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Benzimidazole based Mesogenic Schiff-Bases: Synthesis and characterization

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Abstract

Two homologous series of mesogenic Schiff-bases, *N*-4-((alkoxy)-(phenyl-3-hydroxy-4-(4-(5-methylbenzimidazol))-2-alkoxysalisylaldimine)benzoate (**7a-d**) and *N*-4'-(5-methylbenzimidazole)-phenyl-4-alkoxysalisylaldimine (**8a-d**) incorporating benzimidazole moiety have been prepared and the molecular structures studied by FT-IR, NMR and ESI-MS spectrometry. Mesogenic behaviour was investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and variable temperature powder X-ray diffraction (PXRD) techniques. Changing the spacer (ester-linked to non-ester linked) of the Schiff-base results in enhancement of thermal stability and phase transition temperature. The members of series-I show monotropic *SmA* while those of series-II reflect enantiotropic *SmA* mesomorphism. An electrochemical study of a representative Schiff base in each series (**7d** and **8c**) showed an electrical band gap 1.26 eV and 1.22 eV respectively.

Keywords: Liquid crystal, Benzimidazole, Schiff-base, SmA

1. Introduction

Liquid crystals are self assembled dynamic functional soft materials having both order and mobility at molecular, supramolecular and macroscopic levels; thus, they are fascinating materials in many areas of applied science¹. It is believed that mesomorphic behaviour of an organic compound can be varied by modifying its molecular structure²⁻⁴. Recently, there has

been a renewed interest in the incorporation of heterocycles in liquid crystals due to their optical and electronic behaviour⁵⁻⁷. These functional properties arise due to the inclusion of hetero atoms (S, O and N) which considerably change the polarity, polarizability and to a certain extent the geometry of the molecule, thereby influencing the type of mesophase, the phase transition temperatures, dielectric constants and other properties of the mesogens. Liquid crystal containing heterocycles such as 1,3,4-oxadiazole, 1,2,3-triazole, pyrazoles, pyridine, pyrimidine, *etc.*, have recently been explored⁸. On the other hand, heterocyclic rings fused with benzene rings are also becoming popular mesogenic cores to be incorporated into the molecular structure; thus, liquid crystals containing fused heterocyclic ring systems such as coumarin, benzothiazole and benzothiadiazole are reported in literature⁹. However, only few reports on liquid crystal-containing terminal benzimidazole groups are available in literature¹⁰. The type of linking group between the spacer and mesogenic units (*e.g.*, ether, ester, *etc*) is believed to be responsible for stabilising the molecular orientations necessary for liquid crystal phase generation¹¹.

Hence, with a view of expanding the existing literature on mesomorphic properties of heterocyclic-based liquid crystals comprising a benzimidazole unit, we have undertaken a systematic study on synthesis, mesomorphic and photo-physical properties of two homologous series with varying alkyl chains (series-I, with ester link and series-II without ester link) and the results are reported in this paper.

2. Experimental

2.1 Materials and Methods

All reagents are purchased from commercial sources; 2,4-dihydroxybenzaldehyde, 1bromoalkanes and potassium bicarbonate are from Sigma Aldrich, USA, while 4-

nitrobenzaldehyde, 4-methyl-*o*-phenylenediamine, and SnCl₂.2H₂O are from Alfa-aesar and KOH is from Merck. All the required solvents were dried using standard methods¹².

Elemental analyses for C, H & N were performed on Vario EL III Carlo Erba 1108 analyser. ¹H and ¹³C NMR spectra were recorded on JEOL AL-300/500 MHz FT-NMR spectrometer. Mass spectrometric analysis was carried out on WATERS-Q-TOF Premier-HAB213. FT-IR spectra were recorded on JASCO FTIR (model-5300) spectrophotometer in 4000–400 cm⁻¹ region. The UV-visible absorption (Shimadzu spectrophotometer model, Pharmaspec UV-1700) and fluorescence emission spectra (JY HORIBA Fluorescence spectrophotometer) were recorded at room temperature in 10^{-5} M THF solutions. DSC thermograms (at the heating rate of 5.0 °C min⁻¹, accuracy of ± 0.1 °C) were recorded on a METTLER DSC-25 under nitrogen atmosphere. Mesophases were identified by using polarized binocular microscope (LOMO, USA) equipped with hot-stage and digital camera (Nikon Coolpix 4500); TG Analysis was carried out on PerkinElmer-STA 6000 apparatus under nitrogen atmosphere. Powder XRD studies (unoriented samples filled in Lindemann capillary) were made on Panalytical (Empyrean) X-ray diffractometer and electrochemical measurements on a potentiostat/galvanostat (Model CHI 660C, CH Instruments, USA). Quantum chemical calculations were made using DFT as implemented in the GAUSSIAN-09 package.

