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# A Synthesis and Mesophase behaviour of Homologous Series: 4-(((4-acetylphenyl)imino)methyl)-3-methoxyphenyl3-(4-(alkyloxy)phenyl)acrylate

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## ABSTRACT

A new homologous series 4-(((4-acetylphenyl)imino)methyl)-3-methoxyphenyl3-(4-(alkyloxy)phenyl)acrylate was 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 exhibited a smectogenic mesophase. No odd–even effect was observed in the transition curve. The average thermal stability was observed to be 133.25°C and the nematogenic mesophase ranged from 11.0°C to 17.0°C. Thus, the series was found to be of a low ordered melting type with moderate nematogenic range. Analytical data confirmed the structure of the compounds, and the mesomorphism was identified by optical microscopy. The mesogenic properties were compared with structurally similar compounds.

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

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## 1. INTRODUCTION

Because liquid crystal compounds exhibit several transitions during the melting process, but other organic compounds only exhibit one, the behaviour of liquid crystal compounds is completely different from that of organic molecules. While liquid crystal compounds have solid-mesophase transitions, typical organic compounds exhibit solid-liquid transitions. When heating a liquid crystal compound, a molecule goes through a unique spatial arrangement. The compound is unusual because of this particular spatial layout. These configurations allow the liquid crystal to exhibit distinct mesophases, including climatic, nematic, and smectic mesophases. A liquid crystal compound has a specific building block. Investigating how structure affects liquid crystal characteristics is the main goal of the current work. [1-10]

The transition temperature is a specific temperature that is determined by the structural arrangement of the molecule and occurs at a specific temperature. Mesophase length is the total number of mesophases that are accessible for a given temperature range; it is also influenced by the structure's design. Compounds' liquid behaviour is influenced by structural features such the number of hard cores, group positions, number of groups, and types of groups. The current study includes structurally comparable series that were distinguished by the right terminal group. [11-17]

The sole difference between the two series is the polarity of the right terminal group; otherwise, the binding connectivity and molecular length of the structures are identical, as is the group position. Several spectroscopic techniques, including 1H-NMR and IR, were used for the structural confirmation. Elementary analysis is used to determine the percentage of each element present in a compound. The DSC [21–24] and POM [25–26] methods were used to confirm the liquid crystal and mesophase behaviour. The behaviour of liquid crystals is positively influenced by the group's polarity.

## 2. MATERIALS AND METHODS

4-Hydroxy cinnamic acid, n-alkyl bromides ($C_nH_{2n+1}Br$), KOH, dicyclohexylcarbodiimide (DCC), 4-dimethylamino pyridine(DMAP), 4-bromo-3-methyl aniline, phenol, sodium nitrite, sodium hydroxide, pyridine, piperidine, and other solvent used in synthesis were purchased from Spectrochem, Merck, and Sigma –Aldrich. Purity of all these compounds was checked by TLC. It was accomplished on 0.2 mm pre-coated plates of silica gel G60 $F_{254}$-Merck. The homologues of series characterization by elemental analysis on EuroEA Elemental Analyzer, mass spectroscopy recorded on Shimadzu GC-MS Model No. QP-2010, fourier-transform infrared spectroscopy (IR) recorder on Shimanzu FTIR-8400 and proton nuclear magnetic resonance ($^1$H-NMR) recorded on Brucker spectroscopy using $CDCl_3$ solvent. The thermal behaviour recorded on Differential scanning calorimeter model no. Shimadzu, Singapore DSC-60 10.8.

## 3. RESULT AND DISCUSSIONS

### 3.1. Synthesis of 4-*n*-Alkoxy Cinnamic Acid (Compound A)

4-*n*-Alkoxybenzaldehydes 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.[18] The resulting 4-*n*-alkoxy benzaldehydes 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).[19]

