Available online www.worldscientificnews.com

World Scientific News

An International Scientific Journal

WSN 208 (2025) 144-154 EISSN 2392-2192

A Synthesis and Mesophase behaviour of Homologous Series: 4-(4’-n-alkoxy Benzoyloxy) 2-nitro-(4’’-bromo 2’’-methyl) azobenzene

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ABSTRACT

A new homologous series, 4-(4’-n-alkoxy Benzoyloxy) 2-nitro-(4’’-bromo 2’’-methyl) azobenzene, 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. No An odd–even effect is observed in the transition curve. The average thermal stability is 73.5°C and the nematogenic mesophase ranges from 7.0°C to 12.0°C. Thus, the series is of a low 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 25 August 2025; Accepted 18 September 2025; Date of Publication 7 October 2025)

1. INTRODUCTION

The liquid crystal compound exhibits unique molecular behaviour, distinctly differing from organic molecules, since the latter undergoes a singular transition during the melting process, but the liquid crystal compound demonstrates many transitions during melting. 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. This configuration causes 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 qualities is the main goal of the current study [1–7].

The temperature at which a certain transition takes place is referred to as the transition temperature and is determined by the molecular structure. 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. The mesogenic behaviour of compounds is influenced by structural features such as the number of hard cores, group positions, number of groups, and types of groups. Structurally similar series that differ by right terminal group were considered in the current study [8–11].

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 [12] and POM [13–14] 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-hydroxybenzoic acid, acetone, methanol, n-hexane, ethyl acetate, alkyl bromides, anhydrous K_2CO_3, alkyl bromides (R-Br), ortho nitrophenol, HCl, NaOH, DCC, DMAP, and 4-bromo 2-methy aniline 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)

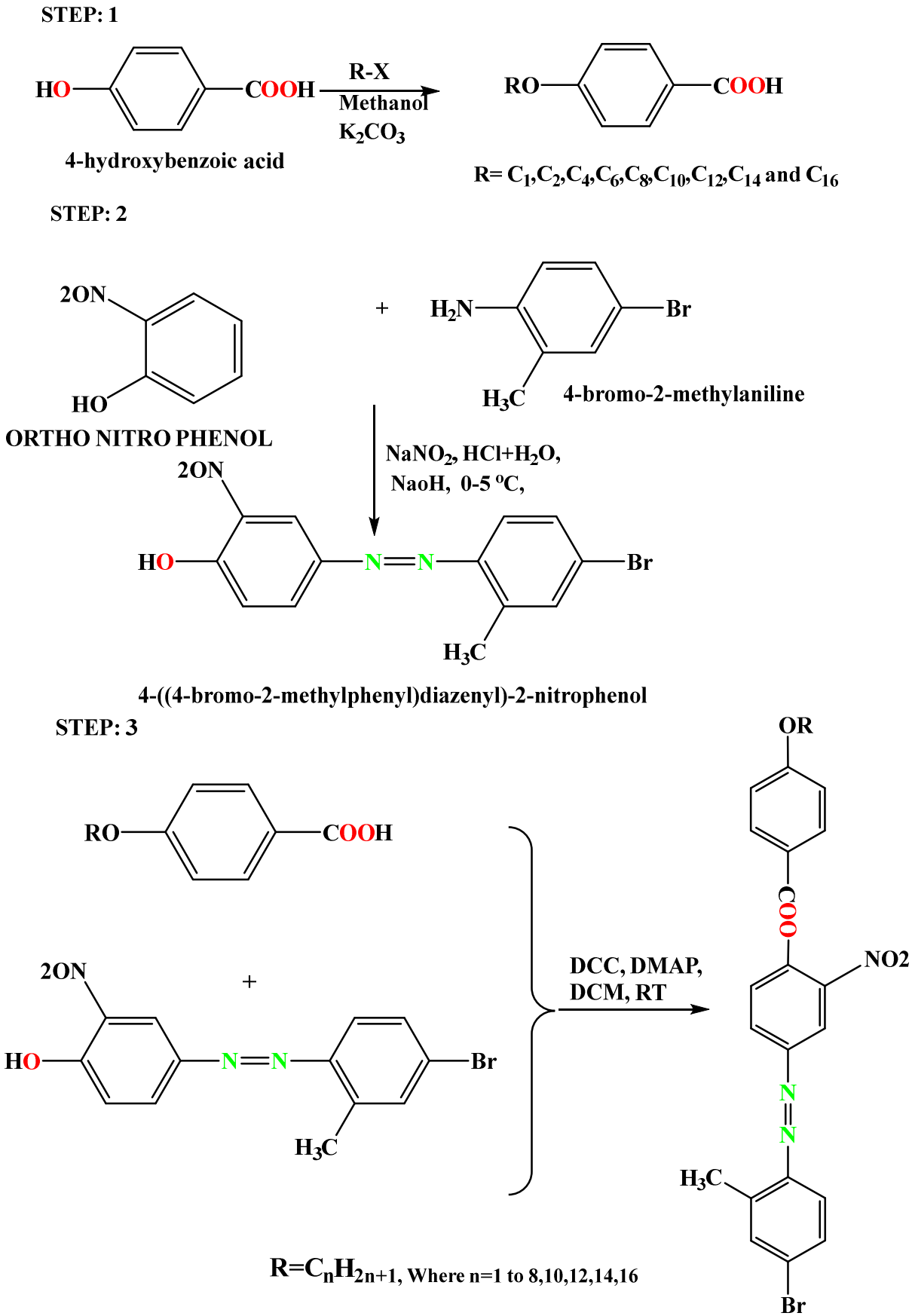
4-*n*-Alkoxybenzoic acid were synthesized by refluxing 4-hydroxybenzoic acid (1 equiv.) with corresponding *n*-alkyl bromides (1 equiv.) in the presence of anhydrous potassium carbonate (1.2 equiv.) using acetone as a solvent.[15] The resulting 4-*n*-alkoxy benzoic acid was purify by crystallization.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