2.2 Synthesis

The synthetic route for preparing the homologous series and intermediates is depicted in **Scheme 1**. The general procedure for alkylation of 2,4-dihydroxybenzaldehyde and its esterification was as earlier reported method¹³⁻¹⁵.

2.2.1 Synthesis of 5-methyl-2-nitro-benzimidazole, 1.

The precursor material, 5-methyl-2-nitro-benzimidazole, **1**, was prepared following literature procedure¹⁶; final crude product was purified by column chromatography on silica gel using hexane/ethyl acetate (10:1,v/v) as eluent to get a brown solid after evaporating the solvent; yield: 5.0 g, 69%; Found: C, 66.39; H, 4.37; N, 16.57 %; Calc. for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59. ¹H NMR (300.40 MHz, DMSO-*d*₆), δ (ppm): 13.08 (b, 1H, -NH), 8.37-8.27 (m, 4H, Ar-H), 7.49-7.37(m, 2H, Ar-H), 7.02 (d, 1H, *J* = 8.4 Hz, Ar-H), 3.50 (s, 3H, -CH₃); ¹³C NMR (75.45 MHz, DMSO-*d*₆), δ (ppm): 152.64, 148.67, 147.61, 136.14, 135.80, 132.94, 127.18, 124.48, 124.17, 118.86, 21.37.

2.2.2 Synthesis of 5-methyl-benzimidazol-2-amine, 2.

The compound, 5-methyl-benzimidazol-2-amine, **2**, was obtained by reducing **1**; yield, 2.7 g, 45%; Found: C, 75.30; H, 5.86; N, 18.80%; Calc. for C₁₄H₁₃N₃: C, 75.31; H, 5.87; N, 18.82. ¹H NMR (300.40 MHz, DMSO-*d*₆), δ (ppm): 12.24 (b, 1H, -NH), 8.32 (d, 2H, J = 6.9 Hz Ar-H),7.81 (d, 2H, J = 8.1 Hz Ar-H) 6.92 (d, 1H, Ar-H, J = 8.1 Hz), 6.65 (m, 2H, Ar-H) 5.53 (s, 2H, -NH₂), 3.34(s, 3H, -CH₃) and ¹³C NMR (75.45 MHz, DMSO-*d*₆), δ (ppm): 164.65, 158.06, 155.86, 150.32, 127.54, 127.15, 124.20, 122.49, 117.59, 113.45, 21.24.

2.2.3 Synthesis of 3-hydroxy-4-(((5-methyl-benzimidazol-2-yl)imino)methyl)phenyl 4-(octyloxy)benzoate,7a;

It was prepared by drop-wise addition of methanolic solution of methylbenzoimidazol-2-amine to a methanolic solution of 4-(octyloxy)phenyl-4-formyl-3-hydroxybenzoate followed by addition of a few drops of glacial acetic acid. The reaction mixture was refluxed for ~4h and then cooled to room temperature. The microcrystalline yellow coloured product was filtered off by suction, thoroughly washed with cold ethanol,