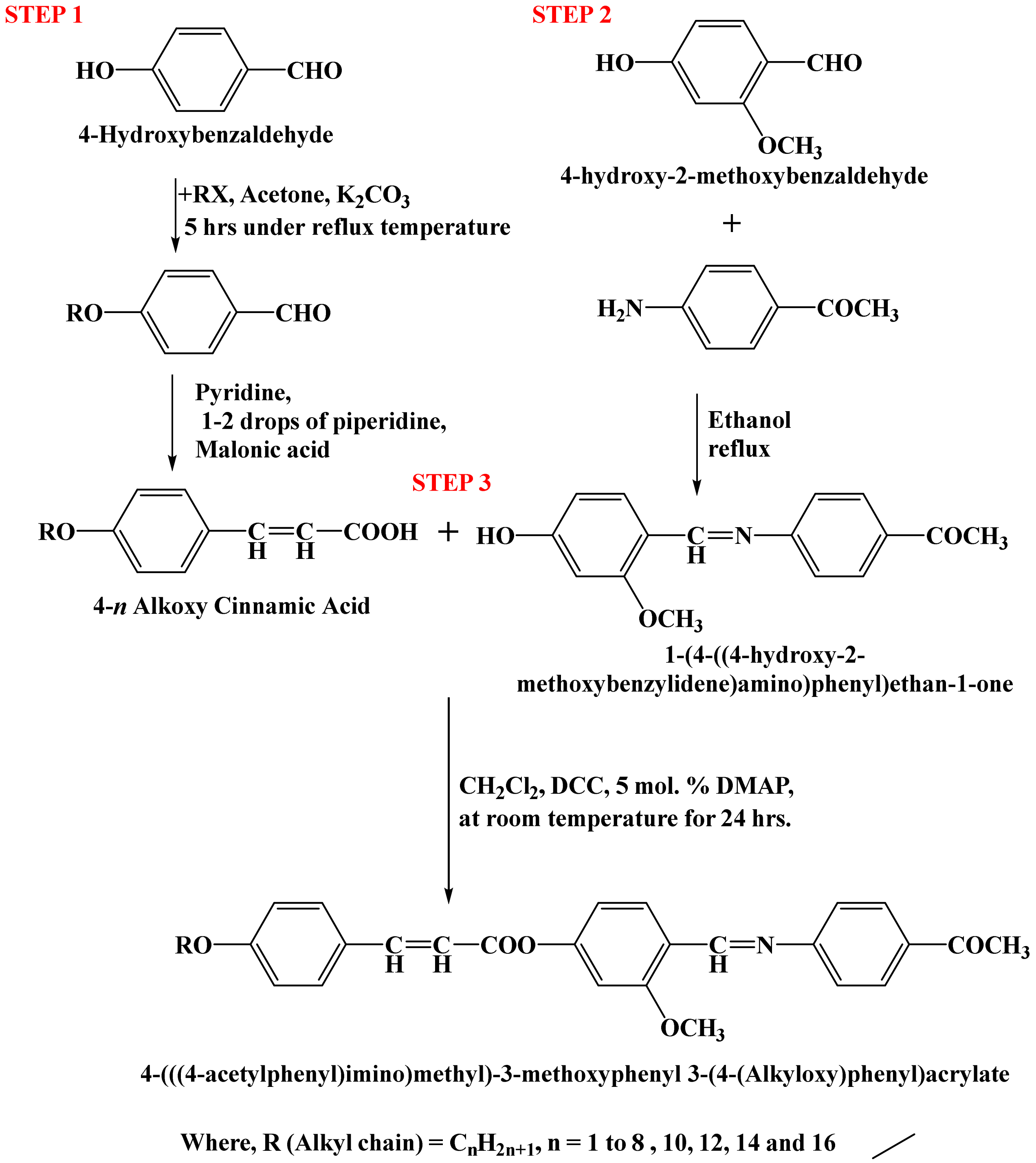
### 3.2. Synthesis of 1-(4-(4-hydroxy 3- methoxy benzylidene) amino) phenyl) ehane-1-one (Compound B)

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

(B) was prepared by previously established method. 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. [20]

### 3.3. Synthesis of 4-(((4-acetylphenyl)imino)methyl)-3-methoxyphenyl3-(4-(alkyloxy)phenyl)acrylate (Compound $AB_1$-$AB_{12}$)