3.2. Synthesis of 4-((4-bromo 2-methylphenyl) diazinyl)-2-nitro phenol (Compound B)

4-((4-bromo 2-methylphenyl) diazinyl)-2-nitro phenol (B) was prepared by previously established method.[28] The diazotization reaction is performed on 4-bromo 2-methy aniline with ortho nitro 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-(4'-n-alkoxy benzoyloxy) 2-nitro-(4''-bromo 2''-methyl) azobenzene (Compound AB_1-AB_{12})

4-*n*-alkoxy benzoic acid were directly condensed with the 4-((4-bromo 2-methylphenyl) diazinyl)-2-nitro phenol 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) ortho-nitrophenol, $NaNO_2$, 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 (ppmδ 8.64 (s, 1H, CH of Aromatic ring), 8.60 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.14 (s, 2H, CH of Ar-H), 7.70 (dd, 2H, Ar-H), 7.56 (dd, 2H, Ar-H), 7.26 (m, 1H, Ar-H), 6.98 (s, 3H, Ar-H), 4.06 (t, 2H, CH_2 of OCH_2), 2.52 (s, 2H, CH2 of OR), 1.83 (m, 2H, CH2 of alkyl Chai), 1.25 (m, 8H, of Poly -CH2-), 0.86 (t, 3H,CH3 of Alkyl chain). **IR in cm^{-1}:** 2927-2860 (C-H str), 1737-1678 (C=O str), 1611-1567 (aromatic stretching), 1542-1516 (Stretching of N-O), 1473-1392 (Aromatic str), 1354-1267 (Stretching of N-O), 1167-1132 (ether linkage), 1073-1030 (N=N Str), 904-883 (str of poly CH_2 Group), 841-821, (Substituted benzene ring), 690-615 (C-Br Str) cm^{-1}.