recrystallised from absolute ethanol and dried at room temperature; yield 3.91 g (68%). Elemental analysis for C₃₆H₃₇N₃O₄, found (calculated) %: C, 75.14 (75.11); H, 6.49 (6.48); N, 7.30 (7.32); ¹H NMR (300.40 MHz, CDCl₃), δ (ppm): 13.46 (b, 1H, OH), 8.64 (s, 1H, CH=N), 8.17 (d, 2H, J = 8.7 Hz), 8.08 (d, 2H, J = 8.7 Hz), 7.41-7.26 (m, 6H, Ar-H, NH), 7.11 (d, 1H, J = 8.1 Hz, Ar-H), 7.00-6.89(m, 3H, Ar-H), 6.82(d, 1H, J = 8.7 Hz, Ar-H), 4.07 (t, 2H, J = 6.6 Hz, -OCH₂), 2.48 (s, 3H, ph-CH₃), 1.82-1.30 (m, 12H, (-CH₂)₆), 0.89 (t, 3H, J= 6.6 Hz, -CH₃), ¹³C NMR (75.45 MHz, CDCl₃, ppm) δ :166.77, 164.88, 163.09, 161.00, 156.41, 150.46, 149.82, 149.58, 136.39, 133.37, 132.41, 131.11, 129.83, 127.51, 127.13, 124.62, 123.33, 121.85, 117.65, 115.55, 114.59, 114.41, 111.33, 68.49, 21.71. IR (KBr) in cm⁻¹: 1169 (C–O_{ether}), 1315 (C–O_{phenolic}), 1623 (C=N), 1721 (C=O_{ester}), 2919–2851 (C–H_{alkyl}). ESI-MS m/z 576.89 [M+H]⁺ calculated 575.27.

2.2.4 Synthesis of 4-(decyloxy)-phenyl-3-hydroxy-4-(((4-(5-methyl-benzimidazol-2-yl) phenyl)imino)benzoate, 7b;

Yield 4.80 g (75%); Elemental analysis for $C_{38}H_{41}N_3O_4$, found (calculated) %: C,75.62 (75.60), H, 6.85 (6.84), N, 6.96 (6.64); ¹H NMR (500.15 MHz, CDCl₃), δ (ppm): 13.46 (b, 1H, OH), 8.62 (s, 1H, CH=N), 8.15 (d, 2H, J = 9.5 Hz, Ar-H,), 8.05 (d, 2H, J = 8.5Hz, Ar-H), 7.33-7.08 (m, 6H, Ar-H, NH), 6.99 (d, 1H, J = 9.5 Hz, Ar-H), 6.89-6.75(m, 3H, Ar-H), 6.92 (d, 1H, J = 8.5 Hz, Ar-H) 4.05 (t, 2H, J = 7.0 Hz, -OCH₂), 2.47 (s, 3H, ph-CH₃), 1.83-1.28 (m, 16H, (-CH₂)₈), 0.99 (t, 3H, J = 6.0 Hz, -CH₃) and ¹³C NMR (125.76 MHz, CDCl₃, ppm) 165.20, 164.74, 163.91, 162.80, 162.07, 155.20, 149.26, 133.49, 132.53, 132.8, 128.59, 127.59, 121.95, 121.09, 117.16, 114.51, 113.38, 110.82, 68.48, 21.83. IR (KBr) in cm⁻¹: 1169 (C–O_{ether}), 1315 (C–O_{phenolic}), 1623 (C=N), 1722 (C=O_{ester}), 2920–2852 (C–H_{alkyl}). ESI-MS m/z 604.75 [M+H]⁺ calculated, 603.75.

2.2.5 Synthesis of 4-(dodecyloxy)-phenyl-3-hydroxy-4-(((4-(5-methyl-benzimidazol-2-yl) phenyl)imino) benzoate, 7c;

Yield 4.52 g (72 %): Elemental analysis for C₄₀H₄₅N₃O₄, found (calculated) %: C, 76.05 (76.07); H, 7.18 (7.19); N, 6.66 (6.67) ; ¹H NMR (300.40 MHz, CDCl₃), δ (ppm): 13.42 (b, 1H, OH), 8.65 (s, 1H, CH=N), 8.16 (d, 2H, *J* = 7.8 Hz, Ar-H), 8.08 (d, 2H, *J* = 6.9 Hz, Ar-H), 7.41-7.19 (m, 6H, Ar-H, NH),7.11(d, 1H, *J* = 7.5 Hz Ar-H), 6.99-6.90(m, 4H, Ar-H), 4.05(t, 2H, *J* = 7.0 Hz, -OCH₂), 2.47(s, 3H, ph-CH₃), 1.82-1.27(m, 20H, (-CH₂)₁₀), 0.86 (t, 3H, *J* = 6.0 Hz, -CH₃) and ¹³C NMR (75.45 MHz, CDCl₃, ppm) 165.82, 162.21, 160.10, 157.25, 152.79, 152.38, 151.29, 140.94, 135.94, 133.63, 132.03, 131.34, 129.66, 127.76, 127.16, 125.71, 125.21, 123.04, 122.82, 121.79, 120.43, 116.06, 115.80, 115.51, 114.48, 68.70, 21.27. IR (KBr) in cm⁻¹: 1169 (C–O_{ether}), 1315 (C–O_{phenolic}), 1623 (C=N), 1722 (C=O_{ester}), 2920–2852 (C–H_{alkyl}). ESI-MS *m/z* 632.56 [M+H]⁺ calculated 631.34.

