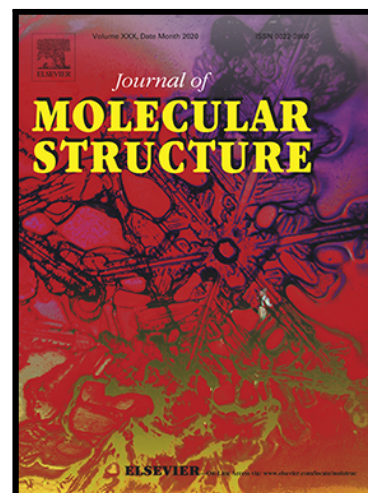


Synthesis of new liquid crystal Schiff's bases bearing ester moiety,
DFT calculation and mesomorphic studies

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PII: S0022-2860(24)02587-0
DOI: <https://doi.org/10.1016/j.molstruc.2024.140078>
Reference: MOLSTR 140078



To appear in: *Journal of Molecular Structure*

Received date: 30 June 2024
Revised date: 8 September 2024
Accepted date: 13 September 2024

Please cite this article as: Jay C. Panchal , Meetkumar Y. Chaudhary , Hemant N. Patel ,
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Sarfaraz Ahmed , Synthesis of new liquid crystal Schiff's bases bearing ester moiety,
DFT calculation and mesomorphic studies, *Journal of Molecular Structure* (2024), doi:
<https://doi.org/10.1016/j.molstruc.2024.140078>

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Highlights:

- A new group of mesogenic compounds from the Schiff's base family with dimethyl substitution around a benzoate center was created.
- The investigation of liquid crystalline phases was carried out using a polarized optical microscope (POM).
- Molecules were built with Gauss View 6 software and optimized with DFT calculations at M06-2X/6-31 G++ (d,p) level in Gaussian 16 quantum chemistry package.
- Anritsu Shockline VNA model MS46322A with SPEAG DAK-TL was used to collect complex permittivity data of samples.

Synthesis of new liquid crystal Schiff's bases bearing ester moiety, DFT calculation and mesomorphic studies.

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Abstract

A new homologues series of liquid crystalline material (E)-4-(((3,4-dimethylphenyl) imino) methyl) phenyl4-*n*-alkoxybenzoate (**SB_n**) synthesized. **SB_n** compounds was subjected to analysis using infrared spectroscopy, proton magnetic resonance, ¹³C NMR, UV- visible and mass spectroscopy for characterization. The investigation of liquid crystalline phases and their transition enthalpies was carried out using a polarized optical microscope and differential scanning calorimetry, respectively. All compounds within the homologous series display mesogenic properties. The **SB₁** -**SB₇** homologues exhibit an enantiotropic nematic mesophase within the temperature range of 180-106 °C, while the **SB₁₄** -**SB₁₈** homologues show a smectic A mesophase at temperatures between 78-75 °C. Additionally, the **SB₈** -**SB₁₀** homologues exhibit a monotropic smectic A mesophase at 61-59 °C. The phase transitions observed in series **SB_n** are compared with those of structurally related compounds to assess the influence of central linkage and lateral tail `substitution on their mesophase behavior. With the help of DFT; E_{HOMO} and E_{LUMO} energy gap were computed to be negative for all derivative molecules, indicating their stability and in the following order: **SB₄** > **SB₆** > **SB₈** > **SB₁₂**. Dielectric through determined values of complex permittivity of the synthesised liquid crystal over a broad frequency range are reported. Determined static permittivity value of liquid crystal is 2.25, at room temperature. The compound **SB_n** exhibited a relaxation peak in the dielectric loss spectra in the microwave frequency range, which may be assigned to the rotation of the end polar group of the molecule.

Key words: Liquid Crystal, Schiff's base, mesogenic, nematic, smectic A.

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1. Introduction

Recently, the synthesis of the liquid crystals along novel structures has been a core vital subject in liquid crystal research. Liquid crystalline materials are widely used in various technological, academic, and scientific fields. They are of great interest due to their applications in coordination chemistry, organic light-emitting diodes, in-plane switching mode liquid crystal display, biological systems, and more [1–4]. An Organic compound's mesophase stability rely on its molecular construction, a slight alteration in the molecular arrangement results in a substantial modification of its mesomorphic characteristics [5]. Notably, changing the structure of central linkages affects its polarity and also the mesophase stability is affected due to changes in the polarity of the molecule. Previously investigated the Schiff base ester synthesis with methoxy, ethoxy and chloroethyl tail [6–8]. Numerous investigations have focused on studying how alterations in terminal substituents, a highly impactful molecular attribute, influence the occurrence of specific liquid crystal phase[9]. Formerly investigated on two novel lateral methyl-substituted Schiff's bases containing cinnamate ester and ester central linkages. The liquid crystals derived from these compounds were synthesized and analyzed in terms of their mesomorphic properties [10]. Various terminal substituents are involved, including small polar compact substituents or alkoxy chain [11]. Designing new thermotropic liquid crystals hinges on crucial criteria such as the choice of a terminal groups, flexible aliphatic chains and mesogenic core [12]. 4-hydroxybenzoic acid is an aromatic compound with high chemical stability, being extensively used in food, pharmaceutical and cosmetic industries and therefore widely distributed in various environments [13].

Since 1864, the initial observation of the interaction between aromatic aldehydes and primary amines resulting in the formation of imine derivatives ($R_1R_2C=NR_3$) was credited to the German chemist [14,15]. Schiff base have many critical practical applications in biological activity [16–21]. Schiff base also play a significant role in another captivating realm of liquid crystal research, specifically concerning the inherent molecular polarization exhibited by certain organic molecules adopting a banana-shaped molecular configuration [22]. The capacity of banana-shaped molecules to autonomously organize and self-assemble introduces a captivating and innovative outlook on the utilization of polar smectogenic compounds. Numerous banana compounds or polar smectic compounds originate from Schiff bases (SBs).[23–25]. Schiff's base imparts a tiered core molecular structure while maintaining

molecular linearity, thereby ensuring increased stability and facilitating the formation of mesophase [26]. The influence of liquid crystal arm number, end group polarity, and central core structure on star-shaped liquid crystal development with Schiff's base linkages [27]. Gold nanoparticles embedded in a composite material, iron dendrimer complexes, and lanthanide complexes of Schiff's base liquid crystals were produced through a synthesis process. The investigation focused on examining their electrical conductivity, photoluminescence characteristics, antioxidant activity, magnetocaloric properties, and quenching behavior [28–32]. The photochemical kinetic characteristics of Schiff's base liquid crystals derived from isoxazole and isoxazoline compounds [33]. Density Functional Theory (DFT) reveal the morphology of the chemical structure [34–37]. Dielectric spectroscopy serves as a crucial technique in the realm of material characterization, offering valuable insights into both intermolecular and intramolecular interactions. This method proves instrumental in unravelling the intricate molecular structures within a given molecular system [38]. Dielectric spectroscopy encompasses the assessment of the material's complex permittivity, examining how it changes concerning frequency at either a consistent temperature or across various temperature points. Effectively deciphered dielectric data prove valuable in diverse fields such as semiconductor design, liquid crystals research [39,40], polymer science [41], as well as colloid and emulsion sciences [42]. A comprehensive analysis of dielectric and electrical characteristics across a spectrum of Paracetamol concentrations in distilled water. The investigation spanned frequencies from 20 Hz to 2 MHz and temperatures range from 293.15K to 323.15K, with intervals of 10K. The acquired dataset underwent thorough analysis, leading to interpretations centered around the dynamics of solute-solvent interactions. Deviations in dielectric properties were observed in correlation with the concentration of PCM in distilled water, displaying anomalous behavior within the specified concentration range [43].

In this contemporary investigation, our aim is to deepen our comprehension of how the mesogenic properties are influenced by variations in alkoxy chain length and terminal substitution. To achieve this, we have synthesized novel liquid crystalline compounds. These compounds feature Schiff's base with ester as well as central linkages. Subsequently, we have conducted a comparative analysis with a structurally related to the liquid crystal compound.

2. Experimental

2.1 Materials and methods

4-Hydroxybenzoic acid, Potassium hydroxide, Ethyl alcohol, *n*-alkyl halides, 4-Hydroxybenzaldehyde, Glacial acetic acid, N, N'-Dicyclohexylcarbodiimide, 4-

Dimethylaminopyridine, Tetrahydrofuran, 3,4-Dimethyl aniline were used as received. Thin layer chromatography was performed (Merck, Kiesel 60F254 pre-coated). Infrared spectra (IR) were recorded using a Shimadzu IR-408 spectrophotometer with potassium bromide (KBr) pellets, while proton nuclear magnetic resonance spectra (400MHz) and ^{13}C NMR (125MHz) were obtained using a Bruker Avance Neo-spectrometer with deuterated chloroform. Mass spectra were recorded using waters-Single quadrupole mass detection (80-1500 ES+, centroid, cv=30). Phase appearance and transition were analysed via thermal polarizing optical microscopy (POM) employing a polarizing optical microscope with a heating stage. Leica DM 2500P polarizing optical microscope with a connected with a Linksys temperature control unit in conjunction with Leica DFC295 camera for image capture. Sample preparation: thin film of powder sample was sandwiched between a glass slide and coverslip. The enthalpies associated with changes in phases, quantified in kilojoules per mole, were determined through the utilization of a Shimadzu DSC-60 plus system, a type of differential scanning calorimeter (DSC), operating at a scanning rate of 10°C per minute. The electronic structures of all four molecules (**SB₄**, **SB₆**, **SB₈** and **SB₁₂**) were studied using quantum mechanical calculations. Each molecule was constructed using gauss view 6 software [44] and was subjected to geometry optimization using DFT calculations at the M06-2X/6-31G++(d,p) level of theory [45] as implemented in gaussian 16 quantum chemistry package [46]. No symmetry constraints were imposed during the optimization. Optimized geometries were used to visualize molecular orbitals and their associated energy values using gauss view 6. In particular, the nature and energetics of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) were characterized. In dielectric complex permittivity measurement of the sample in pallet from were carried out in two frequency regines 200Hz to 2.0 MHz and 500 MHz to 20 GHz.

