World Scientific News

An International Scientific Journal

WSN 206 (2025) 47-55 EISSN 2392-2192

A Synthesis and Mesophase Behaviour of Homologous Series: 2-formyl-4-((E)-phenyldiazenyl)phenyl)diazinyl)phenyl (E)-(3)-(4 alkyloxyphenyl)acrylate

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ABSTRACT

A new homologous series, 2-formyl-4-((E)-phenyldiazenyl)phenyl)diazinyl)phenyl (E)-(3)-(4 alkyloxyphenyl)acrylate is synthesized with a view to understand and establish the relation between mesogenic properties and structure of molecules. The mesophase behaviour of the liniyer-shaped molecular system core with azo-ester linker (E1–E9) was examined in relation to the impacts of alkoxy side groups on three distinct terminal positions. POM and DSC analyses were used to verify the synthetic derivatives' mesogenic behaviour and thermal stability. These compounds based on azo-esters exhibited mesomorphic characteristics of the smectic C. Fan, broken fan, schlieren, and threaded type were the textural patterns of the synthesised chemicals that were observed. At lower temperatures, all derivatives displayed a further stabilised mesophase and a good temperature range. To learn more about how varied side-chains affect liquid crystalline characteristics, the structure-property link was further investigated.

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

(Received 15 June 2025; Accepted 12 July 2025; Date of Publication 11 August 2025)

1. INTRODUCTION

Although they are neither pure crystalline solids nor isotropic liquids, liquid crystals (LCs) are a special kind of matter with high mobility when compared to both [1–3]. The manufacturing of light-emitting materials, electronic display devices, and other electronic applications is increasing demand for these materials [4-6]. Numerous liquid crystalline compounds with a variety of shapes, mesophase behaviours, thermal stability, and uses have been described to far.

The molecular systems' azo (-N=N-) group provides photosensitivity and adjustability for photo-induced applications [7]. However, the existence of confirmation qualities may cause the azo linker to occasionally cause partial distraction in order to produce liquid crystalline properties. The azo linker is inserted into their side arms and supported by various linking groups, most frequently an ester linking unit, for this reason [8–10]. In addition to the ester group conjugation connections between the two phenyl rings that are further coupled with other connecting units such as schiff-base, azo, amide, etc., aromatic esters are known for their thermal stability, ease of synthesis, and relative resistance to hydrolysis [11].

Furthermore, liquid crystalline characteristics are influenced by the functions of the terminal and lateral substituent groups. Therefore, it is evident from the literature that the more lateral adhesion linear molecules have, the more stable a mesophase is. This is further supported by an increase in the polarity and/or polarisability of the molecule's mesogenic area [12–15]. Furthermore, the polarisability of the aromatic ring that is linked throughout the molecular systems is changed by the impact of terminal substituents [16].

We have created new homologous series in this study and examined their liquid crystal properties. Our chemical exhibits nematic and smectic phases, which could be helpful in the creation of display devices. Analytical methods were used to characterise each derivative. For the study of liquid crystalline properties, POM research and DSC analysis were conducted.

2. EXPERIMENTAL

2.1. 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 analyzed 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 a temperature-controlled heating stage.

