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To cite this article: Uhood J. Al-Hamdani, Hanna S. Abbo, Ayat A. Fadhl & Salam J. J. Titinchi (2022): Chloro-benzothiazole Schiff base ester liquid crystals: synthesis and mesomorphic investigation, Liquid Crystals, DOI: [10.1080/02678292.2022.2074558](https://doi.org/10.1080/02678292.2022.2074558)

To link to this article: <https://doi.org/10.1080/02678292.2022.2074558>

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Chloro-benzothiazole Schiff base ester liquid crystals: synthesis and mesomorphic investigation

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ABSTRACT

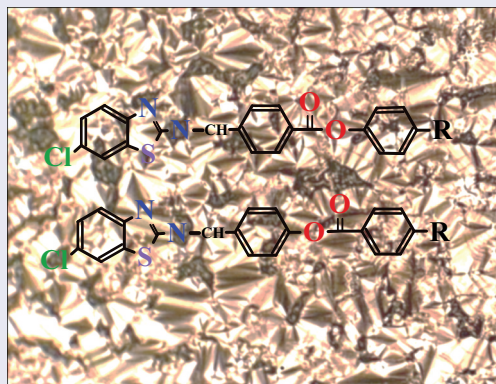
Nine new rod-like chlorobenzothiazole based liquid crystals (**1–9**) containing Schiff base and ester linking groups bearing different terminal substituents are described. Although a few similar chloro substituted benzothiazole compounds are known, none have been studied for their liquid crystal properties. All these compounds possess liquid crystal behaviour except compounds **4** and **8**. The effect of the nature of the terminal groups on thermal stability and optical properties of the mesomorphic compounds was evaluated. With the exception of compound **1**, all the other compounds possess polarity resulting from the polar chloride atom substituted at position-6 of the benzene ring of the benzothiazole moiety which provides a polar group at the one terminal end of the molecules. The presence of the fused-ring system (benzothiazole) adds a molecular width that contributes to increase the molecular breadth, causing a thickening effect which disrupts the liquid crystalline packing. New compounds were prepared *via* reaction of phenolic Schiff bases with the corresponding carboxylic acids or the carboxyl Schiff bases with the corresponding phenols. The synthesized compounds were characterized using ¹H- and ¹³C-NMR and FT-IR spectroscopy, mass spectrometry and elemental analysis. Polarised optical microscope and thermal properties were measured to study the thermal and mesophase behaviours.

ARTICLE HISTORY

Received 3 February 2022
Accepted 3 May 2022

KEYWORDS

Benzothiazole; liquid crystal; Schiff base; ester; terminal group



Introduction


Liquid crystals containing heterocyclic ring units at the central core have received continuous attention due to their effect on distinctive mesomorphic properties [1,2]. Earlier reports demonstrated that the inclusion of a heterocyclic moiety into the molecule has a positive effect on the liquid crystalline properties, forming rod-like molecules due to their unsaturation and/or their more polarisable nature [3]. Benzothiazole, a heterocyclic fused ring system, is an important core unit in liquid crystals and has a great effect on the mesomorphic properties of calamitic

molecules due to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape.

Liquid crystalline compounds that have within their molecular structure a benzothiazole ring as a core unit showed good hole-transporting properties, which have received significant interest as hole transporting materials in organic light-emitting devices [4–6].

Yeap *et al.* synthesised a series of rod-like benzothiazole azo peripheral units attached to a triphenylene central core *via* alkyl chains. Their liquid-crystalline

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 Supplemental data for this article can be accessed online at <https://doi.org/10.1080/02678292.2022.2074558>

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properties were studied and confirmed using differential scanning calorimetry and polarising optical microscopy. The spacers in this series vary by the length of the methylene unit ($n = 5-10$). The disc-shaped liquid crystal having a shorter spacer ($n = 5$) showed the monotropic nematic phase, while the higher homologues ($n = 8-10$) displayed enantiotropic nematic phases and monotropic smectic phases upon cooling [7].