2.2 Synthesis

Synthesis of 4-*n*-alkoxybenzoic acid (A)

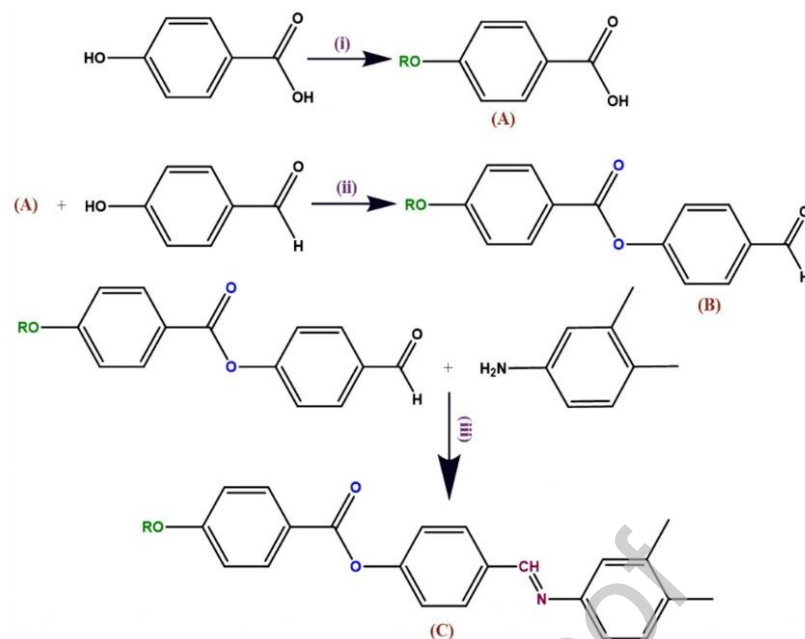
4-*n*-alkoxybenzoic acid (A) were prepared from 4-hydroxybenzoic acid [47]. 4-hydroxybenzoic acid (0.1 mole), 1-bromoalkane (0.12 mole) and potassium hydroxide (0.25 mole) were dissolved in ethanol and refluxed for 7 to 8 hours. 25ml of 10% potassium hydroxide solution was added and refluxed for 2 hours. At room temperature, the mixture was acidified with 1:1 (cold hydrochloric acid): ice. After filtration, collect the solid materials and it was recrystallized from methanol. Purities were checked by thin layer chromatography. The yield was 81–88%.

Synthesis of 4-formylphenyl 4-*n*-alkoxybenzoate (B)

4-*n*-alkoxybenzoic acid (0.10 mole) and 4-hydroxybenzaldehyde (0.15 mole) were dissolved in dry tetrahydrofuran (THF). Actually, 0.1 mole of N, N'-Dicyclohexylcarbodiimide (DCC) [48] and 0.01 mole of 4-Dimethylaminopyridine (DMAP) were added to the reaction mixture. The reaction left under stirring at room temperature overnight. The insoluble solid of 1,3-dicyclohexyl urea was filtered out, and the residue was washed with THF. The solvent from the filtrate was removed using a rotary evaporator, and the solid material was recrystallized from methanol. Purities were checked by thin layer chromatography on Merk kiesel gel 60F254 precoated plates. The yield was generally 65–72%.

Synthesis of (E)-4-(((3,4-dimethylphenyl) imino) methyl) phenyl 4-*n*-alkoxybenzoate (C).

0.01 mole of 4-formylphenyl 4-*n*-alkoxybenzoate for series (**SB_n**) were solubilized in anhydrous ethanol. Subsequently, the solution was carefully added drop-wise to the round bottom flask (RBF) containing 0.01 mole of 3,4-dimethylaniline, which had been previously dissolved in anhydrous ethyl alcohol [49] along with a small quantity of glacial acetic acid, ensuring thorough mixing. The contents of the round bottom flask were then subjected to reflux for a duration of four to six hours. Following this, the resulting reaction mixture was filtered while still hot, leading to the precipitation of the product. The obtained crude product was subjected to multiple recrystallization processes using ethyl alcohol. The purity of Series-SB_n was assessed through the utilization of thin-layer chromatography (TLC). The overall yield 90-96%. The synthetic route of Series- **SB_n** are illustrated in Scheme-1.



$$R = C_nH_{2n+1}$$

[n (number of carbon) = 1 to 8,10,12,14,16,18]

(i) R-Br, KOH, Ethanol (ii) DCC(N, N'-Dicyclohexylcarbodiimide), DMAP(4-Dimethylaminopyridine), THF (iii) Glacial acetic acid, Ethanol.

3. Characterisation

(E)-4-(((3,4-dimethylphenyl) imino) methyl) phenyl 4-ethoxybenzoate (SB₂)

IR Spectrum (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2979, 2882 (aliphatic C-H stretching), 1722 (-C=O stretching, ester), 1601 (-CH=N-), 1504 (-C=C- stretching), 1417 (C-H bending, -CH₃), 1261 (C-O stretching, ester), 1064 (C-O stretching, ether), 862 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 1.46 (t, 3H, -CH₃), 2.28 (s, 3H, Ar-CH₃), 2.30 (s, 3H, Ar-CH₃), 4.12 (m, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.05 (d, 2H, ArH), 7.16 (d, H, ArH), 7.24 (s, H, ArH), 7.32 (d, 2H, ArH), 7.96 (d, 2H, ArH), 8.14 (d, 2H, ArH), 8.47 (s, H, -Ar-CH=N-). ¹³C NMR (125 MHz, CDCl₃): δ 14.66 (H₃C-C-O-Ar), 19.33, 19.86 (H₃C-Ar), 63.99 (-H₂C-O-Ar), 114.32, 118.09, 121.29, 122.10, 129.84, 130.28, 132.35, 133.97, 134.53, 137.36, 149.65, 153.29 for aromatic carbons, 158.20 (-CH=N), 163.46 (O-C, aromatic carbon), 164.62 (-COO-). Mass Spectrum: m/z calculated for C₂₄H₂₃NO₃: 373.17, Found: 374.29. Colour: Yellow. Melting point: 161°C. Yield: 86.0%.

(E)-4-(((2-methyl-4-nitrophenyl) imino) methyl) phenyl 4-*n*-butyloxy benzoate (SB₄)

IR Spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2951, 2928 (aliphatic C-H stretching), 1725 (C=O stretching, ester), 1602 (CH=N-), 1510 (C=C- stretching), 1423 (C-H bending, -CH₃), 1251 (C-O stretching, ester), 1056 (C-O stretching, ether), 848 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 0.99 (t, 3H, -CH₃), 1.83–1.52 (m, 4H, 2 X -CH₂-), 2.28 (s, 3H, Ar-CH₃), 2.31 (s, 3H, Ar-CH₃), 4.06 (t, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.01 (d, 2H, ArH), 7.15 (d, H, ArH), 7.26 (s, H, ArH), 7.31 (d, 2H, ArH), 7.96 (d, 2H, ArH), 8.14 (d, 2H, ArH), 8.48 (s, H, -Ar-CH=N-). Colour: Yellow. Melting point: 145 °C. Yield: 84.0%.

(E)-4-(((3,4-dimethylphenyl) imino) methyl) phenyl 4-(hexyloxy) benzoate (SB₆)

IR Spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2929, 2850 (aliphatic C-H stretching), 1728 (C=O stretching, ester), 1604 (CH=N-), 1508 (C=C- stretching), 1421 (C-H bending, -CH₃), 1251 (C-O stretching, ester), 1058 (C-O stretching, ether), 844 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 0.92 (t, 3H, -CH₃), 1.48–1.35 (m, 8H, 3 X -CH₂-), 1.82 (m, 2H, -CH₂-C-O-), 2.28 (s, 3H, Ar-CH₃), 2.30 (s, 3H, Ar-CH₃), 4.05 (t, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.01 (d, 2H, ArH), 7.15 (d, H, ArH), 7.26 (s, H, ArH), 7.33 (d, 2H, ArH), 7.96 (d, 2H, ArH), 8.14 (d, 2H, ArH), 8.48 (s, H, -Ar-CH=N-). ¹³C NMR (125 MHz, CDCl₃): δ 14.03 (-H₃C-O-Ar), 19.34, 19.87 (H₃C-Ar), 22.59, 25.66, 29.06, 31.54 for methylene carbons (CH₃-(CH₂)₄-O-), 68.36 (-H₂C-O-Ar), 114.36, 118.09, 121.23, 122.26, 129.86, 130.29, 132.35, 133.97, 134.55, 137.38, 149.66, 153.31 for aromatic carbons, 158.27 (CH=N-), 163.46 (O-C, aromatic carbon), 164.63 (-COO-); Mass Spectrum: m/z calculated for C₂₈H₃₁NO₃: 429.23, Found: 430.39. Colour: Yellow. Melting point: 114°C. Yield: 84.0%.

(E)-4-(((2-methyl-4-nitrophenyl) imino) methyl) phenyl 4-*n*-heptyloxy benzoate (SB₇)

IR Spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2929, 2850 (aliphatic C-H stretching), 1728 (C=O stretching, ester), 1604 (CH=N-), 1508 (C=C- stretching), 1421 (C-H bending, -CH₃), 1251 (C-O stretching, ester), 1058 (C-O stretching, ether), 844 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 0.90 (t, 3H, -CH₃), 1.59–1.31 (m, 10 H, 4 X -CH₂-), 1.76 (m, 2H, -CH₂-C-O-), 2.28 (s, 3H, Ar-CH₃), 2.30 (s, 3H, Ar-CH₃), 4.05 (t, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.01 (d, 2H, ArH), 7.15 (d, H, ArH), 7.26 (s, H, ArH), 7.33 (d, 2H, ArH), 7.96 (d, 2H, ArH), 8.14 (d, 2H, ArH), 8.47 (s, H, -Ar-CH=N-). ¹³C NMR (125 MHz, CDCl₃): δ 14.09 (-H₃C-O-Ar), 19.34, 19.87 (H₃C-Ar), 22.61, 25.95, 29.03, 29.10, 31.76 for methylene carbons (CH₃-(CH₂)₅-O-), 68.36 (-H₂C-O-Ar), 114.36, 118.08, 121.24, 122.26, 129.85, 130.28, 132.35, 133.99, 134.54, 137.38, 149.68, 153.31 for aromatic carbons, 158.23 (CH=N-), 163.69 (O-C, aromatic carbon), 164.62 (-COO-); Mass Spectrum: m/z calculated for C₂₉H₃₃NO₃: 443.25, Found: 444.43. Colour: Yellow. Melting point: 106°C. Yield: 84.0%.