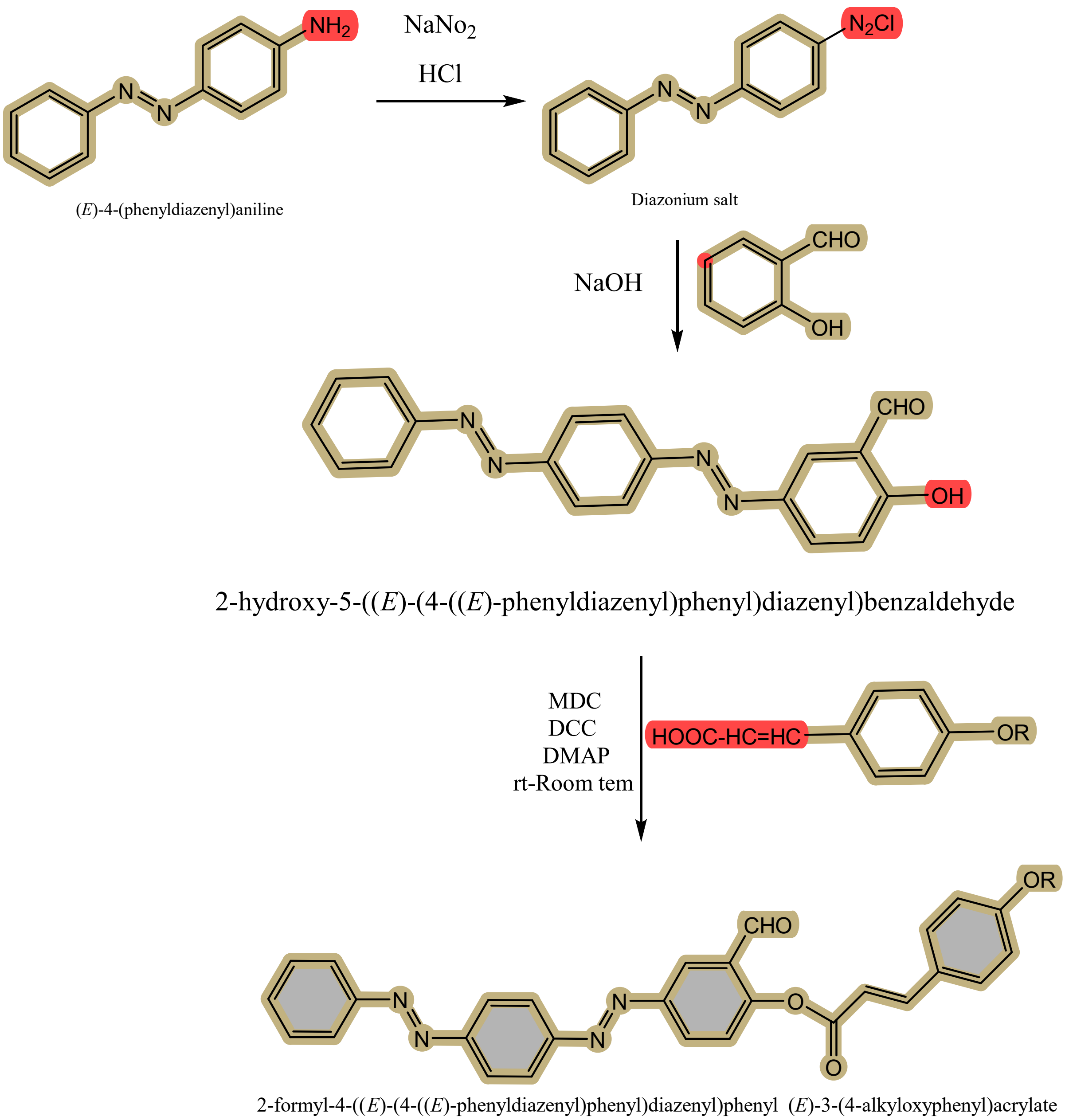
2.2. Measurements

The Opti-Melt (automated melting point system) was used to measure melting points. Shimadzu's KBr pellets were used to record the FT-IR spectra, which ranged from 3800 to 600 cm-1. A trinocular polarising optical microscope (POM) with a digital camera and a heated plate was used to examine the texture images. A 400MHz Bruker Advance was used to record 1H NMR in the 0.5–16 ppm range using CDCl3 solvent.

The Shimadzu DSC-50 was used to measure the phase transition temperatures at heating and cooling speeds of 10 oC/min. The nematic phase's texture pictures were identified using the miscibility method. There includes a qualitative discussion of the thermodynamic quantities entropy ($\Delta S=\Delta H/T$) and enthalpy (ΔH).

For the POM measurement, the freshly synthesized chemical is positioned between a coverslip and a glass slide, and it is heated and cooled at rates of 10 oC/min.

2.3. Reaction Scheme



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) 2-hydroxy benzaldehyde, $NaNO_2$, HCl, NaOH, 0-5 °C; (v) DCC, DMAP, DCM, 12 hours, rt.

2.4. Synthesis of Compounds in Present Series

2.4.1. Synthesis of 4-*n*-Alkoxy Cinnamic Acid

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.[15] 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.[16]

2.4.2. Synthesis of 2-hydroxy-5-((E)-(phenyldiazenyl)phenyl)diazinyl)benzaldehyde

2-hydroxy-5-((E)-(4-((E)-phenyldiazenyl)phenyl)diazinyl)benzaldehyde was prepared by previously established method.[17] The diazotization reaction is performed on (E)-4-(phenyldiazenyl) aniline with 2-hydroxy benzaldehyde 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.