P-n-alkoxy cinnamic acid were directly condensed with the 4-Hydroxy phenyl azo-4”-bromo-3”-methyl benzene dissolved in MDC in portions with DCC & DMAP as catalyst by stirring reaction mixture. Products were decomposed, filtered, washed, dried, and purified, till the constant transition temperatures obtained. 4-*n*-Alkoxybenzaldehyde, alkyl halides (R-X), methanol, 4-Hydroxy cinnamic acid, malonic acid, $K_2CO_3$, DCC, DMAP, MDC, acetone, etc., required for synthesis were used as received, except solvents, which were dried and distilled prior to use. 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) malonic acid, piperidine, pyridine, reflux, 3-4 h; (iii) HCl; (v) 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):** 8.43 (s, 1H, CH of CH=N), 8.04 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.86 (s, 1H, CH of CH=CH), 7.73 (dd, 2H, Ar-H), 7.57 (dd, 2H, Ar-H), 7.41 (m, 1H, Ar-H), 7.25 (s, 2H, Ar-H), 6.96 (s, 2H, Ar-H), 6.54 (s, 1H, CH of CH=CH), 4.03 (t, 2H, $CH_2$ of $OCH_2$), 3.97 (s, 3H, $CH_3$ of $OCH_3$), 2.65 (s, 3H, CH3 of $COCH_3$), 1.83 (m, 2H, CH2 of alkyl chain), 1.49 (m, 2H), 1.32 (m, 8H, of Poly -CH2-), 0.92 (t, 3H,CH3 of Alkyl chain).
**IR in cm$^{-1}$:** 3072-3041 (stretching of CH=CH),2925-2858 ( C-H str ), 1726 (C=O str), 1678 (CH=N str), 1627-1593(aromatic stretching ), 1509-1420 (Aromatic str ), 1357 ( Stretching of C-O) , 1261-1134 (ether linkage ), 1019 ( C-C Str ), 869 ( str of poly $CH_2$ group), 831-777 ( Substituted benzene ring) cm$^{-1}$
**Compound $AB_{10}$; $^1$H NMR δ (ppm):** 8.44 (s, 1H, CH of CH=N), 8.04 (dd, *J* = 8.0 Hz, 2H, Ar-H), 7.88 (s, 1H, CH of CH=CH), 7.69 (dd, 2H, Ar-H), 7.56 (dd, 2H, Ar-H), 7.42 (m, 1H, Ar-H), 7.25 (dd, 2H, Ar-H), 6.95 (s, 2H, Ar-H), 6.56 (s, 1H, CH of CH=CH), 4.03 (t, 2H, $CH_2$ of $OCH_2$), 3.97 (s, 3H, $CH_3$ of $OCH_3$), 2.65 (s, 3H, CH3 of $COCH_3$), 1.83 (m, 2H, CH2 of alkyl chain), 1.56 (m, 2H, CH2 of alkyl chain), 1.31 (m, 12H, of Poly -CH2-), 0.91 (t, 3H,CH3 of Alkyl chain).

**IR in cm$^{-1}$:** 3017-3040 (stretching of CH=CH), 2927-2856 ( SP$^3$ C-H str ), 1712 (C=O str), 1637 (CH=N str ), 1592-1420 (Aromatic str ), 1380 ( Stretching of C-O) , 1256-1127 (ether linkage), 1021 ( C-C str), 868 ( str of poly $CH_2$ Group ), 832-781 ( Substituted benzene ring) cm$^{-1}$

**Table 1.** Elemental analysis for compounds $AB_8$ and $AB_{10}$.

| Sr. No. | Molecular Formula | Elements % Found (% Calculated) | | |
|---|---|---|---|---|
| | | C | H | N |
| 1. | $C_{34}H_{39}NO_5$ | 75.21% (74.79%) | 7.26% (7.45%) | 2.59% (2.64 %) |
| 2. | $C_{36}H_{43}NO_5$ | 75.46% (75.89%) | 7.39% (7.61%) | 2.61% (2.46 %) |

### 3.4. POM and DSC investigation

Transition temperatures were 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.[21-26] In this series, most compound showing one type of phases. First compound converts solid to nematic phase than after 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 $AB_8$ & $AB_{10}$ was selected for spectral analysis. DSC spectra showed one peaks which indicates nematic to isotropic conversion mesophase present in molecules. Compound $AB_8$ showed peak at 128 °C**(Figure 2)**. and $AB_{10}$ showed peak at 82 °C for the conversion of crystal to nematic phase **(Figure 3)**.