(E)-4-(((2-methyl-4-nitrophenyl) imino) methyl) phenyl 4-*n*-octyloxy benzoate (SB₈)

IR Spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2924, 2854 (aliphatic C-H stretching), 1725 (C=O stretching, ester), 1605 (CH=N-), 1510 (C=C- stretching), 1417 (C-H bending, -CH₃), 1263 (C-O stretching, ester), 1070 (C-O stretching, ether), 843 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 0.90 (t, 3H, -CH₃), 1.51–1.30 (m, 10H, 5 X -CH₂-), 1.83 (m, 2H, -CH₂-C-O-), 2.29 (s, 3H, Ar-CH₃), 2.31 (s, 3H, Ar-CH₃), 4.05 (t, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.01 (d, 2H, ArH), 7.15 (d, H, ArH), 7.26 (s, H, ArH), 7.33 (d, 2H, ArH), 7.95 (d, 2H, ArH), 8.15 (d, 2H, ArH), 8.48 (s, H, -Ar-CH=N-). Mass Spectrum: m/z calculated for C₃₀H₃₅NO₃: 457.26, Found: 458.53. Colour: Yellow. Melting point: 101°C. Yield: 84.0%.

(E)-4-(((2-methyl-4-nitrophenyl) imino) methyl) phenyl 4-*n*-decyloxy benzoate (SB₁₀)

IR Spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2924, 2854 (aliphatic C-H stretching), 1725 (C=O stretching, ester), 1605 (CH=N-), 1510 (C=C- stretching), 1417 (C-H bending, -CH₃), 1263 (C-O stretching, ester), 1070 (C-O stretching, ether), 843 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 0.91 (t, 3H, -CH₃), 1.51–1.33 (m, 14 H, 7 X -CH₂-), 1.83 (m, 2H, -CH₂-C-O-), 2.29 (s, 3H, Ar-CH₃), 2.30 (s, 3H, Ar-CH₃), 4.06 (t, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.01 (d, 2H, ArH), 7.15 (d, H, ArH), 7.26 (s, H, ArH), 7.33 (d, 2H, ArH), 7.96 (d, 2H, ArH), 8.16 (d, 2H, ArH), 8.48 (s, H, -Ar-CH=N-). ¹³C NMR (125 MHz, CDCl₃): δ 14.09 (H₃C-C-O-Ar), 19.34, 19.87 (H₃C-Ar), 22.60, 25.95, 29.06, 31.76, for methylene carbons (CH₃-(CH₂)₈-O-), 68.35 (-H₂C-O-Ar), 114.35, 118.09, 121.23, 122.26, 129.85, 130.28, 132.35, 133.98, 134.53, 137.37, 149.67, 153.31 for aromatic carbons, 158.21 (CH=N-), 163.68 (O-C, aromatic carbon), 164.61 (-COO-); Colour: Yellow. Melting point: 97°C. Yield: 84.0%.

(E)-4-(((2-methyl-4-nitrophenyl) imino) methyl) phenyl 4-*n*-dodecyloxy benzoate (SB₁₂)

IR Spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2919, 2854 (aliphatic C-H stretching), 1724 (C=O stretching, ester), 1604 (CH=N-), 1510 (C=C- stretching), 1423 (C-H bending, -CH₃), 1262 (C-O stretching, ester), 1072 (C-O stretching, ether), 846 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 0.96 (t, 3H, -CH₃), 1.47–1.29 (m, 18 H, 9 X -CH₂-), 1.74 (m, 2H, Ar-O-C-CH₂-), 2.25 (s, 3H, Ar-CH₃), 2.28 (s, 3H, Ar-CH₃), 4.07 (t, 2H, Ar-O-CH₂-), 2.29 (s, 3H, Ar-CH₃), 2.31 (s, 3H, Ar-CH₃), 4.05 (t, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.01 (d, 2H, ArH), 7.15 (d, H, ArH), 7.26 (s, H, ArH), 7.33 (d, 2H, ArH), 7.95 (d, 2H, ArH), 8.15 (d, 2H, ArH), 8.48 (s, H, -Ar-CH=N-). Colour: Yellow. Melting point: 86°C. Yield: 82.0%.

(E)-4-(((2-methyl-4-nitrophenyl) imino) methyl) phenyl 4-*n*-hexadecyloxy benzoate (SB₁₆)

IR Spectrum (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2956, 2924 (aliphatic C-H stretching), 2859, 1742 (C=O stretching, ester), 1659 (CH=N-), 1598 (C=C- stretching), 1417 (C-H bending, -CH₃), 1269 (C-O stretching, ester), 1054 (C-O stretching, ether), 862 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 0.91 (t, 3H, -CH₃), 1.97–1.26 (m, 26 H, 13 X -CH₂-), 1.74 (m, 2H, -CH₂-C-O-), 2.29 (s, 3H, Ar-CH₃), 2.31 (s, 3H, Ar-CH₃), 4.05 (t, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.01 (d, 2H, ArH), 7.15 (d, H, ArH), 7.26 (s, H, ArH), 7.33 (d, 2H, ArH), 7.95 (d, 2H, ArH), 8.15 (d, 2H, ArH), 8.48 (s, H, -Ar-CH=N-). Colour: Yellow. Melting point: 76°C. Yield: 79.0%.

(E)-4-(((2-methyl-4-nitrophenyl) imino) methyl) phenyl 4-*n*-octadecyloxy benzoate (SB₁₈)

IR Spectrum (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2956, 2859 (aliphatic C-H stretching), 1742 (C=O stretching, ester), 1659 (CH=N-), 1598 (C=C- stretching), 1417 (C-H bending, -CH₃), 1269 (C-O stretching, ester), 1054 (C-O stretching, ether), 862 (aromatic C-H bending). ¹H-NMR Spectrum (400 MHz, CDCl₃) δ in ppm: 0.90 (t, 3H, -CH₃), 2.08–1.22 (m, 30 H, 15 X -CH₂-), 2.29 (s, 3H, Ar-CH₃), 2.29 (s, 3H, Ar-CH₃), 3.74 (m, 2H, -CH₂-C-O-), 4.22 (t, 2H, Ar-O-CH₂-), 6.99 (d, H, ArH), 7.09 (d, 2H, ArH), 7.22 (d, H, ArH), 7.28 (s, H, ArH), 7.31 (d, 2H, ArH), 7.97 (d, 2H, ArH), 8.01 (d, 2H, ArH), 8.16 (d, 2H, ArH), 9.89 (s, H, -Ar-CH=N-). Colour: Yellow. Melting point: 75°C. Yield: 74.0%.

4. Results and discussion

4.1 Spectral analysis

Upon analysis of the ¹H-NMR spectrum, it was observed that a solitary proton from the imine group exhibited a singlet peak within the range of 9.89–8.47 (s, H, -CH=N-). A total of eleven aromatic protons manifested themselves in the form of six doublet peaks (d) spanning the regions of 8.16–8.14 (d, 2H, ArH), 7.97–7.95 (d, 2H, ArH), 7.33–7.31 (d, 2H, ArH), 7.22–7.15 (d, H, ArH), 7.09–7.01 (d, 2H, ArH) and 6.99 (d, H, ArH) for Series **SB_n**. Conversely, a single aromatic proton was detected as a singlet peak in the region of 7.28–7.24 (s, H, ArH) for the series **SB_n**. The ether (-CH₂-O-Ar) protons of the alkoxy chain showcased resonance signals within the range of 4.22–4.05 (J = 6.1–6.4 Hz), appearing as a triplet. Similarly, the methyl proton linked to the terminal phenyl ring resonated at δ 2.31–2.28, presenting as a singlet. The methylene protons belonging to the alkoxy chain resonated between 3.74–1.22, displaying a multiplet pattern. Lastly, the methyl group of the alkoxy chain resonated at 1.46–0.90 (J = 7.3–7.9 Hz) in the form of a triplet. The infrared spectrum ($\nu_{\max}/\text{cm}^{-1}$) exhibits absorption bands of moderate intensity in the range of 2979–2850 cm^{-1} attributed to aliphatic C-H (Sp³

hybridized) functional groups. The stretching related to carbonyl (-C=O) in the vicinity of $1742\text{--}1722\text{ cm}^{-1}$ was detected in the context of Series **SB_n**. Within the range of $1659\text{--}1601\text{ cm}^{-1}$, there was observed a moderate intensity stretching associated with the bond of imine (-C=N-). The C=C stretching frequency observed at $1598\text{--}1504\text{ cm}^{-1}$, notably the absorption at $1423\text{--}1417\text{ cm}^{-1}$ is related to the bending vibration of C-H bonds in methyl groups (-CH_3). $1269\text{--}1054\text{ cm}^{-1}$ are associated with the stretching vibrations of C-O bonds in ester and ether groups, respectively. $862\text{--}843\text{ cm}^{-1}$ serves as a marker for the bending vibrations associated with aromatic C-H bonds. UV-Visible spectra (**Figure 1**) of Series **SB₄** reveal distinctive features, characterized by dual peaks. The initial peak, observed at 275 nm with an intensity of 1.75 , is associated with the dispersion of electron density from the alkoxy oxygen donor towards the aromatic nucleus. This phenomenon significantly influences intermolecular attraction, subsequently impacting the mesophase behaviour of the compound. Concurrently, a second peak emerges at 321 nm with a hyperchromic shift of 0.70 , attributable to the extension of conjugation. This extension enhances the $\eta\text{-}\pi^*$ adsorption, contributing to the observed spectral characteristics.

