4-*n*-alkoxy benzoic acid were directly condensed with **1-(4-(4-hydroxy 3- methoxy benzylidene) amino) phenyl) ehane-1-one** 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$_3$; ^{1}H NMR δ (ppm): 8.39 (s, 1H, CH of CH=N), 8.24 (dd, 2H, Ar-H), 8.11 (dd, 2H, Ar-H), 7.66 (dd, 2H, Ar-H), 7.37 (m, 3H, Ar-H), 7.11 (m, 2H, Ar-H), 4.1 (t, 2H CH$_2$ of OCH$_2$), 3.98 (s, 3H, CH$_3$ of OCH$_3$), 2.70 (s, 3H, CH$_3$ of COCH$_3$), 1.83 (m, 2H, CH$_2$ of Alkyl Chain), 1.58 (m, 2H, CH$_2$ of Alkyl Chain), 1.25 (m, 12H (-CH$_2$-)n), 0.90 (s, 3H CH$_3$ of alkyl chain) **IR in cm^{-1}: :** 2942-2871 (C-H str), 1739 (C=O str), 1668 (CH=N str), 1508-1414 (Aromatic str), 1351 (Stretching of C-O in aster) , 1266-1134 (ether linkage), 1060 (C-C Str), 858 (str of poly CH$_2$ Group), 849-758 (Substituted benzene ring) cm^{-1}.

Compound AB$_4$; ^{1}H NMR δ (ppm): 8.44 (s, 1H, CH of CH=N), 8.18 (dd, 2H, Ar-H), 8.05 (dd, 2H, Ar-H), 7.73 (dd, 2H, Ar-H), 7.43 (m, 3H, Ar-H), 7.01 (m, 2H, Ar-H), 4.07 (t, 2H CH$_2$ of OCH$_2$), 3.94 (s, 3H, CH$_3$ of OCH$_3$), 2.65 (s, 3H, CH$_3$ of COCH$_3$), 1.85 (m, 2H, CH$_2$ of Alkyl Chain), 1.62 (m, 2H, CH$_2$ of Alkyl Chain), 1.28 (m, 12H (-CH$_2$-)n), 0.91 (s, 3H CH$_3$ of alkyl chain). **IR in cm^{-1}:** 2921-2854 (C-H str), 1743 (C=O str), 1677 (CH=N str), 1512-1410 (Aromatic str), 1366 (Stretching of C-O in aster) , 1270-1165 (ether linkage), 1026 (C-C Str), 852 (str of poly CH$_2$ Group), 844-761 (Substituted benzene ring) cm^{-1}

Table 1. Elemental analysis for compound AB$_1$ and AB$_2$.

Sr. No.	Molecular Formula	Elements % Calculated (% Found)		
		C	H	N
1.	$C_{33}H_{39}NO_5$	74.83% (74.51%)	7.42% (7.75%)	2.64% (2.32 %)
2.	$C_{31}H_{35}NO_5$	74.23% (74.71%)	7.03% (7.39%)	2.51% (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 one type of phases. First compound converts solid to nematic phase than after nematic convert into isotropic phase. The phase behaviour texture of AB$_3$ (octyloxy) captured during POM investigation was showed in **Figure 1**. In the DSC analysis, one compounds AB$_4$ was selected for spectral analysis. DSC spectra showed one peaks which indicates peaks for nematic phase, and then, after isotropic conversion, mesophase present in molecules. Compound AB$_4$ showed peak at 85 °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)**.