2.2.6 Synthesis of 4-(tetradecyloxy)phenyl-3-hydroxy-4-(((4-(5-methyl-benzimidazol-2-yl)phenyl)imino)methyl)benzoate, 7d;

Yield 4.50 g (66 %): Elemental analysis for $C_{34}H_{41}N_3O_4$, found (calculated) %: C, 73.49 (73.50); H, 7.49 (7.48); ¹H NMR (300.40 MHz, CDCl₃), δ (ppm): 13.63 (b, 1H, OH), 8.63 (s, 1H, CH=N), 8.14-8.06 (m, 4H, Ar-H), 7.72-7.13(m, 6H, Ar-H, NH), 7.13(d, 1H, J =9.9 Hz, Ar-H), 6.97-6.86(m, 4H, Ar-H), 4.05 (t, 2H, J = 7.0 Hz, -OCH₂), 2.48 (s, 3H, ph-CH₃), 1.82-0.98 (m, 24H, (-CH₂)₁₂), 0.88 (t, 3H, J = 6.0 Hz, -CH₃) and ¹³C NMR (75.45 MHz, CDCl₃, ppm) 165.10, 161.70, 160.98, 156.14, 152.61, 152.15, 140.92, 135.03, 133.38, 132.74, 131.24, 127.81, 127.47, 127.21, 125.35, 124.98, 121.92, 115.04, 114.50, 68.67, 21.97. IR (KBr) in cm⁻¹: 1169 (C–O_{ether}), 1315 (C–O_{phenolic}), 1623 (C=N), 1722 (C=O_{ester}), 2920–2852 (C–H_{alkyl}); ESI-MS m/z 660.56 [M+H]⁺ calculated, 659.34.

2.2.7 Synthesis of (4'-(5"-methyl-1H-benzimidazole)-phenyl)-4-octyloxysalisylaldimine,

8a:

It was prepared by drop-wise addition of methanolic solution of methylbenzimidazole amine to a methanolic solution of 4-octyloxy-2-hydroxybenzaldehyde and refluxing the reaction mixture in presence of a few drops of glacial acetic acid for ~4h followed by cooling to room temperature. The microcrystalline yellow coloured product was filtered off by suction, washed with cold ethanol; the product was recrystallised from absolute ethanol and dried at room temperature; Yield 3.10 g, 68%; Found C, 76.47; H, 7.29; N, 9.20%; Calc for C₂₉H₃₃N₃O₂: C, 76.45; H, 7.30; N, 9.22%; 1H NMR (300.40 MHz,CDCl₃), δ (ppm): 13.69 (b, 1H, OH), 8.42 (s, 1H, -CH=N), 8.08(d, 2H, *J* =7.8 Hz, Ar-H), 7.53(d, 1H, *J* = 7.5 Hz, Ar-H), 7.25-7.16 (m, 4H, Ar-H, NH), 7.07(d, 1H, *J* = 7.8 Hz, Ar-H), 6.52-6.42(m, 3H, Ar-H), 3.93 (t, 2H, *J* = 7.5 Hz, -OCH₂), 2.43(s, 3H, ph-CH₃), 1.79-1.31 (m, 12H, (-CH₂)₆), 0.86 (t, 3H, *J* = 6.3 Hz -CH₃), and ¹³C NMR (75.45 MHz, CDCl₃), δ (ppm): 164.24, 163.86, 161.26, 150.93, 148.96, 135.20, 133.54, 132.65, 127.68, 127.49, 124.27, 121.30, 112.93, 112.54, 107.69, 101.69, 68.07, 21.46 ;IR (KBr pellet, cm⁻¹) 3415, ν (OH/NH); 1629, ν (CH=N); ESI-MS *m/z* 456.20 [M+H]⁺ calculated, 455.53.