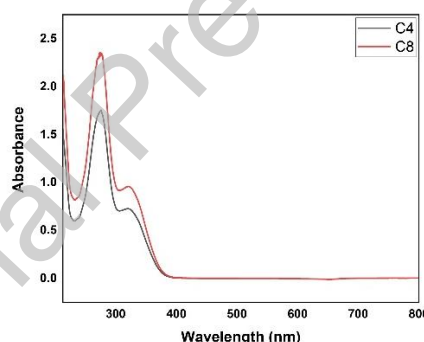


Figure 1. UV-V is absorption spectra of series **SB₄ & SB₈**)

4.2 Mesomorphic behaviour

In this study, a series of derivatives of (E)-4-(((3,4-dimethylphenyl) imino) methyl) phenyl 4-*n*-alkoxybenzoate **SB_n** were investigated for their mesomorphic behavior. It was found that all the derivatives in this series exhibited mesogenic properties. The derivatives with *n*-alkoxy groups ranging **SB₁** to **SB₇** demonstrated an enantiotropic nematic mesophase. These nematic mesophases were enantiotropic, indicating they could reversibly transform between the nematic phase and isotropic liquid phase with changes in temperature. On the other hand, the derivatives with *n*-alkoxy groups, specifically **SB₁₄** to **SB₁₈**, exhibited an enantiotropic smectic A mesophase. Smectic A phase was also enantiotropic, allowing reversible transformation with

temperature changes. Notably, **SB₈** and **SB₁₀**, displayed monotropic mesophase. **SB₈** exhibits a nematic mesophase in the heating stage, while a smectic A mesophase is exhibited in the cooling stage. The middle member of the series **SB₁₂** displayed both Smectic A and nematic mesophases. This observation suggested that it had a border temperature range in which could exist in either the smectic or nematic phase. **Table 1** recorded the transition temperature data for these derivatives, providing valuable information about the temperature. Additionally, **Figure 2** illustrated the mesomorphic behavior of the **SB_n** compounds, showing their clearing and melting points of all derivatives. Notably, a consistent trend of decreasing clearing temperatures across the series was observed. The relationship between the nematic to isotropic transition temperatures (N–I) and the alkoxy-chain length (n) follows a proportional decrease. These findings are consistent with the research findings of Gray [50] and Imeri [51]. In other words, as the alkoxy-chain length increases, the N–I temperatures decrease in a manner supported by the studies conducted by Gray and Imrie.

Table 1: Phase transition temperatures (°C) of series **SB_n** compounds.

Compound	R =-					
	C_nH_{2n+1}	Cr	SmA	N	I	
	n =					
SB₁	1	•	-	•	180	• 210
SB₂	2	•	-	•	161	• 192
SB₃	3	•	-	•	156	• 182
SB₄	4	•	-	•	145	• 174
SB₅	5	•	-	•	126	• 163
SB₆	6	•	-	•	114	• 146
SB₇	7	•	-	•	106	• 148
SB₈	8	•	(61)	•	101	• 155
SB₁₀	10	•	(59)	•	97	• 151
SB₁₂	12	•	86	•	103	• 137
SB₁₄	14	•	78	•	-	• 112
SB₁₆	16	•	76	•	-	• 106
SB₁₈	18	•	75	•	-	• 104

() = monotropic value; Cr=crystalline solid; SmA=smectic A phase; N=nematic phase; I=isotropic liquid phase; •=phase exists.

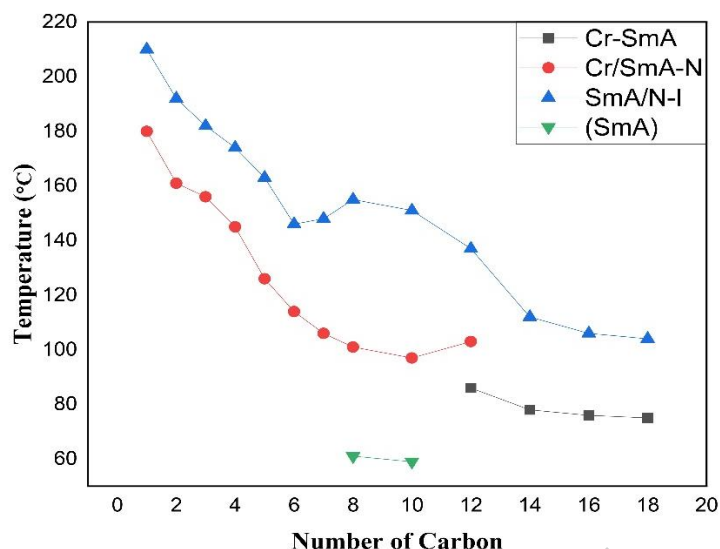


Figure 2. LCs phase behaviour of series **SB_n**

() = monotropic value; Cr=crystalline solid; SmA=smectic A phase; N=nematic phase; I=isotropic liquid phase.

4.3 Polarising optical microscope study

The examination of mesomorphic characteristics in every derivative within the synthesized Series **SB_n** was conducted utilizing a polarized optical microscope equipped with a heating and cooling platform. The experimental procedure involved creating a slender sample layer by carefully placing the derivatives between coverslip and glass slide, forming a sandwich-like arrangement. This method allowed for the subsequent analysis of mesogenic characteristics. The derivatives of series **SB_n** were discovered to exhibit mesogenic properties. Notably, in series **SB₁** to **SB₇** derivatives displayed an enantiotropic nematic mesophase. Similarly, **SB₁₄** to **SB₁₈** derivatives of series **SB_n** showed an enantiotropic smecticA mesophase. Derivative **SB₈** exhibited a schlieden nematic phase at 101°C to the isotropic (155°C) phase, (POM texture shown in **Figure 3**) while a smectic A mesophase is exhibited in the cooling stage at 61°C. On other hand **SB₁₂** demonstrated a focal conical smectic A phase on heating from the crystalline state to 86°C followed by nematic mesophase at 103°C and isotropic range at 137°C. Derivative **SB₁₈** display smectic A mesophase at 78 °C to the isotropic (112°C) while heating.

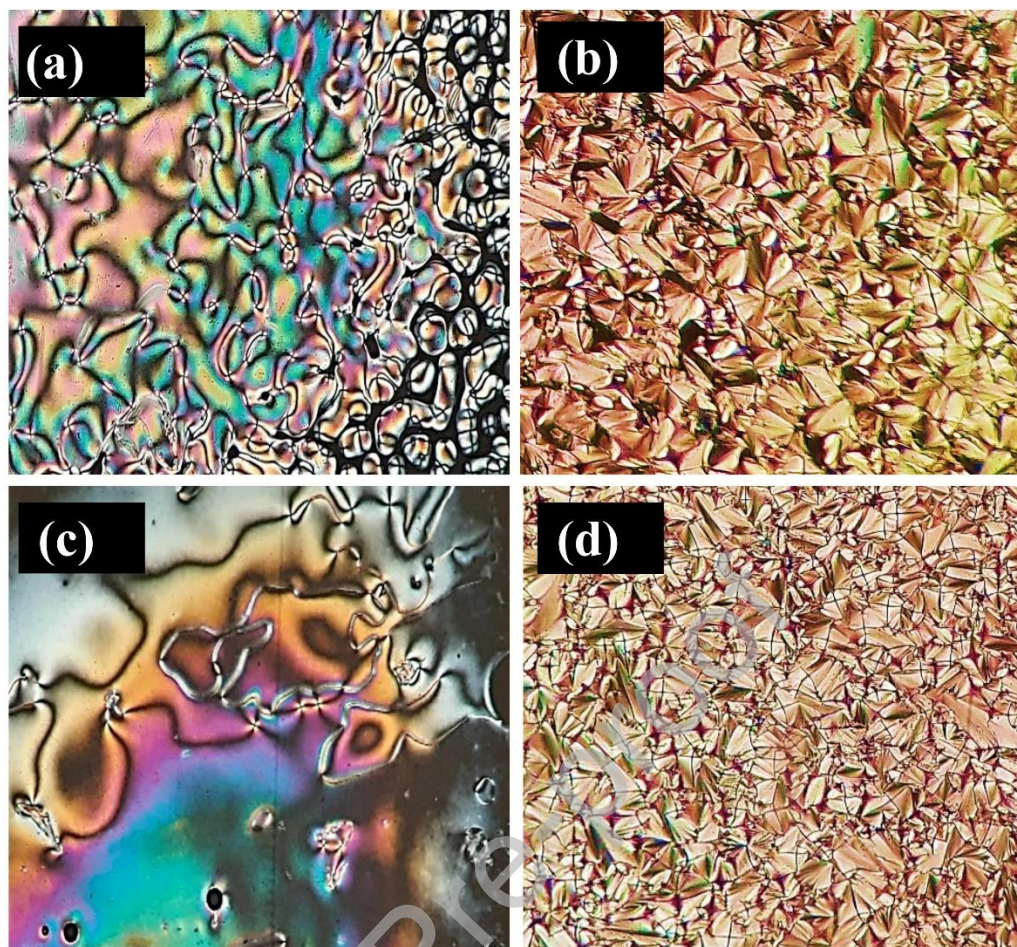


Figure 3. Optical microphotographs of Nematic (while heating) & Smectic phase (while cooling) at 101°C and 61°C of compound **SB₈** (a & b). Optical microphotographs of Smectic & Nematic phase (while cooling) at 86°C and 103°C of compound **SB₁₂** (c & d).

4.4 Differential Scanning calorimetry analysis (DSC)

Calorimetry serves as a valuable technique for investigating phase transitions, offering precise data that allows us to derive meaningful insights about the characteristics of the phases involved in these transitions. In our current research, we conducted measurements to determine the enthalpies associated with the mesogenic homologues within series **SB_n**. The enthalpies of phase transitions upon heating are documented in units of kJ/mol, and these measurements were obtained using a scanning rate of 10°C per minute. We confirmed the thermal stability of these compounds by consistently obtaining identical thermograms during repeated heating cycles. In **Figure 4**, shows the DSC thermograms for the **SB_n** compounds, which were generated during the initial heating cycle at 10°C per minute.