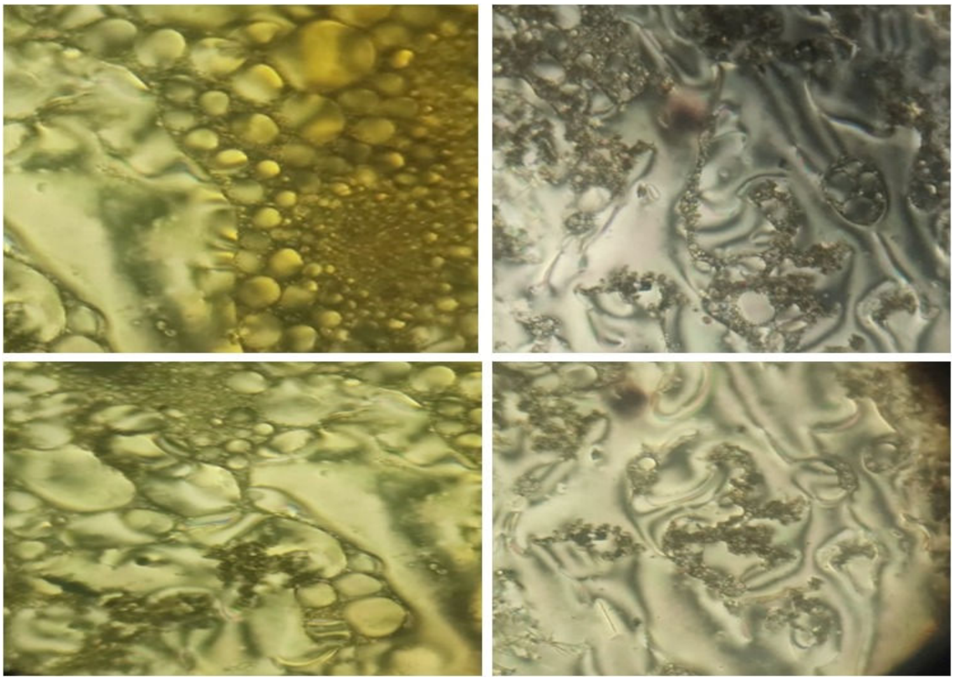


Figure 1. POM images of compound AB_3.

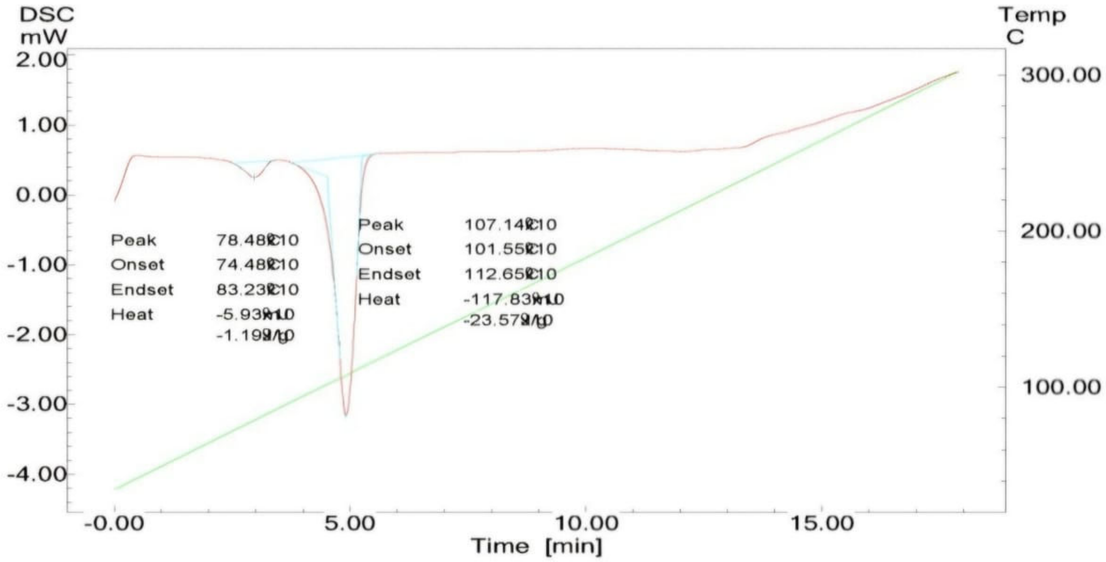


Figure 2. DSC data of compound AB_4 (decyloxy).

Homologous series **(**4’-n-alkoxy Benzoyloxy) 1-(4-(4-hydroxy 3- methoxy benzylidene) amino) phenyl) ehane-1-one is entirely mesomorphic in character. AB_3 after compound of the series, displays mesomorphism in enantiotropic manner with enough range of liquid crystallinity. All the homologues display mesomorphism of nematic type mesophase. 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 3**. Smooth curves are drawn through like or related points. The solid-mesomorphic transition curve follows a parallel path of falling nature.

The nematic –isotropic transition curve exhibits also falling tendency as the series is ascended homologue of the series. Well known linier effect is observed in the nematic-isotropic transition curve with parallar of transition temperatures. 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 79.0 °C and 145.0 °C with mesomorphic range varying from 4.0 °C at the tetradecyloxy homologue to a maximum of 6.0 °C at the octaloxy homologue of the series. Thus, the present homologues series is considered as middle ordered melting type with wide range of liquid crystallinity. Terminal –COCH3 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 falls in parallel manner. 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. Compounds	***n*-Alkyl Group**	**Transition temperatures in °C**		
		Smectic	**Nematic**	**Isotropic**
1	Butyl	-	-	145
2	Hexyl	-	-	132
3	Octyl	-	105	111
4	Decyl	-	93	98
5	Dodecyl	-	87	91
6	Tetradecyl	-	75	79