All the other members of the series were prepared in a similar manner. The yield, IR, NMR and elemental data for the compounds are summarised below:

2.2.8 Synthesis of 4'-(5"-methyl-benzimidazole)-phenyl)-4-decyloxysalisylaldimine, 8b:

Yield, 3.20 g, 66%; Found: C, 76.92; H, 7.70; N, 8.71%; Calc. for $C_{31}H_{37}N_3O_2$: C, 76.98; H, 7.71; N, 8.69;¹H NMR (300.40 MHz, CDCl₃), δ (ppm): 13.68 (s, 1H, OH), 8.43 (s, 1H, -CH=N), 8.09(d, 2H, J = 6.3 Hz, Ar-H), 7.53 (d, 1H, J = 6.0 Hz), 7.37-7.05(m, 6H, Ar-H, NH), 6.44(m, 2H, Ar-H) 3.95 (t, 2H, -OCH₂, J = 6 Hz), 2.43 (s, 3H, ph-CH₃), 1.77-0.88 (m, 16H (-CH₂-)₈), 0.88 (t, 3H, -CH₃, J = 6.3 Hz) and ¹³C NMR (75.45 MHz, CDCl₃), δ (ppm):

164.41, 164.04, 161.47, 151.1, 149.16, 140.79, 133.74, 130.72, 130.10, 127.92, 127.52, 124.44, 121.50, 112.75, 107.82, 101.52, 68.17, 21.68; IR (KBr pellet, cm⁻¹) 3415, υ (-OH/NH); 1627, υ (CH=N); ESI-MS *m*/*z* 484.20, [M+H]⁺ calc: 483.28.

2.2.9. Synthesis of 4'-(5"-methyl-benzimidazole)-phenyl)-4-dodecyloxysalisylaldimine,

8c:

Yield, 3.4 g, 65%; mp, 287 °C; Found C,77.45; H, 8.05; N, 8.20%; Calc for $C_{33}H_{41}N_3O_2$: C, 77.46; H, 8.08; N, 8.21%; ¹H NMR (300.40 MHz,CDCl₃), δ (ppm): 13.61 (b, 1H, OH), 8.49 (s, 1H, CH=N), 8.07(d, 2H, J = 8.4 Hz, Ar-H), 7.54(d, 2H, J = 9.0 Hz, Ar-H), 7.39(s, 1H, Ar-H), 7.28-7.21(m, 3H, Ar-H, NH), 7.09(d, 1H, J = 8.1Hz), 6.47-6.45 (m, 2H, Ar-H) 3.99 (t, 2H, J = 6.6 Hz), 2.46 (s, 3H, ph-CH₃), 1.76-1.26 (m, 20H, (-CH₂-)₁₀), 0.85 (t, 3H, -CH₃, J = 6.9 Hz) and ¹³C NMR (75.45 MHz, CDCl₃), δ (ppm): 164.29, 164.06, 161.72, 150.56, 149.56, 133.88, 133.01, 127.77, 125.14, 124.58, 122.20, 121.63, 115.31, 112.87, 107.97, 101.58, 68.22; ESI-MS : m/z 512.20, [M+H]⁺; calc. 511.28; IR (KBr pellet, cm⁻¹): 3415, v(-OH/NH); 1627, v(CH=N).

2.2.10. Synthesis of 4-(5'-methyl-benzimidazole)-phenyl)-4-tetradecyloxysalisylaldimine, 8d:

Yield 3.90 g, 70%; Found C, 77.95; H, 8.45; N, 7.82%; Calc. for $C_{35}H_{45}N_3O_2$: C, 77.88; H, 8.40; N, 7.79%; ¹H NMR (300 MHz, CDCl₃), δ (ppm): 13.67 (b, 1H, OH), 8.43 (s, 1H, -CH=N), 8.08(d, 2H, J = 8.4 Hz, Ar-H), 7.53(d, 1H, J = 7.5 Hz, Ar-H), 7.38(s, 1H, Ar-H), 7.25-7.05(m, 5H, Ar-H, NH), 6.44-6.42 (m, 2H, Ar-H), 3.92 (t, 2H, -CH₂, J = 6.3 Hz), 2.43 (s, 3H, ph-CH₃), 1.79-0.85 (m, 24H, (-CH₂-)₁₂), 0.85(t, 3H, -CH₃, J = 6.0 Hz) and ¹³C NMR (75.45 MHz, CDCl₃): δ (ppm): 164.45, 164.09, 161.49, 151.31, 149.22, 142.56, 138.24, 133.76, 132.88, 127.92, 127.70, 124.56, 121.40, 112.50, 107.92, 101.07, 68.18, 21.68; IR

(KBr pellet, cm⁻¹): 3416, υ (-OH/NH); 1628, υ (CH=N); ESI-MS *m*/*z* 540.35, [M+H]⁺ calc. 539.75.