SB₄ showed two clear peaks while heating, at 145°C and 174°C. These represent the transitions from a crystalline state to a nematic state (Cr-N) and from the nematic state to an isotropic state

(N-I). The enthalpy changes for these transitions are 51.6130 kJ/mol and 0.8241 kJ/mol, respectively. As well as compound **SB₈** displays two peaks 101°C and 155°C at heating stage. while a smectic A mesophase is exhibited in the cooling stage at 60°C. The enthalpy changes for these transitions are 45.1124 kJ/mol and 0.5871 kJ/mol, as well as smectic A mesophase enthalpy changes value is 10.93 kJ/mol respectively. Compound **SB₁₂** displays three peaks at temperatures of 86°C, 103°C, and 137°C. These temperature points correspond to the transitions from crystal to Smectic A (Cr-SmA), Smectic A to nematic (SmA-N), and nematic to isotropic (N-I) phases, respectively. These transitions are accompanied by changes in enthalpy, with values of 44.8818 kJ/mol, 0.0410 kJ/mol, and 0.5592 kJ/mol, in the same order. Additionally, the consistency of these findings was further confirmed through polarized optical microscopy (POM) analysis.

Table-2 shows the phase sequences, transition temperatures, as well as enthalpies and entropies for the mesogenic members within Series **SB_n**. Notably, the data underscores the remarkable stability exhibited by all the mesomorphic compounds, with particular emphasis on the heightened stability observed in the lower members of the homologous series **SB_n**.

Table-2 highlights a noteworthy observation: within Series **SB_n**, the enthalpy values associated with transitions are significantly higher compared to the enthalpy values corresponding to melting. The variation in enthalpy and entropy alterations observed during the transformation from a crystalline state to a smectic A phase within the synthesized series **SB_n** could be attributed to structural variances in **SB_n**. Variances in planarity and length of **SB_n** molecules can affect intermolecular interactions, thereby impacting the phase transition enthalpy in relation to the length of the alkoxy chain. Similarly, a comparable trend is noted in the nematic transition. The enthalpy during the shift from crystalline to nematic exceeds that from nematic to isotropic. As evident in **Table 2**, the slight changes in enthalpy during N-I transitions can be attributed to factors like the aspect ratio, the inclusion of the vinyl group for improved alignment, and enhanced molecular biaxiality due to dimethyl substitution on the side. These aspects collectively contribute to a reduction in entropy change during the specified transition. [52,53].

Table: -2 Phase transition temperatures ($^{\circ}\text{C}$), enthalpy change, entropy change and normalised entropy of the series- **SB_n** by DSC and POM measurement.

Compound	Transition	Peak temp./ $^{\circ}\text{C}$	$\Delta H/\text{kJmol}^{-1}$	$\Delta S/\text{kJmol}^{-1} \text{K}^{-1}$
SB₄	Cr-N	145	51.613	0.1235
	N-I	174	0.8241	0.0024
SB₈	Cr-N	101	45.1124	0.1216
	N-I	155	0.5871	0.0014
	SmA	61	10.93	0.0327
SB₁₂	Cr-SmA	86	44.8818	0.1250
	SmA-N	103	0.0410	0.00011
	N-I	137	0.5592	0.0014

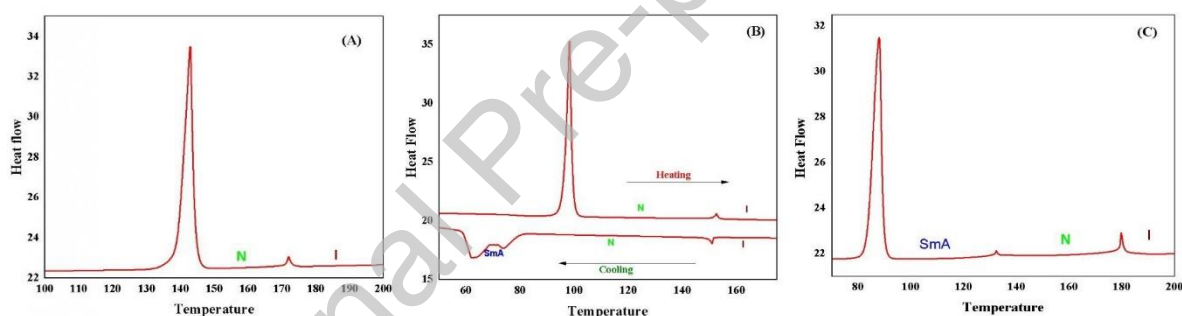


Figure 4. DSC thermogram of series **SB** (4, 8 & 12).

(A=SB₄, B=SB₈ & C=SB₁₂)

4.5 Dielectric study

0.73 gm of compound **SB_n** was compressed into a pellet using a Press-Well Hydraulics unit at 4 ton/MPa pressure to measure dielectric properties, with complex permittivity tests conducted at frequencies ranging from 200 Hz to 20 GHz using an Agilent precision LCR meter E4980A and Agilent 16451B dielectric test fixture. [54,55] The test fixture was calibrated to eliminate the systematic measurement error prior to initiate the experiment. The complex dielectric function $\epsilon^*(f)$ of the sample was determined at 161 frequency points on log scale in the frequency range of 200 Hz to 2 MHz [47,48]. Anritsu Shockline Vector Network Analyser (VNA) model no. MS46322A along with SPEAG DAK-TL (Dielectric Assessment Kit for Thin Layers) was utilized [56,57] to obtain complex permittivity data of samples at 391

frequency points in the frequency range of 500 MHz to 20 GHz. All the dielectric measurements were taken at room temperature, 300.15 K.

Frequency dependence of dielectric constant (ϵ') and dielectric loss (ϵ'') of synthesised LC in two frequency spans: $200 \text{ Hz} \leq f \leq 2 \text{ MHz}$ and $500 \text{ MHz} \leq f \leq 20 \text{ GHz}$ at 300.15 K temperature, is represented in **Figure 5**. It can be seen that the values of ϵ' is almost frequency independent over the entire frequency range. Frequency independent value in the static frequency region $200 \text{ Hz} \leq f \leq 2 \text{ MHz}$ is taken as static dielectric constant (ϵ_s), which is 2.25, suggesting polar nature of the compound. Molecules of the studied compound become locked in a solid or rigid lattice at room temperature, hence cannot contribute to orientational polarization causing smaller value of static dielectric constant. From the dielectric loss against frequency plot shown in **Figure 5**, it can be seen that dielectric loss values of this compound are order of magnitude higher in the low frequency regime and decreases rapidly with frequency. Higher value of dielectric loss at the lower end of the frequency range may be attributed to the translational diffusion of ionic impurities in the sample. In the microwave frequency range, a peak in dielectric loss at frequency 10.9 GHz is observed, providing relaxation time value of 14.6 pS. This loss due to the rotation of the end polar groups of the molecule.

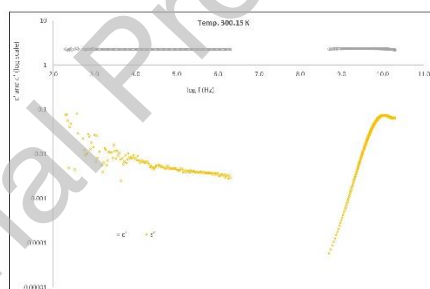


Figure 5. Plots of dielectric constant (ϵ') and dielectric loss (ϵ'') vs frequency of synthesised **SB_n**.

4.6 DFT

All four series **SB_n** molecules (**SB₄**, **SB₆**, **SB₈** and **SB₁₂**) were optimized using the DFT methods at the M06-2X/6-31G++(d,p) level of theory. The optimized geometries are shown in **Figure 6** and the various electronic properties are presented in **Table 3**. For each molecule, we calculated the energy gap ($E_{\text{HOMO}} - E_{\text{LUMO}}$), which is an important parameter to assess the thermal stability and the chemical reactivity of a molecule. The E_{HOMO} and E_{LUMO} energy gap were computed to be negative for all derivative molecules, indicating their stability and in the following order: **SB₄** > **SB₆** > **SB₈** > **SB₁₂**. Interestingly, E_{LUMO} energy values were calculated

to be negative for all four molecules, indicating their reactive nature. Further, Frontier Molecular Orbital analysis illustrates that for all molecules, the highest occupied molecular orbital (HOMO) orbital is localized on the terminal phenyl ring of the Schiff's base (**Figure 7**). Whereas the lowest occupied molecular orbital (LUMO) orbital is localized on the π orbitals of the phenyl ring connecting the base with the alkoxy group.

Table 3. The calculated E_{HOMO} , E_{LUMO} (eV), $E_{\text{HOMO}} - E_{\text{LUMO}}$ (ΔE , eV), and dipole moment (Debye) for molecules as calculated at the M06-2X/6-31G ++(d,p) level of theory.

	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)	Dipole Moment (Debye)
SB₄	-5.8524	-0.5794	-5.2730	3.52
SB₆	-5.8504	-0.5875	-5.2629	3.54
SB₈	-5.8510	-0.6011	-5.2499	3.59
SB₁₂	-5.8477	-0.6147	-5.2330	3.41

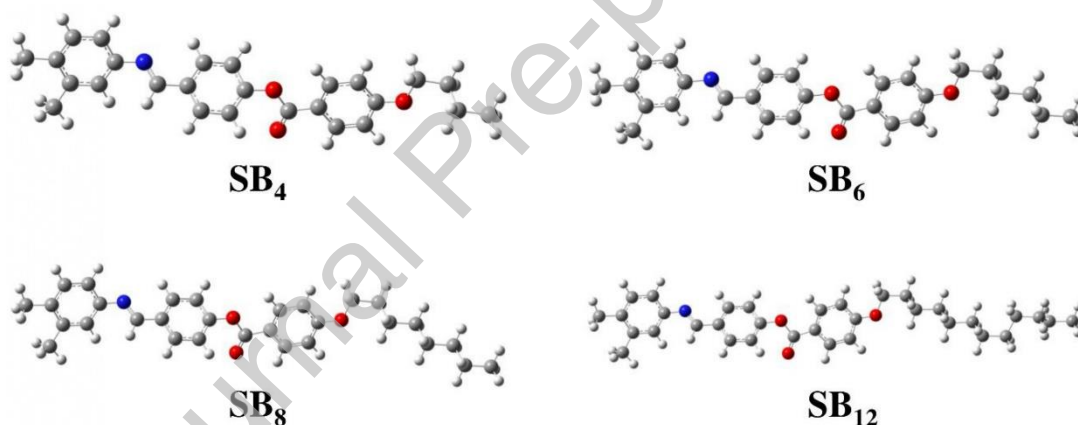


Figure 6: The geometry of **SB₄**, **SB₆**, **SB₈** and **SB₁₂** molecules optimized at the M06-2X/6-31G++(d,p) level of theory.