Compound AB$_{10}$; ^{1}H NMR δ (ppm): 8.64 (s, 1H, CH of Aromatic ring), 8.62 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.15 (s, 2H, CH of Ar-H), 7.84 (dd, 2H, Ar-H), 7.66 (dd, 2H, Ar-H), 7.26 (m, 1H, Ar-H), 6.98 (s, 3H, Ar-H), 4.04 (t, 2H, CH_2 of OCH_2), 2.53 (s, 2H, CH2 of OR), 1.28 (m, 2H, CH2 of alkyl Chai), 1.26 (m, 12H, of Poly -CH2-), 0.87 (t, 3H,CH3 of Alkyl chain). **IR in cm^{-1}:** 2928-2860 (C-H str), 1742-1672 (C=O str), 1610-1585 (aromatic stretching), 1539-1516 (Stretching of N-O), 1476-1391 (Aromatic str), 1352-1265 (Stretching of N-O), 1175-1135 (ether linkage), 1069-1030 (N=N Str), 902-844 (str of poly CH_2 Group), 758-716, (Substituted benzene ring), 691-650 (C-Br Str) cm^{-1}.

Table 1. Elemental analysis for compound AB_1 and AB_2.

Sr. No.	Molecular Formula	Elements % Calculated (% Found)		
		C	H	N
1.	C28H30BrN3O5	59.56% (59.16%)	5.95% (5.32%)	7.81% (7.39 %)
2.	C30H34BrN3O5	60.43% (59.98%)	5.81% (5.75%)	7.40% (7.07 %)

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. [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**.

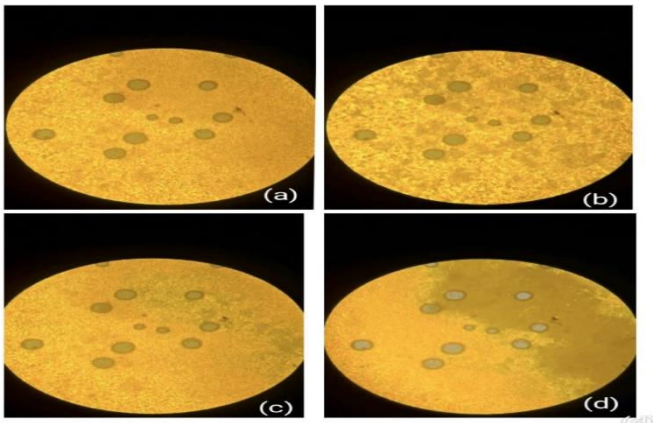


Figure 1. POM images of compound AB_3.

Homologous series 4-(4'-n-alkoxy Benzoyloxy) 2-nitro-(4''-bromo 2''-methyl) azobenzene is entirely mesomorphic in character. AB_3 after compound of the series display 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 2**. 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 48.0 ºC and 118.0 ºC with mesomorphic range varying from 7.0 ºC at the tetradecyloxy homologue to a maximum of 12.0 ºC 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. 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 Temperature.

Sr. Compounds	*n*-Alkyl Group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Butyl	-	-	118
2	Hexyl	-	106	94
3	Octyl	-	82	75
4	Decyl	-	69	57
5	Dodecyl	-	55	49
6	Tetradecyl	-	55	48