On the other hand, liquid crystalline compounds containing a Schiff base linkage also have great potential and important applications based on their preparation [8] and showed liquid crystal properties at room temperature. The molecular structure of thermotropic liquid crystal compounds is influenced by several factors *viz.*, a mesogenic core, terminal groups and an appropriate length of the flexible chain [9].

It has been reported that incorporating the $-CH=N-$ linkages to already rigid moieties such as phenyl rings leads to these molecules retaining their structural linearity and enhances the mesophase's stability [10]. Rod-like mesogenic compounds having aromatic rings substituted at the *para*-position provide for the molecule to have a linear molecular structure, as well as a high polarisation, which, in turn, makes it capable of demonstrating liquid crystalline properties [11].

It has been reported that the liquid crystalline properties of these compounds are affected by the nature of the terminal groups (\times). All these compounds show liquid crystalline properties on heating and cooling with different thermal ranges. Another study reported the synthesis of non-symmetric dimers substituted with different terminal groups. All these dimers exhibited an enantiotropic nematic phase. However, the substituted dimers with halogens and ethyl groups do exhibit SmA behaviour in addition to the nematic phase [12].

Naoum and his group and Hagar et al. studied the effect of either a methyl or a methoxy terminal group on two compounds [13,14]. The two compounds showed an enantiotropic nematic phase, but with different thermal ranges of 150°C (OCH_3) and 85°C (CH_3). The results showed that the nematic range is broadened by the presence of the more electron-donating substituent.

A study on thiazolo[5,4-*d*]thiazole based liquid crystals found that the lengths of the aliphatic chain ($\text{C}_n\text{H}_{2n+1}$) at the terminal ends of the molecule affect their liquid crystalline properties [15]. The results showed that the nematic phase appeared with short alkyl chains ($n = 2$), while the SmA and nematic phases appeared with medium chain lengths ($n = 4$). The nematic phase disappeared and only two types of the SmA phase remained with long chains ($n = 8$). The thermal range of the nematic phase decreases with increasing chain length. On the other hand,

asymmetric diphenylacetylenes bearing a hexylthio group at one end and different alkyl groups ($n = 0-8$ and 12) at the other end showed only the nematic phase [16]. Interestingly, symmetric diphenyldiacetylenes having both terminal thioalkyl groups were found to not demonstrate liquid crystalline properties [17-23].

Other non-symmetric ester/cholesterol-based liquid crystal dimers containing a thioalkyl moiety at one end have also been reported. All these compounds showed phase transitions having a typical cholesteric phase. The liquid crystalline properties of these dimers were compared with the analogous dimers substituted by an alkoxy chain at one end instead of the thioalkyl group. It was found that the transition temperature for asymmetrical liquid crystals containing a thioalkyl moiety is lower and has a narrower cholesteric phase. This is ascribed to its high polarisability in conjunction with the flexibility via the small bend angle of the C-S-C bond [24].

There are a few reports on benzothiazole liquid crystalline compounds [25-28]

A key structural feature in these compounds is the Schiff base-ester linkages, which has led to the discovery of the twist-bend in the smectic phases [29,30]

However, no report on chloro substituted benzothiazole-type systems has been reported. Herein, we report the synthesis and characterisation of new nine rod-like Schiff-base/ester-chlorobenzothiazole based liquid crystals (1-9) having different substituents on one terminal position as shown in Figure 1 to understand the structure-property relationship of these intriguing liquid crystalline compounds. We have also evaluated the effect of these terminal groups on the thermal stability and mesomorphic properties of the synthesised compounds.