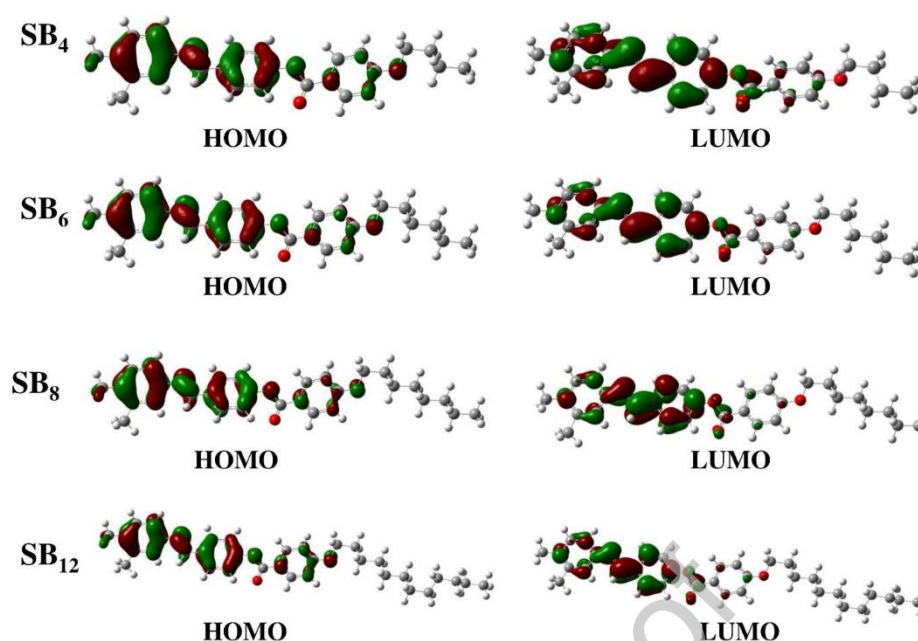


Figure 7: The HOMO and LUMO orbitals **SB₄**, **SB₆**, **SB₈** and **SB₁₂** molecules as calculated at the M06-2X/6-31G++(d,p) level of theory.

5. Comparative study

The properties of the mesophase in a liquid crystal compound are greatly impacted by its molecular structure. Relationship can be established between the transition process, stability of the mesophase, and the temperature span of the mesophase through an examination of the molecule's geometry and form. **Table 4** provides a concise overview of the phase transition temperatures, the temperature range of the nematic mesophase, and the onset of the nematic phase for the synthesized series. Additionally, comparative data for Series-X [58], Series-Y [59], and Series-Z [10] is included for reference. The molecular structures of the comparison series are depicted in **Figure 8**.

The comparison presented in **Table 4** indicates that the width of the nematic mesophase and the N-I transition temperature of the **SB₈** series are 11°C and 60°C lower, respectively, when compared to the X series. This discrepancy can be attributed to the structural difference between the molecules of **SB₈** and X, which is limited to the terminal linkages. While both series share the same central ester linkages, **SB₈** features a terminal dimethyl group, whereas X has a methyl terminal group. The distinction between **SB₈** and X lies solely in the terminal substitution, where the methyl group in X is positioned para, while in **SB₈**, it is positioned ortho

and para laterally. This alteration in the electron-donating methyl group impacts the overall polarity of the molecule, ultimately leading to a decrease in the melting point.

In a similar vein, the Series-Y exhibits a difference in the presence of a terminal fluoro (-F) group at the meta position, resulting in a reduction of 36°C in the nematic mesophase length of SB₈, along with a 14°C lower N-I transition temperature in comparison to series SB₈. This alteration in the location of the electron-donating dimethyl group impacts the stability of the terminal ring, subsequently influencing the thermal stability of the compound. The lateral substitution within the phenyl ring connected to Schiff's base introduces a twisting steric effect within the molecule.

Series-Z and SB₈ differ in terms of the end polar nitro (-NO₂) and methyl (-CH₃) substituted phenyl ring that is connected with Schiff's base in Series- Z, while a dimethyl substituted ring is connected with Schiff's base in series SB₈. The nematic mesophase length of SB₈ is reduced by 3°C, and the N-I transition temperature of series-Z is lower by 33°C respectively, in comparison to that of series SB₈. This alteration in the position of electron contributing dimethyl group influences the stability of the end ring which consequently impacts the thermal stability of the molecule.

Table:-4 Comparison of the phase transition temperatures, nematic mesophase range and comparative molecular structures of compounds **SB₈**, **X**, **Y** and **Z**.

Compound	Nematic	Isotropic	Mesophase range/°C	Commencement of nematic phase
SB₈	101	155	54	C ₈
X	112	215	103	C ₈
Y	137	141	4	C ₈
Z	104	122	18	C ₈

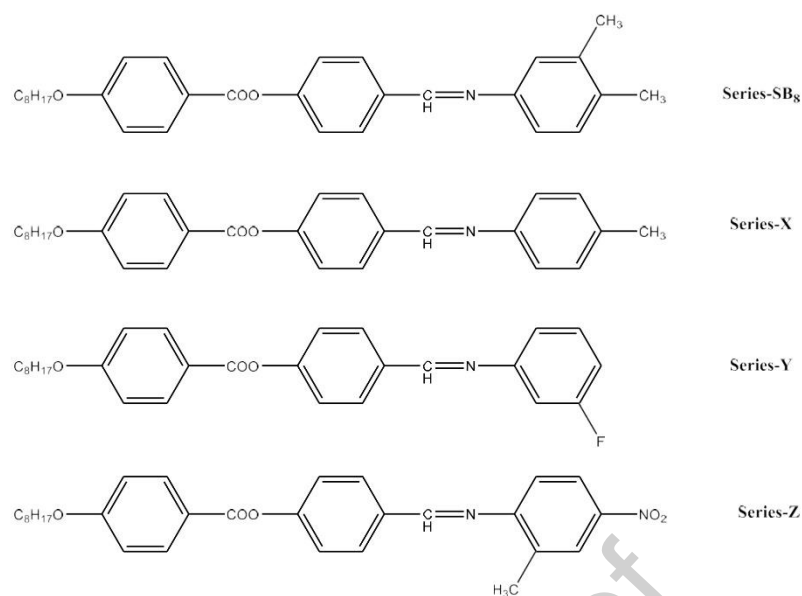


Figure 8. Comparative geometry of Series-SB₈, X, Y and Z.

6. Conclusion

New liquid crystal Schiff's bases bearing ester moiety **SB_n** were synthesised and investigated for their mesophase and DFT calculation. Our study involved investigating how the behavior of compounds is affected by varying the terminal attachments, including changes in the alkyl chain and the addition of terminal dimethyl groups. Additionally, the presence of a tail substituent influences the mesomorphic properties of reported series. The homologs of series **SB_n** from [**SB₁** to **SB₇**] demonstrated an enantiotropic nematic mesophase within the temperature range of 180-106 °C, from [**SB₁₄** to **SB₁₈**] exhibited an enantiotropic smectic A mesophase at temperatures between 78-75 °C, as well as [**SB₈** and **SB₁₀**] exhibits a nematic mesophase in the heating stage at 101-97 °C, while a smectic A mesophase is exhibited in the cooling stage at 61-59 °C. With the help of DFT; E_{HOMO} and E_{LUMO} energy gap were computed to be negative for all derivative indicating their stability in the following order: **SB₄** > **SB₆** > **SB₈** > **SB₁₂**. Dielectric study through determined values of complex permittivity of the synthesised liquid crystal over a broad frequency range reported. Also determined static permittivity value of liquid crystal is 2.25, at room temperature. The compound exhibited a relaxation peak in the dielectric loss spectra in the microwave frequency range, which may be assigned to the rotation of the end polar group of the molecule.

Acknowledgment

The authors thankful specially the Principal Prof. Dr Keyur Shah of Shri M. M. Patel Institute of Sciences and Researches, Department of Chemistry (KSV) Gandhinagar for providing research facilities. The authors extend their appreciation to the Researchers Supporting Project number (RSP2024R380), King Saud University, Riyadh, Saudi Arabia.