2.4.3. Synthesis of 2-formyl-4-((E)-phenyldiazenyl)phenyl)diazinyl)phenyl(E)-(3)-(4alkyloxyphenyl)acrylate

4-*n*-alkoxy cinnamic acid were directly condensed with the 2-hydroxy-5-((E)-(4-((E)-phenyldiazenyl)phenyl)diazinyl)benzaldehyde 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 above in Scheme 1**.**

2.5. Selected Data of Synthesized Compounds

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_{10}; ^{1}H NMR δ (ppm): 0.91 (t, 3H, $-CH_3$ of $–OC_{10}H_{21}$), 1.28 (m, 12H, $-CH_2-$ of alkyl chain), 1.65 (m, 2H, $-CH_2$ of alkyl chain), 2.00 (m, 2H, $-CH_2-$ of alkyl chain), 4.00 (t, 2H, $-OCH_2-$ of alkyl chain), 6.61 (d, 1H of -CH=CH-), 6.92 (2H, of Ar-H), 7.44 (dd, 4H, Ar-H), 7.56 (m, 3H, (2) Ar-H also split 1H of -CH=CH-), 7.65 (dd, 4H, Ar-H), 7.99 (m, 2H, Ar-H), 8.12 (m, 2H, Ar-H), 8.56 (s, 1H of CH=N-), 10.34 (s, 1H of -CHO). **IR in cm^{-1}:** 690 (substitute aromatic ring), 771 (aromatic ring), 831 poly($-CH_2-)_n$ group), 989 (*p*-di substituted benzene ring),, 1033 (-C-H hydrocarbon), 1149-1175 (C-N), 1236 (ether linkage), 1303 (C-H banding of HC=CH), 1418-1460 (-N=N-), 1461-1593 (C=C- of aromatic ring), 1641 (-C=C- alkene), 1702 (C=O of CHO), 1737 (-COO), 2856 (doublet of CHO), 2927 (-C-H str), 3047-3254 (C-H streching of HC=CH).

Compound AB_8; ^{1}H NMR δ (ppm): 0.89 (t, 3H, $-CH_3$ of $–OC_{10}H_{21}$), 1.25 (m, 8H, $-CH_2-$ of alkyl chain), 1.62 (m, 2H, $-CH_2$ of alkyl chain), 1.98 (m, 2H, $-CH_2-$ of alkyl chain), 3.98 (t, 2H, $-OCH_2-$ of alkyl chain), 6.58 (d, 1H of -CH=CH-), 6.89 (2H, of Ar-H), 7.42 (dd, 4H, Ar-H), 7.54 (m, 3H, (2) Ar-H also split 1H of -CH=CH-), 7.64 (dd, 4H, Ar-H), 7.97 (m, 2H, Ar-H), 8.10 (m, 2H, Ar-H), 8.53 (s, 1H of CH=N-), 10.31 (s, 1H of -CHO).

IR in cm^{-1}: 687 (substitute aromatic ring), 768 (aromatic ring), 841 poly(-CH_2-)$_n$ group), 983 (*p*-di substituted benzene ring),, 1067 (-C-H hydrocarbon), 1144-1170 (C-N), 1247 (ether linkage), 1302 (C-H banding of HC=CH), 1384 (-N=N-), 1473-1597 (C=C- of aromatic ring), 1634 (-C=C- alkene), 1697 (C=O of CHO), 1739 (-COO), 2857 (doublet of CHO), 2926 (-C-H str), 3066 (C-H streching of HC=CH).

Table 1. Elemental analysis for compounds AB_1 and AB_2

Sr. No.	Molecular Formula	Elements % Found (% Calculated)		
		C	H	N
1.	$C_{29}H_{21}N_4O_4$	71.11% (71.16%)	4.20% (4.29%)	11.2% (11.4 %)
2.	$C_{30}H_{23}N_4O_4$	71.50% (71.57%)	4.50% (4.57%)	11.1% (11.3 %)

3. RESULT AND DISCUSSION

3.1. 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. In this series most compound showing one type of phases. First compound converts solid to sematic phase than after sematic convert into isotropic phase. The phase behaviour texture of AB_6 (octyloxy) captured during POM investigation was showed in **Figure 1**. In the DSC analysis, one compound, AB_5 was selected for spectral analysis. DSC spectra showed one peaks which indicates smectic phase present in molecules. Compound AB_9 showed peak at 159 °C for the conversion of crystal to smectic phase **(Figure 2)**.