Experimental

General

Infrared spectra were recorded with KBr pellets on a Buck - M500 spectrometer (Buck Scientific, USA). ^1H - and ^{13}C -NMR spectra were recorded on a Bruker instrument using CDCl_3 as solvent and TMS as internal standard. Transition temperatures were determined using a Perkin Elmer-Pyris DSC-8000 differential scanning calorimeter with a heating rate of $10^\circ\text{C min}^{-1}$. The phase transitions were observed with a LeitzLaborlux 12 Pol optical microscope with polarised light in conjunction with a Leitz 350 hot stage (Germany) equipped with a Vario-Orthomat. Mass spectra were recorded on an Agilent technologies 5957C spectrometer. Elemental analysis was performed on a Euro Vector EA 3000A instrument.

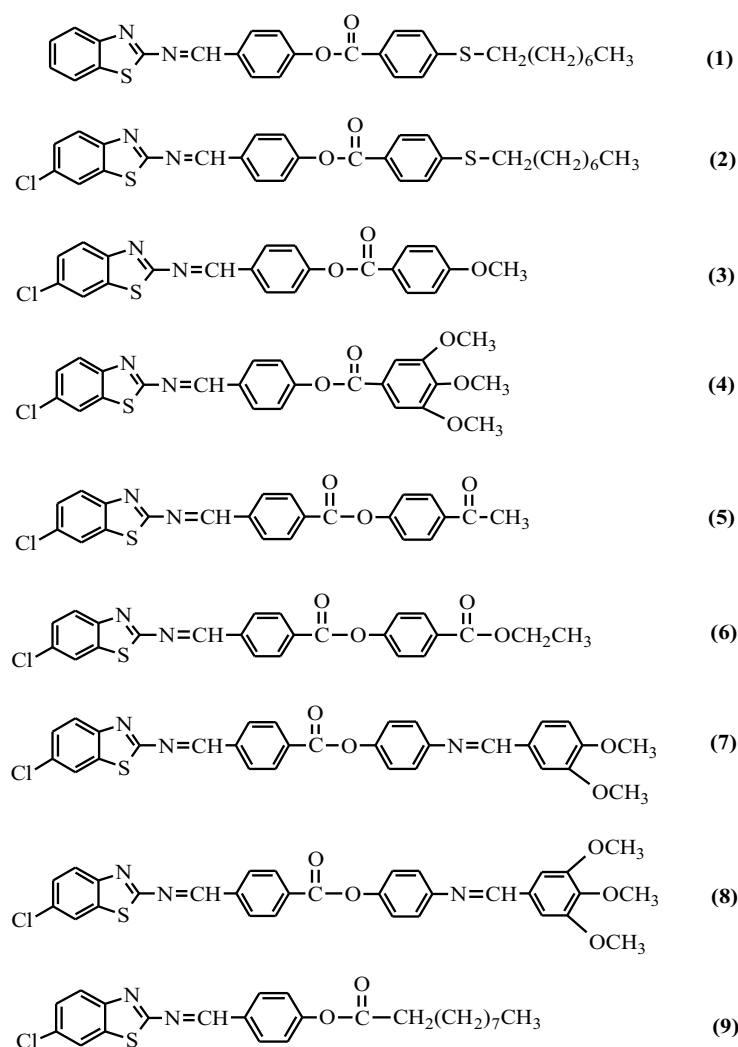


Figure 1. Schiff-base-benzothiazole based compounds.

Synthesis of Schiff bases

One molar equivalent of the appropriately substituted aniline was added to a solution of the appropriate benzaldehyde in ethanol (1:1) to which a few drops of acetic acid were added according to the earlier reported method [31]. The mixture was heated under reflux for 2 h, and the solid obtained upon cooling was filtered and twice recrystallised from ethanol to give pure compounds (Schemes 1–4).