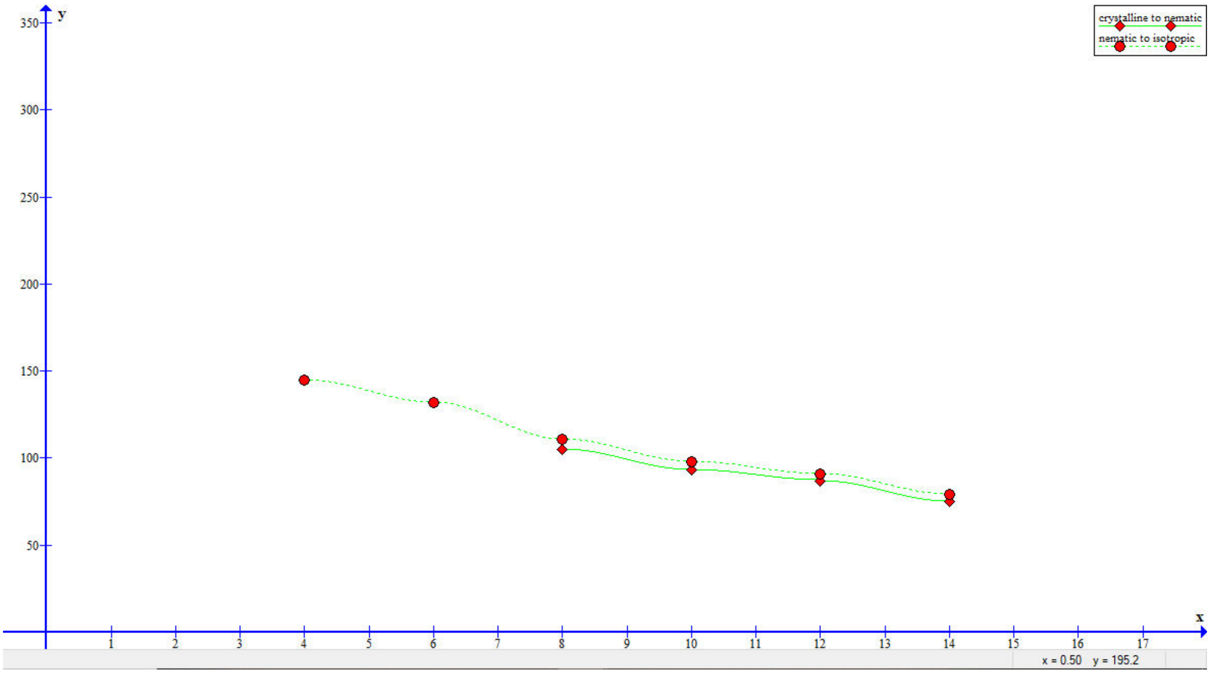
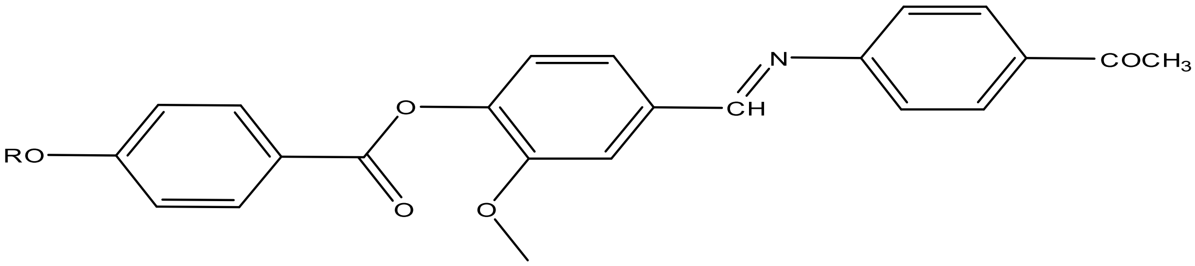
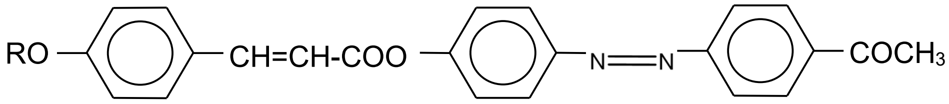


Figure 3. Phase behaviour of compound AB_1-AB_6: No of carbon in alkyl chain vs Temperature.

Series – 1



Series – A



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 –CH=N-, –N=N- left n-alkoxy group, and right terminal $–COCH_3$ 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 –CH=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	109.33°C (C_4 - C_{14})	136.83°C (C_1 - C_{16})
Commencement of nematic Phase	C_8	C_1
Total mesophase length in °C (Nm-Iso)	4 °C – 6°C	25 °C – 120°C
Cn_1 Cn_2	C_{14} - C_8	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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