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References

- [1] B. Naskar, D.K. Maiti, A. Bauzá, A. Frontera, C. Prodhan, K. Chaudhuri, S. Goswami, Synthetic Modulation of a Chemosensor Affords Target Metal Ion Switch from Zn²⁺ to Al³⁺, *ChemistrySelect* 2 (2017) 5414–5420. <https://doi.org/10.1002/slct.201700861>.
- [2] S. Setia, S. Sidiq, J. De, I. Pani, S.K. Pal, Applications of liquid crystals in biosensing and organic light-emitting devices: future aspects, *Liq Cryst* 43 (2016) 2009–2050. <https://doi.org/10.1080/02678292.2016.1213002>.
- [3] H. Yu, G. Zhu, Y. Wang, Preparation of polyimide alignment films with high photosensitivity and low solid content, *Liq Cryst* 48 (2021) 598–606. <https://doi.org/10.1080/02678292.2020.1799446>.
- [4] E. Ritter, P. Przybylski, B. Brzezinski, F. Bartl, Schiff Bases in Biological Systems, *Curr Org Chem* 13 (2009) 241–249. <https://doi.org/10.2174/138527209787314805>.
- [5] J.W. Goodby, Free volume, molecular grains, self-organisation, and anisotropic entropy: machining materials, *Liq Cryst* (2017) 1–9. <https://doi.org/10.1080/02678292.2017.1347293>.
- [6] A.K. Prajapati, N.L. Bonde, Mesogenic Schiff's Base Esters with a Methoxyethyl Tail, *Molecular Crystals and Liquid Crystals* 461 (2006) 15–28. <https://doi.org/10.1080/15421400600914882>.
- [7] A.K., and H.N.Patel. Prajapati, Mesogenic cinnamate with ethoxyethyl tail, *Myscience* 1 (2006) 105–114.
- [8] A.K. Prajapati, N.L. Bonde, H.N. Patel, Mesogenic Schiff's base ester with chloroethyl tail, *Phase Transitions* 78 (2005) 507–513. <https://doi.org/10.1080/01411590500188876>.
- [9] G.-Y. Yeap, T.-C. Hng, S.-Y. Yeap, E. Gorecka, M.M. Ito, K. Ueno, M. Okamoto, W.A.K. Mahmood, C.T. Imrie, Why do non-symmetric dimers intercalate? The synthesis and characterisation of the α -(4-benzylidene-substituted-aniline-4'-oxy)- ω -(2-methylbutyl-4'-(4''-phenyl)benzoateoxy)alkanes, *Liq Cryst* 36 (2009) 1431–1441. <https://doi.org/10.1080/02678290903271504>.
- [10] R.R. Koshti, A. Vyas, K.A. Patel, H.S. Patel, M.B. Patel, H.N. Patel, New Schiff's base cinnamates/benzoates liquid crystals with lateral methyl substitutes: characterisation, mesomorphic behaviour and DFT calculation, *Liq Cryst* 49 (2022) 248–263. <https://doi.org/10.1080/02678292.2021.1957163>.
- [11] G.-Y. Yeap, F. Osman, C.T. Imrie, Non-symmetric dimers: effects of varying the mesogenic linking unit and terminal substituent, *Liq Cryst* 42 (2015) 543–554. <https://doi.org/10.1080/02678292.2015.1004843>.
- [12] Gray GW., *Thermotropic liquid crystals*, John Wiley & Sons, New York, 1987.
- [13] E. Tsagogiannis, S. Asimakoula, A.P. Drainas, O. Marinakos, V.I. Boti, I.S. Kosma, A.-I. Koukkou, Elucidation of 4-Hydroxybenzoic Acid Catabolic Pathways in

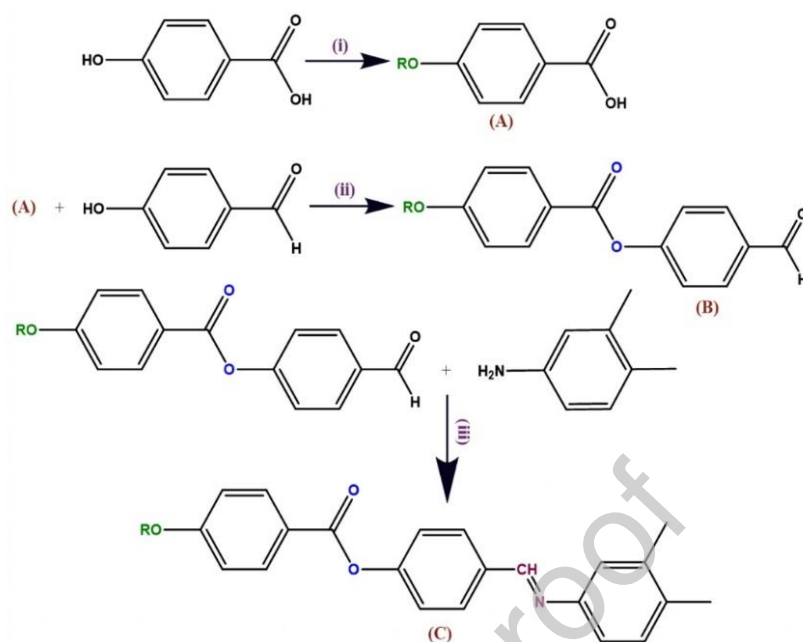
- Pseudarthrobacter phenanthrenivorans Sphe3, *Int J Mol Sci* 25 (2024) 843. <https://doi.org/10.3390/ijms25020843>.
- [14] H. Schiff, Mittheilungen aus dem Universitätslaboratorium in Pisa: Eine neue Reihe organischer Basen, *Justus Liebigs Ann Chem* 131 (1864) 118–119. <https://doi.org/10.1002/jlac.18641310113>.
- [15] W. Qin, S. Long, M. Panunzio, S. Biondi, Schiff Bases: A Short Survey on an Evergreen Chemistry Tool, *Molecules* 18 (2013) 12264–12289. <https://doi.org/10.3390/molecules181012264>.
- [16] S.A. Hassan, J.B. Ziwar, D. muhammed Aziz, M.N. Abdullah, Sonochemical synthesis of New Thiazolidin-4-one derivatives as potent anticancer and antimicrobial agents with Docking design, and Energy gap estimation, *J Mol Struct* 1301 (2024) 137282. <https://doi.org/10.1016/j.molstruc.2023.137282>.
- [17] S.A. Hassan, D.M. Aziz, M.N. Abdullah, A.R. Bhat, R.S. Dongre, T. Ben Hadda, F.A. Almalki, S.M.A. Kawsar, A.K. Rahiman, S. Ahmed, M.H. Abdellattif, M. Berredjem, S.A. Sheikh, J. Jamalis, *In vitro* and *in vivo* evaluation of the antimicrobial, antioxidant, cytotoxic, hemolytic activities and *in silico* POM/DFT/DNA-binding and pharmacokinetic analyses of new sulfonamide bearing thiazolidin-4-ones, *J Biomol Struct Dyn* 42 (2024) 3747–3763. <https://doi.org/10.1080/07391102.2023.2226713>.
- [18] S.A. Hassan, D.M. Aziz, M.N. Abdullah, A.R. Bhat, R.S. Dongre, S. Ahmed, A. Kalilur Rahiman, T. Ben Hadda, M. Berredjem, J. Jamalis, Design and synthesis of oxazepine derivatives from sulfonamide Schiff bases as antimicrobial and antioxidant agents with low cytotoxicity and hemolytic prospective, *J Mol Struct* 1292 (2023) 136121. <https://doi.org/10.1016/j.molstruc.2023.136121>.
- [19] D.M. Aziz, S.A. Hassan, O.Q. Hamad, Azo-azomethine complex activity and sensor potential toward Ca(II) ion in life samples: The spectroscopic and morphological studies, *J Mol Struct* 1293 (2023) 136204. <https://doi.org/10.1016/j.molstruc.2023.136204>.
- [20] D. muhammed Aziz, S.A. Hassan, D.M. Mamand, K. Qurbani, New azo-azomethine derivatives: Synthesis, characterization, computational, solvatochromic UV–Vis absorption and antibacterial studies, *J Mol Struct* 1284 (2023) 135451. <https://doi.org/10.1016/j.molstruc.2023.135451>.
- [21] Molecular Study of IL-7R Gene Polymorphism and their Associations with Male Multiple Sclerosis Patients in Erbil Province., *Zanco J Pure Appl Sci* 33 (2021). <https://doi.org/10.21271/ZJPAS.33.1.3>.
- [22] H. Kim, S. Lee, T.J. Shin, Y.J. Cha, E. Korblova, D.M. Walba, N.A. Clark, S.B. Lee, D.K. Yoon, Alignment of helical nanofilaments on the surfaces of various self-assembled monolayers, *Soft Matter* 9 (2013) 6185. <https://doi.org/10.1039/c3sm50637a>.
- [23] D.M. Walba, E. Korblova, R. Shao, N.A. Clark, bow-phase mesogen showing strong, robust analog electro-optics., *J Mater Chem* 11 (2001) 2743–2747. <https://doi.org/10.1039/b102732h>.