Synthesis of octylthiobenzoic acid

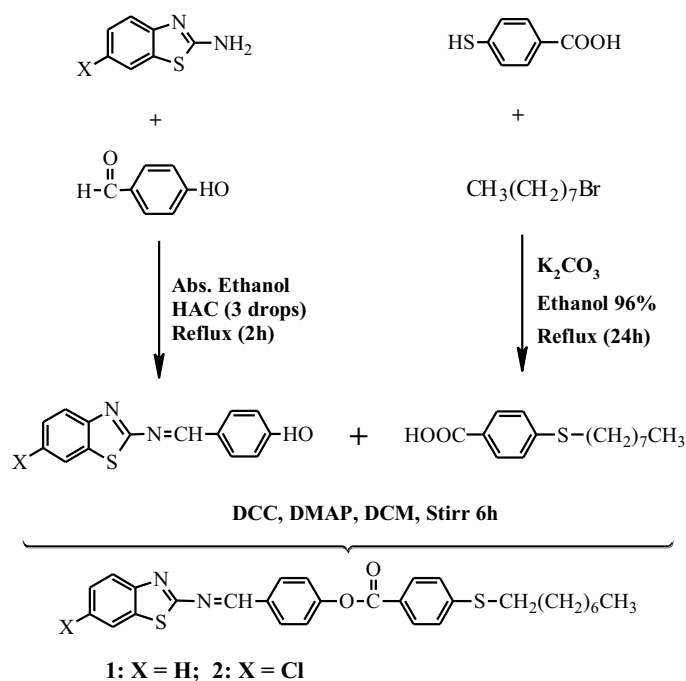
4-Octylthio-benzoic acid was synthesised according to the literature procedure [32] (Scheme 1) by refluxing 4-mercaptobenzoic acid, 1-bromooctane and potassium carbonate in ethanol for 24 h. At the end of the reaction, solvent was evaporated, and water was added, and the aqueous solution was heated to boiling and then cooled

to room temperature. A few drops of conc. HCl were added until a solid precipitated. The solid was filtrated and washed with water to afford the target compound.

Synthesis of esters

Molar equivalents of acids and phenols (0.01 mol) were dissolved in 25 ml of DCM. To the resulting mixture, DCC (0.002 mol) and DMAP (0.002 mol) were added and the mixture was kept stirring at room temperature for 6 h following the reported procedure [33,34]. The precipitated solid (by product) was filtered off, and the filtrate was evaporated, and the residue was twice crystallised from ethanol (Schemes 1–4).

4-[(Benzothiazolyl imino)methyl]phenyl-4-(octylthio)benzoate (1): Chemical Formula: $C_{29}H_{30}N_2O_2S_2$; yellow solid; yield 70%; 1H -NMR spectrum ($CDCl_3$, 400 MHz): δ (ppm) 0.89 (t, $J = 6.8$ Hz, 3 H, H_a), 1.25–1.33 (m, 8 H, H_b , H_c , H_d , H_e), 1.47 (pent, $J = 7.3$ Hz, 2 H, H_f), 1.73 (pent, $J =$



Scheme 1. Synthesis of compounds **1** and **2**.