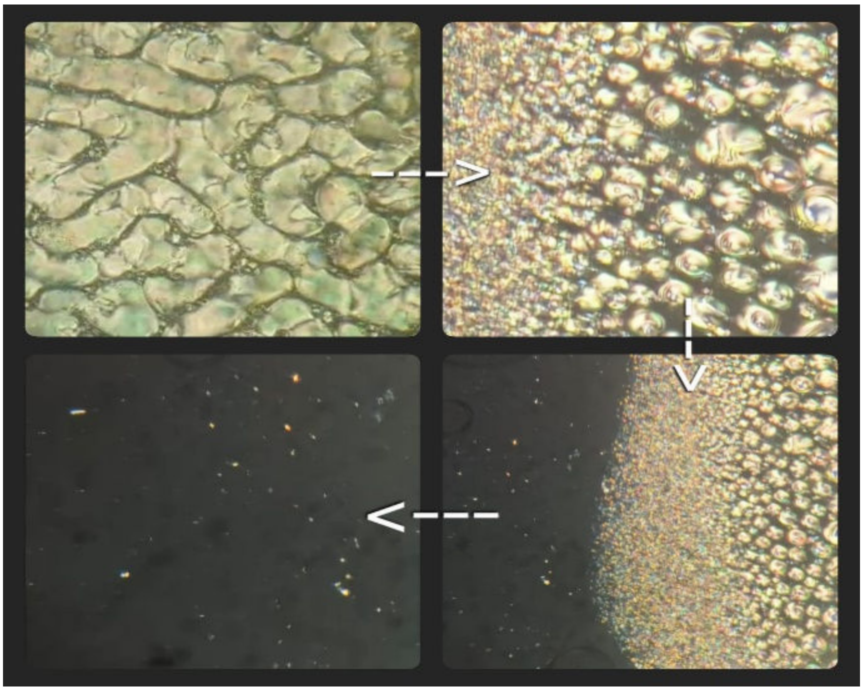


**Figure 1**. POM images of compound $AB_8$: solid (a); nematic phase (b); sematic phase (c).

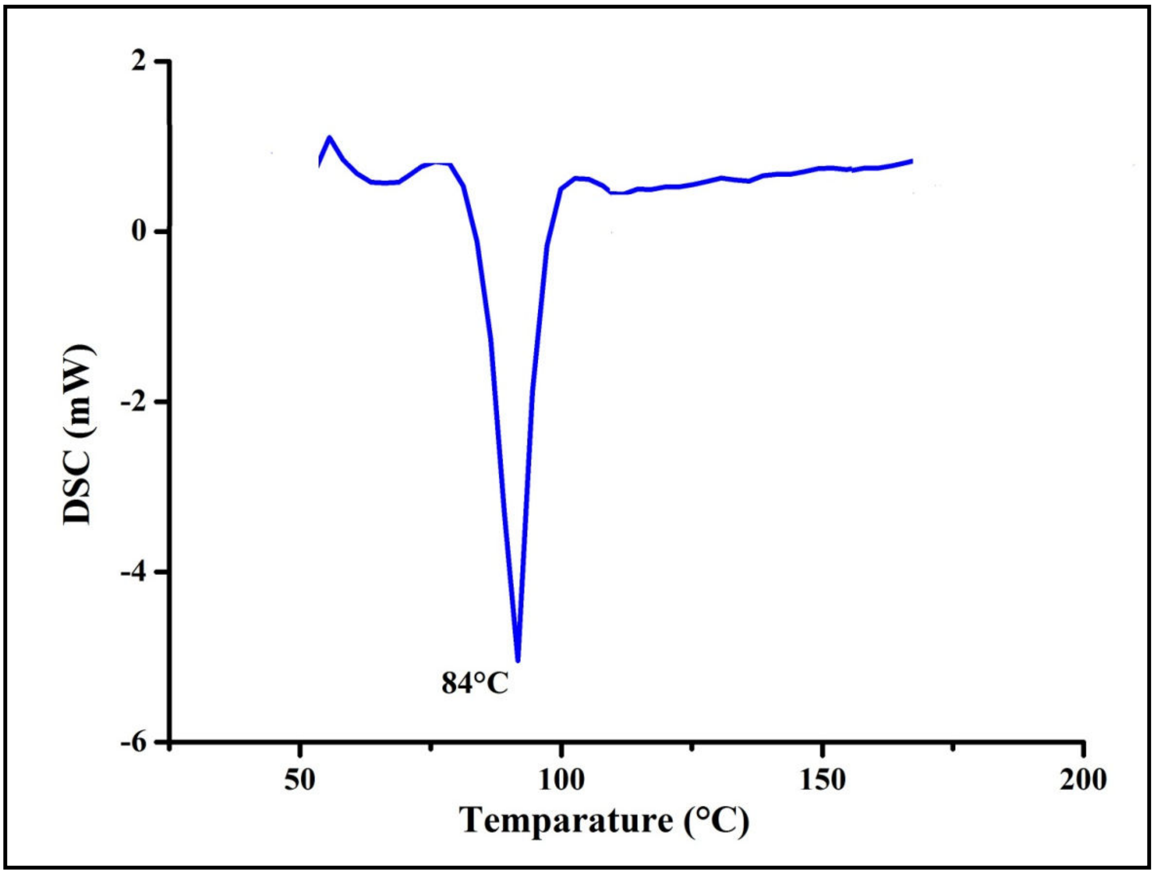