3. Results and Discussion

3.1 Synthesis and Chemical structure characterisation

Synthetic routes of the compounds are outlined in the scheme 1. The Schiff bases were obtained by condensation reaction of 5-methyl-benzimidazol-2-amine with appropriate aldehyde in refluxing methanol. All the ligands were characterized by elemental analyses and standard spectroscopic techniques.

The FT-IR spectra of compounds in both the series showed considerable similarities; the diagnostic absorption band of the azomethine (C=N) group appeared in the 1620-1623 cm⁻¹ range. The spectral bands appearing within the frequency ranges of 2921-2923 cm⁻¹ and 2851-2854 cm⁻¹ may be respectively attributed to v(C–H)_{asy} and v(C–H)_{sym} of –CH₃. The broad band centred at 3351-3354 cm⁻¹ is characteristic of v(O–H/N-H) frequency. The members of series-I are characterized by v(C=O)_{ester} band appearing at 1721-1723 cm⁻¹. Further, resemblance of both the series was also reflected in their ¹H NMR spectra; phenolic-OH appeared as a singlet at 13.43-13.69 ppm, the aromatic protons gave rise to multiplets over the range of 8.62-6.23 ppm and –C<u>H</u>=N of the Schiff-base moiety appeared as a singlet at 8.42-8.62 ppm. ¹³C NMR spectral data (given below in the running text under 'synthesis') is used to further substantiate the molecular structures of the compounds.

3.2 Mesomorphic study of the benzimidazole based Schiff bases

Thermotropic behavior of the benzimidazole based Schiff-base ligands was studied on the basis of data obtained from thermogravimetric analyses (TGA), differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray scattering on powder

samples XRD studies (in selected cases). Table 1 presents the phase sequence, transition temperatures and enthalpies of the transitions; the phase transition temperatures are deduced from calorimetric measurements of the second heating \leftrightarrow cooling cycles at a rate of 5 °C min⁻¹. In the absence of transition peaks in DSC traces, wherever applicable, the phase transition temperatures (noted during the POM study) are taken as such.

Thermal stability of these compounds (series-I) up to ~250 °C (Fig. 1(a)) has been inferred from TGA measurements and monotropic behaviour implied¹⁷ by DSC studies: endotherms observed during heating [corresponding to the crystal phase \rightarrow the isotropic liquid at 228 °C (n = 8) and at 214 °C (n = 14)] and exotherms in cooling cycle [characteristic of isotropic \rightarrow mesophase transition (213 °C (n = 8), 208 °C (n = 14) and mesophase \rightarrow crystal transitions at 149 °C (n = 8) and at 68° C (n = 14), Fig. 2]. It was observed that the clearing temperatures of the compounds and the phase transition temperatures decreased slightly with the increase of chain length (Table 1). A broken fan-shaped SmA mesophase (from 208 to 68 °C; Fig. 3) was implied by POM studies of 7d of series-I; similar optical textures were observed for the rest of the members of Series-I. The wide range of the mesophase of 7d was further corroborated by XRD diffraction patterns at 204 °C (Fig. 4); these patterns consist of (i) a sharp intense low angle peak ($2\theta = 2.15$ Å), and (ii) a weak broad diffuse peak at wide angles ($2\theta = 17$ Å) characteristic of liquid-like arrangement of the molecules within the layers. These features, in agreement with the POM observations, confirm the SmA mesophase. A comparison of the experimental *d*-spacing (d, 40.57 Å) with the DFT-calculated [B3LYP/6-311G (d,p)] molecular length (l, 41 Å, Fig. 5) implies d/l ratio of ~ 1 , which suggests a monolayer arrangement¹⁸.