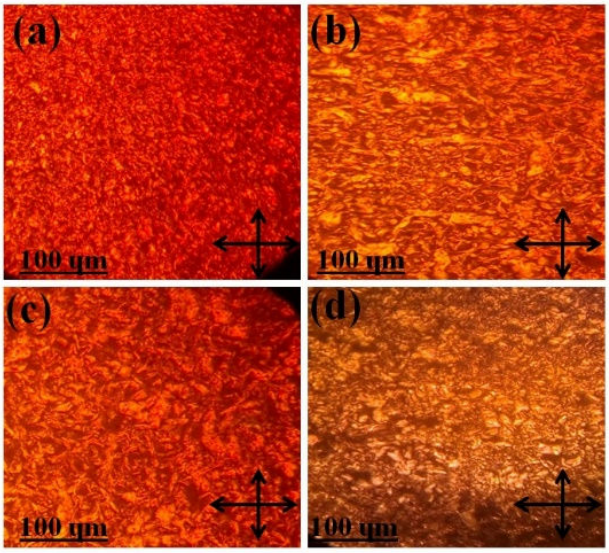


Figure 1. POM images of compound AB_6: solid (a); nematic phase (b); smectic phase (c).

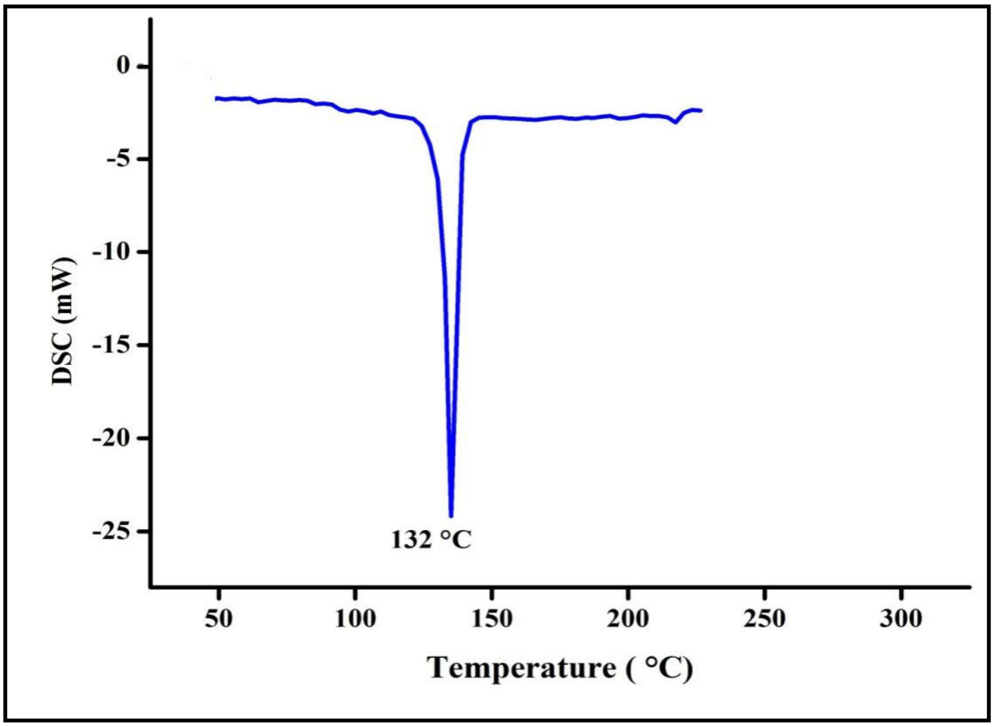


Figure 2. DSC data of compound AB_9 **(**Tetradecyloxy**).**

Homologousseries2formyl4((E)phenyldiazenyl)phenyl)diazinyl)phenyl(E)(3)(4alkyloxyphenyl)acrylate is entirely mesomorphic in character. After AB_4 all the members of the series display mesomorphism in enantiotropic manner with enough range of liquid crystallinity. All the homologues display mesomorphism exhibition of smectic mesophase **(Figure 1)**. 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 liniyer path of rising and falling nature. The nematic–isotropic transition curve exhibits falling tendency as the series is ascended.. Well known odd-even effect is not observed in the smactic-isotropic transition curve, with alternation of transition temperatures and merges into each other at the eight homologue. The texture of nematic mesophase is threaded type as clearly judged from the field of view of hot stage polarizing microscope while observing the samples. The mesomorphic-isotropic transitions are between 167.0 ºC and 312.0 ºC with mesomorphic leangth varying from 5.0 ºC at the 0ctyl homologue to a maximum of 14.0 ºC at the heptyl homologue of the series. Thus, the present homologues series is considered as middle ordered melting type with wide range of liquid crystallinity.

Table 2. Transition temperatures.