**Figure 2.** DSC data of compound $AB_8$ **(**0ctyloxy**)**

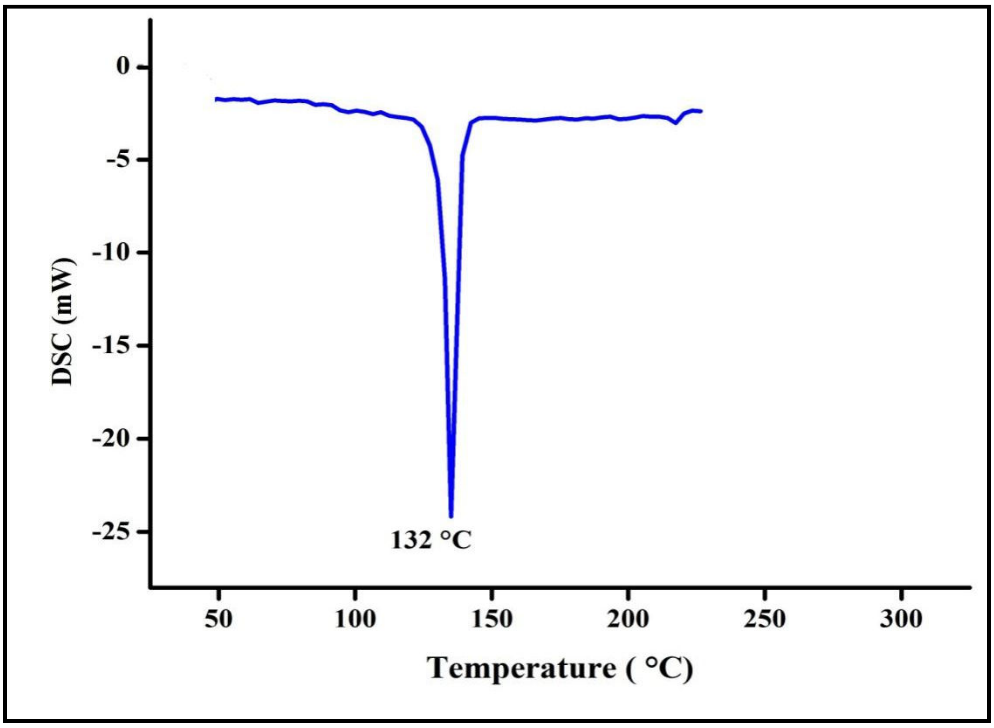
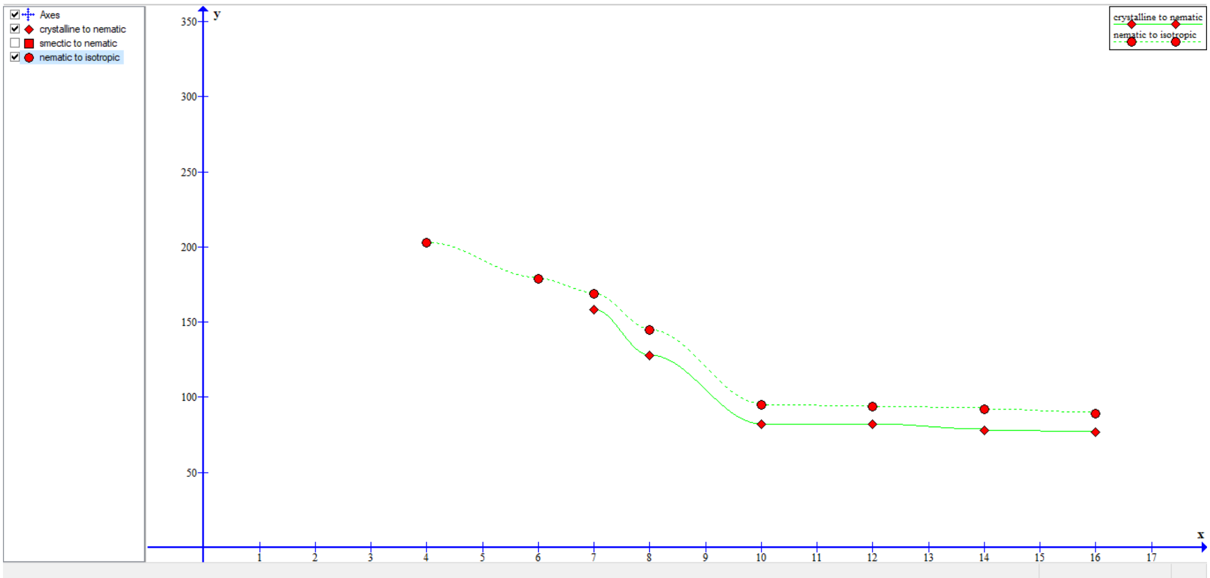