- [24] D.K. Yoon, Y. Yi, Y. Shen, E.D. Korblova, D.M. Walba, I.I. Smalyukh, N.A. Clark, Orientation of a Helical Nanofilament (B4) Liquid-Crystal Phase: Topographic Control of Confinement, Shear Flow, and Temperature Gradients, *Advanced Materials* 23 (2011) 1962–1967. <https://doi.org/10.1002/adma.201004482>.
- [25] A. Gowda, A. Roy, S. Kumar, Synthesis and mesomorphic properties of novel Schiff base liquid crystalline EDOT derivatives, *J Mol Liq* 225 (2017) 840–847. <https://doi.org/10.1016/j.molliq.2016.11.010>.
- [26] R.W. Date, C.T. Imrie, G.R. Luckhurst, J.M. Seddon, Smectogenic dimeric liquid crystals. The preparation and properties of the α,ω -bis(4-*n*-alkylanilinebenzylidene-4'-oxy)alkanes, *Liq Cryst* 12 (1992) 203–238. <https://doi.org/10.1080/02678299208030393>.
- [27] Q.-Q. He, Y. Lan, Y.-Y. Quan, C.-Y. Li, Y.-P. Liu, X.-J. Wang, Y.-G. Jia, M. Tian, D.-S. Yao, The influence of the structure of terminal groups and cores on the properties of schiff base star-shaped liquid crystals, *Liq Cryst* 48 (2021) 1309–1320. <https://doi.org/10.1080/02678292.2020.1861346>.
- [28] N. Das, H. Acharya, S.K. Prasad, D.S.S. Rao, C.R. Bhattacharjee, Mesomorphic Schiff base amine tethered giant gold nanoparticles, *Liq Cryst* 44 (2017) 2259–2266. <https://doi.org/10.1080/02678292.2017.1370144>.
- [29] K.K. Abid, S.M. Al-barody, Synthesis, characterisation and liquid crystalline behaviour of some lanthanides complexes containing two azobenzene Schiff base, *Liq Cryst* 41 (2014) 1303–1314. <https://doi.org/10.1080/02678292.2014.919670>.
- [30] M.S. Gruzdev, V. V. Korolev, A.G. Ramazanova, U. V. Chervonova, O. V. Balmasova, Magnetocaloric properties of dendrimer complexes of Fe(III) with substituted Schiff base, *Liq Cryst* 45 (2018) 907–911. <https://doi.org/10.1080/02678292.2017.1397783>.
- [31] N. Das, D. Borah, H. Acharya, S. Choudhury, S.K. Prasad, D.S.S. Rao, C.R. Bhattacharjee, Grafting a mesomorphic Schiff base onto gold nanoparticle via ester link – photoluminescence, mesomorphism, electrical conductivity and antioxidant activity, *Liq Cryst* 46 (2019) 609–617. <https://doi.org/10.1080/02678292.2018.1515372>.
- [32] H. Karaca, Redox chemistry, spectroelectrochemistry and catalytic activity of novel synthesized phthalocyanines bearing four schiff bases on the periphery, *J Organomet Chem* 822 (2016) 39–45. <https://doi.org/10.1016/j.jorganchem.2016.08.013>.
- [33] L. Fritsch, V. Lavayen, A.A. Merlo, Photochemical behaviour of Schiff base liquid crystals based on isoxazole and isoxazoline ring. A kinetic approach, *Liq Cryst* 45 (2018) 1802–1812. <https://doi.org/10.1080/02678292.2018.1488280>.
- [34] S. Hassan, An efficient One-pot three-component synthesis, Molecular docking, ADME and DFT predictions of new series Thiazolidin-4-one derivatives bearing a Sulfonamide moiety as potential Antimicrobial and Antioxidant agents, *Egypt J Chem* 0 (2022) 0–0. <https://doi.org/10.21608/ejchem.2022.104381.4819>.
- [35] M.N. Abdullah, P. Osw, S.A. Hassan, S. Othman, Two new cyclohexenone derivatives: Synthesis, DFT estimation, biological activities and molecular docking study, *J Mol Struct* 1301 (2024) 137361. <https://doi.org/10.1016/j.molstruc.2023.137361>.

- [36] H. Karaca, S. Kazancı, The metal sensing applications of chalcones: The synthesis, characterization and theoretical calculations, *J Mol Struct* 1248 (2022) 131454. <https://doi.org/10.1016/j.molstruc.2021.131454>.
- [37] H. Karaca, N.Ç. Delibaş, S. Sağlam, H. Pişkin, S. Sezer, T. Hökelek, M. Teker, Metallophthalocyanines derived with phenyl sulfide by bridging triazole using click chemistry: Synthesis, Computational Study, Redox Chemistry and Catalytic Activity, *J Mol Struct* 1236 (2021) 130225. <https://doi.org/10.1016/j.molstruc.2021.130225>.
- [38] C.M. Trivedi, Dielectric and other physical properties of some polar molecules of pharmaceutical importance, Gujarat University, 2016.
- [39] S.M., Y.L. and K.K.Ng. Sze, Physics of semiconductor devices, fourth, John wiley & sons, 2021.
- [40] A.S. Grove, Physics and technology of semiconductor devices., (1967).
- [41] B.E.R. N. McCrum, Anelastic and Dielectric Properties of Polymeric Solids, G. Williams (Ed.) (1967).
- [42] P. Sherman, Academic Press, Emulsion Science (1968).
- [43] V.A. Rana, T.R. Pandit, Dielectric spectroscopic and molecular dynamic study of aqueous solutions of paracetamol, *J Mol Liq* 290 (2019) 111203. <https://doi.org/10.1016/j.molliq.2019.111203>.
- [44] R.D.I.I., T.A.K. and J.M.Millam. Dennington, GaussView, version 6.0. 16, Semichem Inc Shawnee Mission KS (2016).
- [45] M. ea, G.W.T.H.B.S.G.E.S.Ma.R.J.R.C.G.S. et al. Frisch, Gaussian 16, (2016).
- [46] Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06 functionals and 12 other functionals, *Theor Chem Acc* 119 (2008) 525–525. <https://doi.org/10.1007/s00214-007-0401-8>.
- [47] J.S. Dave, R.A. Vora, Mesomorphic Behaviour of the Cholesteryl Esters-I: p-n-Alkoxybenzoates of Cholesterol, in: *Liquid Crystals and Ordered Fluids*, Springer US, Boston, MA, 1970: pp. 477–487. https://doi.org/10.1007/978-1-4684-8214-0_38.
- [48] A. Hassner, V. Alexanian, Direct room temperature esterification of carboxylic acids, *Tetrahedron Lett* 19 (1978) 4475–4478. [https://doi.org/10.1016/S0040-4039\(01\)95256-6](https://doi.org/10.1016/S0040-4039(01)95256-6).
- [49] J.S. Dave, P.R. Patel, Influence of Molecular Structure on Liquid Crystalline Properties and Phase Transitions in These Structures, Part I, *Molecular Crystals* 2 (1966) 103–114. <https://doi.org/10.1080/15421406608083063>.
- [50] Gray GW., *Molecular structure and the properties of liquid crystals*, London,UK., 1962.

- [51] C.T. Imrie, L. Taylor, The preparation and properties of low molar mass liquid crystals possessing lateral alkyl chains, *Liq Cryst* 6 (1989) 1–10. <https://doi.org/10.1080/02678298908027317>.
- [52] G.-Y. Yeap, T.-N. Chan, W.-S. Yam, K. Madrak, D. Pocięcha, E. Gorecka, Non-symmetric chiral isoflavone dimers: synthesis, characterisation and mesomorphic behaviour, *Liq Cryst* 39 (2012) 1041–1047. <https://doi.org/10.1080/02678292.2012.693628>.
- [53] C.T. Imrie, Laterally substituted dimeric liquid crystals, *Liq Cryst* 6 (1989) 391–396. <https://doi.org/10.1080/02678298908034184>.
- [54] Technologies, Precision LCR Meter-E4980 Manual, Keysight (2013).
- [55] 16451B Dielectric Test Fixture, Keysight (2008).
- [56] V.A. Rana, T.R. Pandit, Microwave dielectric relaxation spectroscopy of paracetamol and its aqueous solutions, *J Mol Liq* 314 (2020) 113673. <https://doi.org/10.1016/j.molliq.2020.113673>.
- [57] DAK-TL Handbook, SPEAG, 2017.
- [58] M. Hagar, H.A. Ahmed, G.R. Saad, Mesophase stability of new Schiff base ester liquid crystals with different polar substituents, *Liq Cryst* 45 (2018) 1324–1332. <https://doi.org/10.1080/02678292.2018.1435831>.
- [59] H.A. Ahmed, M. Hagar, O.A. Alhaddad, Mesomorphic and geometrical orientation study of the relative position of fluorine atom in some thermotropic liquid crystal systems, *Liq Cryst* 47 (2020) 404–413. <https://doi.org/10.1080/02678292.2019.1655809>.

Scheme -1

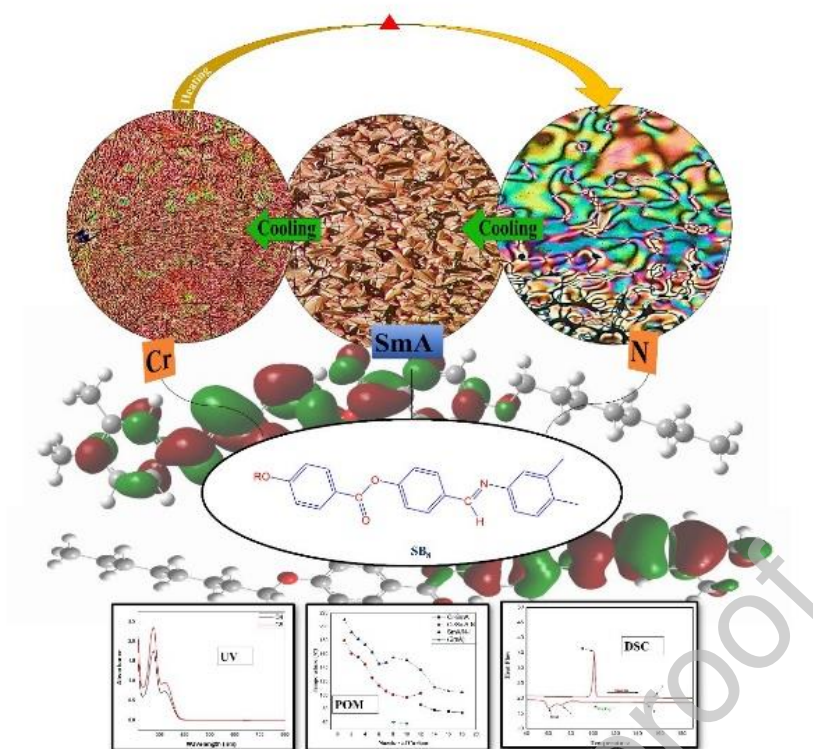


$$R = C_nH_{2n+1}$$

[n (number of carbon) = 1 to 8,10,12,14,16,18]

(i) R-Br, KOH, Ethanol (ii) DCC(N, N'-Dicyclohexylcarbodiimide), DMAP(4-Dimethylaminopyridine), THF (iii) 3, 4 dimethyl aniline, Glacial acetic acid, Ethanol.

Graphical Abstract



Author Statement

Author	Contribution
Jay C. Panchal	Experimental work and manuscript preparation
Meetkumar Y. Chaudhary	Experimental work.
Hemant N. Patel	manuscript preparation.
Tarun M. Patel	Manuscript preparation.
Shavi Thakur	DFT calculation.
Sumit Mittal	DFT calculation and writing related part of this manuscript.
Komal M. Vyas	Dielectric property measurement and manuscript writing.
Chetan B. Sangani	Revised manuscript

Sarfaraz Ahmed Diversity oriented synthetic idea, experimental work and Manuscript Preparation

Conflicts of interest

There are no conflicts of interest associated with this paper.

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