Sr. No.	***n*-Alkyl Group**	**Transition temperatures in °C**		
		Smectic	**Nematic**	**Isotropic**
1	Methyl	-	-	312°C
2	Ethyl	-	-	305°C
3	Butyl	-	-	294°C
4	Hexyl	-	-	257°C
5	Heptyl	212°C	-	226°C
6	Octyl	197°C	-	202°C
7	Decyl	178°C	-	189°C
8	Dodecyl	179°C	-	185°C
9	Tetradecyl	159°C	-	167°C

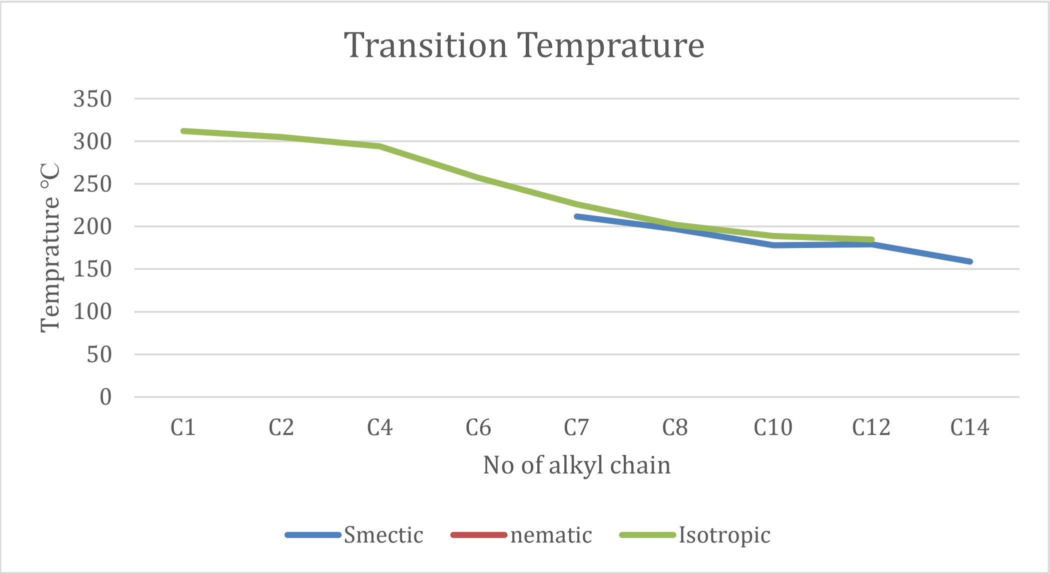
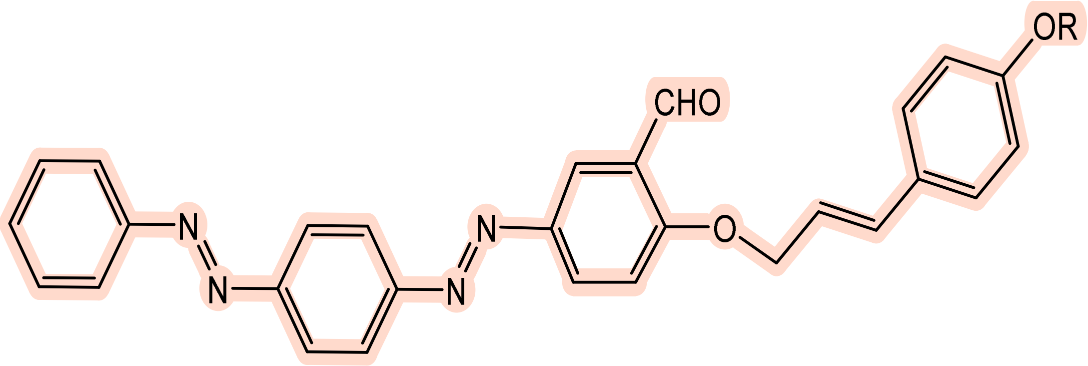


Figure 3. Phase behaviour of compound AB_1-AB_{12}: No of carbon in alkyl chain vs. Temperature.

Series - 1



2-formyl-4-((*E*)-(4-((*E*)-phenyldiazenyl)phenyl)diazenyl)phenyl (*E*)-3-(4-alkyloxyphenyl)acrylate

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

Table 3. Average thermal stability.

Series	**Series - 1**
Nematic -isotropic Commencement of Nematic Phase	237.44°C (C_1 - C_{14}) C_7
Total mesophase length in °C (Nm-Iso) Cn_1 Cn_2	5 °C – 14°C C_8 - 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 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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