TGA measurements performed on the members of Series-II (having no ester linkage) imply thermal stability up to ~300 °C (Fig. 1(b)); POM studies show that the initial batonnets got transformed into typical fan-shaped focal conic smectic textures, characteristic of SmA

mesophase (the representative textures of **8a** and **8c** are shown in Figs. 6 & 7); in case of **8c** DSC thermogram showed three sharp endothermic peaks (at 81 °C, 122 °C and 294 °C) and two sharp exothermic peaks (at 284 °C and 67 °C) (Fig. 8) while POM studies reveal that heating beyond 225 °C leads to formation of fully grown focal conic SmA mesophase having fluid property with higher viscosity. The DSC data thus, implies crystal transformation (Cr– Cr₁) characteristic of polymorphism^{2,17,19-20}. Powder XRD patterns (Fig. 9) of **8c** at 225 °C show a sharp reflection in the low-angle region ($2\theta = 2.48$ Å) presumably due to the layered structure of the smectic A phase, and a broad peak in the wide-angle region ($2\theta = 4.45$ Å) characteristic of liquid-like arrangement of the molecules within the layers. On the basis of the d/l ratio (d/l ~1) of **8c** (d, the interlayer distance calculated from XRD, 35.6 Å, and *l*, the calculated length of the optimized structure, 32.7 Å, Fig.10) the SmA phase was suggested to have a monolayer arrangement.

3.3 Structure-mesomorphic property relationship

The observed differences in the mesomorphic properties and thermal stability of the members of series-I (having ester linkage) and series-II (similar to series-I devoid of ester linkage) may be attributed to their structural differences. Although both the series exhibited SmA mesophase, the mesogenic behaviour of series-I, with thermal stability upto ~250 °C, is limited to monotropic type while that of the series-II is expanded to enantiotropic type with thermal stability upto ~300 °C. Further, the transition temperatures of series-II are spanned relatively over a wider range. These differences may be understood in terms of restricted rotation/flexibility in series-I due to ester linkage which alters the polarity and intermolecular interactions between the layers²¹; on the contrary, members of series-II (with no such ester linkage) tend to be more linear with a higher degree of self-assembly, thus resulting in a wider of SmA phase.

3.4 Photo physical properties

The photo physical properties of these mesogens were recorded in micromolar solutions of THF (Table 2); both the series showed similar absorption patterns with the lowest energy band arising at 363–365 nm (Fig. 11). The high molar absorption coefficients (ϵ , ~28,000 dm³ mol⁻¹ cm⁻¹), attributed to π - π * transitions in the hetero-aromatic and aromatic rigid portions of the molecules, are in accordance with the conjugated nature of the systems. Emission spectral bands of the compounds (λ_{ex} , 330 nm, Fig. 12) span over the range of 380-410 nm with small stokes shift (Table 2). No significant difference in the absorption and emission spectra has been observed across the homologous series (n = 8 to n = 14).

The theoretical HOMO-LUMO plots (TD-DFT/B3LYP/6-311G (d,p)) of **7d** and **8c** (Fig. 13) imply that the electron density in the HOMO is confined mainly onto the benzimidazole and benzene moieties, while that of the LUMO is distributed onto the benzene moiety (imine system).

3.5 Electrochemical properties

Cyclic voltammetry (CV) studies of one representative compound from each series (**7d, 8c**) (Fig. 14) have been carried out in micromolar dichloromethane solution (potential range of -2 V to +2 V at a scan rate of 50 mVs¹ under nitrogen atmosphere) for investigating electrochemical behaviour. For these studies 0.1*M* solution of tetrabutylammonium hexafluorophosphate was used as supporting electrolyte; a single compartment cell fitted with a Ag/AgNO₃ reference electrode, a platinum wire counter electrode, and a glassy carbon working electrode was used for the experiment; the reference electrode was calibrated with ferrocene/ferrocenium (Fc/Fc+) redox couple (with an absolute energy level of -4.80 eV with respect to vacuum)²². On the basis of the cyclic voltammograms for **7d** & **8c** the HOMO

energies have been calculated as -5.06 eV and -4.92 eV, and the LUMO energy values as -3.80 eV and -3.70 eV respectively. The electrical band gaps (as per the CV data; Table 3) were calculated as 1.26 eV and 1.22 eV for of **7d** and **8c** which are much smaller than optical band gaps²³.