**Figure 3.** DSC data of compound $AB_{10}$ **(**decayloxy**)**

Homologous series 4-(((4-acetylphenyl)imino)methyl)-3-methoxyphenyl3-(4-(alkyloxy)phenyl)acrylate 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 without exhibition of smectic 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 4. Smooth curves are drawn through like or related points. The solid-mesomorphic transition curve follows a linear path of falling nature. The nematic –isotropic transition curve exhibits linear tendency transition curve behaves in a normal manner. Well known odd-even effect is not observed in the nematic-isotropic transition curve with alternation 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 203.0 ºC and 89.0 ºC with mesomorphic range varying from 11.0 ºC at the heptyl homologue to a maximum of 17.0 ºC at the octyl homologue of the series Table 2. Thus, the present homologues series is considered as low ordered melting type with wide range of liquid crystallinity. Display of nematic mesophase without exhibition of any 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, which resulted in absence of smectic mesophase for all the homologue. Terminal –COCH3 is 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 nematic transition curve falls in linear manner.

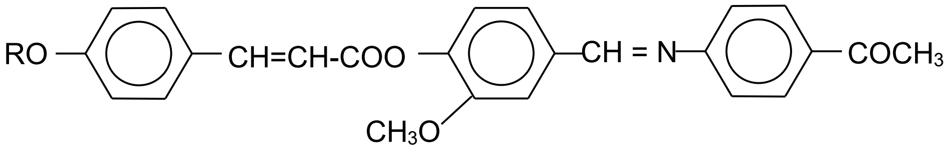
**Table 2.** Transition temperatures.

| **Sr. No.** | ***n*-Alkyl Group** | **Transition temperatures in °C** | | |
|---|---|---|---|---|
| | | **Smectic** | **Nematic** | **Isotropic** |
| 1 | Methyl | - | - | - |
| 2 | Ethyl | - | - | - |
| 3 | Propyl | - | - | - |
| 4 | Butyl | - | - | 203 |
| 5 | Pentyl | - | - | - |
| 6 | Hexyl | - | - | 179 |
| 7 | Heptyl | - | 158 | 169 |
| 8 | Octyl | - | 128 | 145 |
| 9 | Decyl | - | 82 | 95 |
| 10 | Dodecyl | - | 82 | 94 |
| 11 | Tetradecyl | - | 78 | 92 |
| 12 | Hexadecyl | - | 77 | 89 |

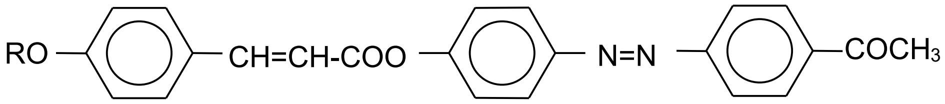


**Figures 4**. Phase behaviour of compound AB$_1$-AB$_{12}$: No of carbon in alkyl chain vs. Temperature.

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 series (1) 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 series-1 contain CH=N-,secound phenyl ring having -OCH3 group,left n-alkoxy group, and right terminal –COCH3 functional group at para position. And series(A) Contain -N=N, -COCH3 group in pera 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 at secound phenyl ring In series(1) -OCH3 grops present and also having -CH=N- and In series (A) -OCH3groups absent and -N=N- azo group present. 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. In case of series (1) as compared to series (A) melting and transition temperatures of titled homologous series (1) are relatively nearly low 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 low than series (A). Thus, nematic group efficiency order with respect to type of linking terminal, i.e., last 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 | 133.25°C<br>($C_1$ - $C_{16}$) | 136.83 °C<br>($C_1$ - $C_{16}$) |
| Commencement of nematic Phase | $C_7$ | $C_1$ |
| Total mesophase length in °C (Nm-Iso) | 11 °C – 17°C | 25.0°C - 120.0°C. |
| $Cn_1$ $Cn_2$ | $C_7$ - $C_8$ | $C_{14}$ - $C_7$ |

## 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 phase. Present investigation supports 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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