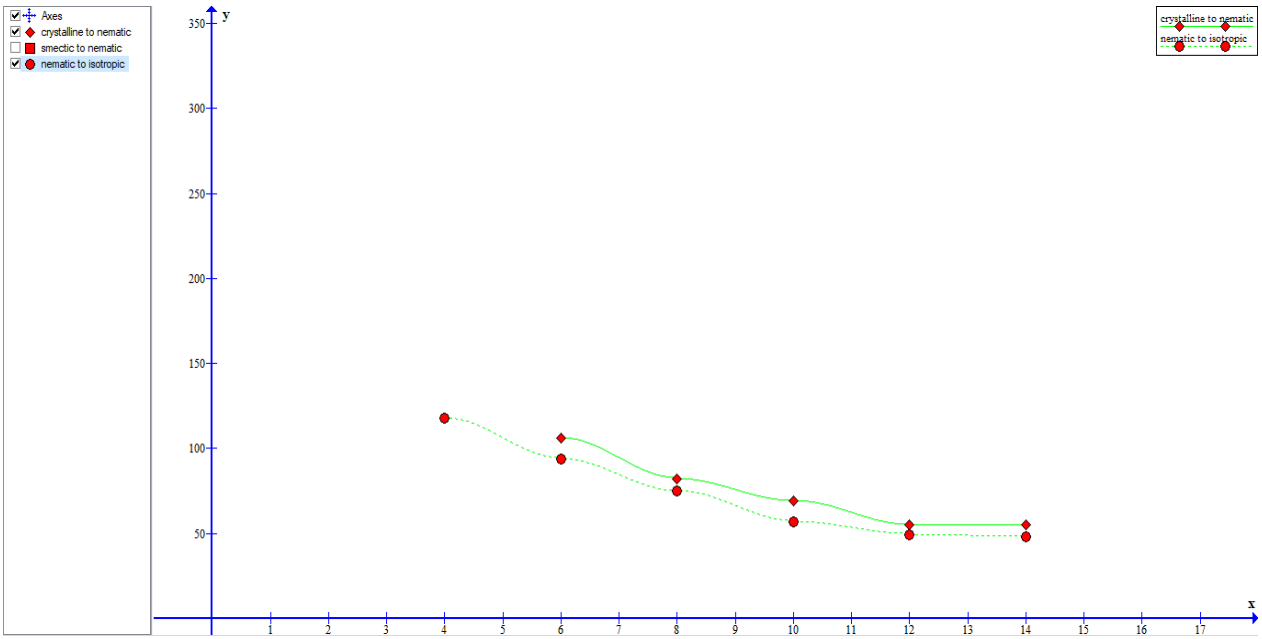
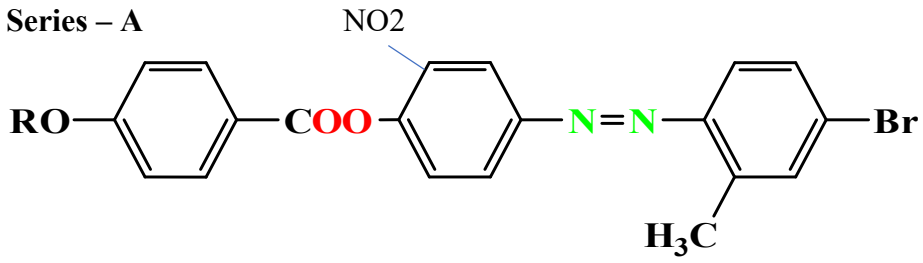
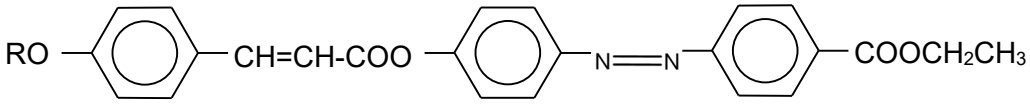


Figure 2. Phase behaviour of Compound AB_1-AB_6: No of carbon in alkyl chain vs. Temperature.



Series – 1



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.**

Table 3. Average thermal stability.

Series	**Series – 1**	**Series – A**
Nematic -isotropic Commencement of nematic Phase	293.66°C (C_1 - C_{16}) C_8	73.5°C (C_4 - C_{14}) C_6
Total mesophase length in °C (Nm-Iso) Cn_1 Cn_2	10 °C – 130°C C_{16} - C_1	12 °C – 7°C C_6 - C_8

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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