4. Conclusion

In summary, two homologous series of benzimidazole based mesogenic Schiff-bases were synthesised and characterised. Series-I (having ester linkage) showed monotropic SmA mesophase while series-II (with no ester linkage) corresponded to enantiotropic SmA mesophase. Enhanced thermal stability of the members of series-II has been discussed on the basis of structure-mesomorphism relationship. Electrochemical studies of a representative compound from each series imply low HOMO-LUMO band gap (1.22 & 1.26 eV).

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Scheme 1. Reagents and conditions: (i) RBr, K₂CO₃, DMF, ~5h reflux; (ii) KOH, ethanol, ~2h reflux; (iii) 2,4-dihydroxybenzaldehyde, DCC, DMAP, DCM, stirring about ~24h; (iv) RBr, K₂CO₃, DMF, ~5h reflux; (v) KI, DMF, 24h reflux; (vi) SnCl₂2H₂O, dry ethanol, ~4h reflux; (vii) & (viii) few drops of acetic acid, ethanol, ~4h reflux







Fig. 2. DSC thermograms of (a) 7c and (b) 7d



Fig. 3. Optical textures (broken-fan like, SmA) of (a) 7c at 210 °C and (b) 7d at 206 °C





Fig. 5. DFT optimized structure of 7d and its molecular length



Fig. 6. Optical textures (SmA) of **8a**: (a) Batonnets at 274 °C (b) at 220 °C (c) at 187 °C and (d) transition from SmA to Crystalline state at 79 °C





Fig. 8. DSC thermograms of (a) 8a and (b) 8c



Fig. 10. DFT optimized structure of 8c and its molecular length





Fig. 13. HOMO & LUMO orbitals of 7d & 8c



Compounds	T, °C [ΔH ^b , kJ/ mol]			
	Heating	Cooling		
Series-I				
7a	Cr 184.9 (6.0) Cr ₁ 228 ^c I	I 226 ^c SmA 149.1 (5.1) Cr		
7b	Cr 184.4 (5.1) Cr ₁ 223 ^c I	I 219 ^c SmA 138.6 (4.3) Cr		
7c	Cr 165 (9.3) Cr ₁ 220 ^c I	I 212 (0.3) SmA 130.9 (6.1) Cr		
7d	Cr 157.7 (8.5) Cr ₁ 214 ^c I	I 208 (1.7) SmA 68 (1.2) Cr		
Series-II				
8a	Cr 73 (17.9) Cr ₁ 146 (13.6) SmA 283 ^c I	I 276 ^c SmA 78 (1.2) Cr		
8b	Cr 79 (34) Cr ₁ 120 (14.5) SmA 287 ^c I	I 275 (0.5) SmA 71.4 (4.5) Cr		
8c	Cr 81 (17) Cr ₁ 122 (15) SmA 294 (7.11) I	I 284 (1.6) SmA 67 (2.7) Cr		
8d	Cr 76(3.8), Cr ₁ 113 (3.2) SmA 279 ^c I	I 276 (0.4) SmA 60 (1.2) Cr		

Table 1: Thermal Transitions and thermodynamic parameters

 Cr = crystalline state; SmA = Smectic A mesophase; i = isotropic liquid; b = Data as obtained from DSC; c = Observed by POM

Table 2: Optic	al absorption	and emission	data (nm)
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Compound	Band maximum			
	absorption	Emission		
7a	363	385		
7b	365	385		
7c	364	386		
7d	365	388		
8a	364	409		
8b	365	409		
8c	364	410		
8d	363	411		

Table 3: Electrochemical data

Compounds	HOMO ^a (eV)	LUMO ^a (eV)	$\Delta E_{g} (eV)^{b}$	$\Delta E_{g}(eV)^{c}$
7d	-5.06	-3.80	1.26	2.57
8c	-4.92	-3.70	1.22	2.67

^a= Calculated from ferrocene standard. ^b= Calculated as the difference between HOMO & LUMO. ^{c=} Optical band gap determined from the onset of the lower energy of the absorption maxima.

Graphical abstract



highlights:

- 1. Two homologous series of benzimidazole-based Schiff-bases have been synthesized.
- Structural, thermal and optical studies made by FTIR, NMR, ESI-MS, POM, DSC and PXRD techniques.
- 3. Monotropic and enantiotropic mesomorphism identified in series-I and series-II respectively.
- 4. Differences in mesomorphism and thermal stability correlated to structural variations.
- 5. Low electrochemical band gaps found for representative members.

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