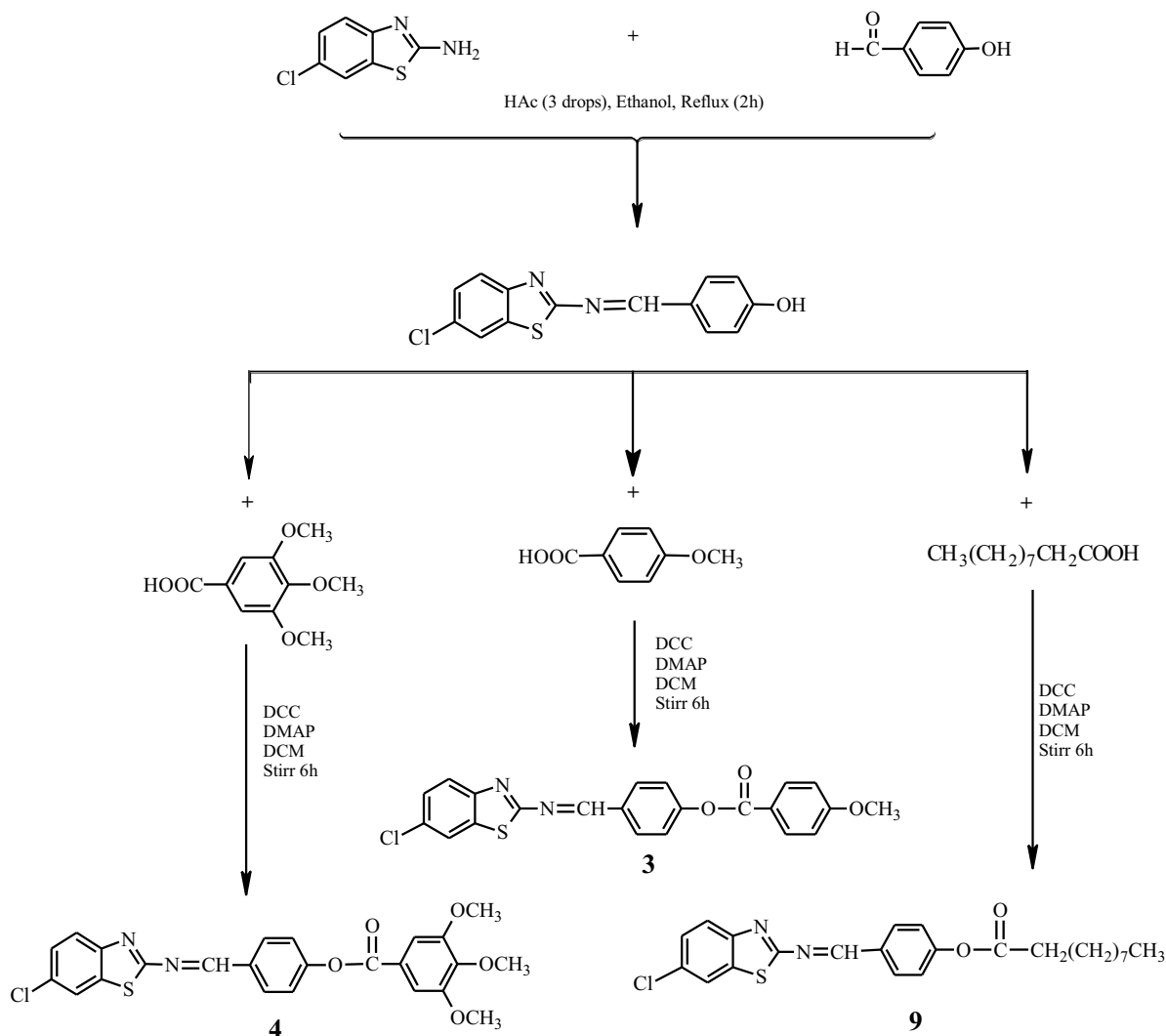
7.5 Hz, 2 H, H_g), 3.02 (t, $J = 7.4$ Hz, 2 H, H_h), 7.36 (d, $J = 8.4$ Hz, 2 H, H_8, H_8'), 7.40 (d, $J = 8.4$ Hz, 2 H, H_6, H_6'), 7.48 (d, $J = 4.0$ Hz, 1 H, H_3), 7.50 (d, $J = 4.0$ Hz, 1 H, H_2), 7.85 (d, $J = 8.0$ Hz, 1 H, H_4), 7.98 (d, $J = 6.0$ Hz, 2 H, H_5, H_5'), 8.10 (dd, $J = 8.5$ Hz, 11.5 Hz, 3 H, H_1, H_7, H_7'), 9.10 (s, 1 H, H_k); ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 14.10 (C_a), 22.65 (C_b), 28.70 (C_c), 28.93 (C_d), 29.15 (C_e), 29.72 (C_f), 30.93 (C_g), 31.79 (C_h), 120.92, 121.72, 122.39, 122.57, 123.13, 125.14, 126.21, 126.51, 130.55, 131.27, 131.61, 132.39, 134.03, 134.73, 154.89 for Ar-carbons, 165.17 (CH=N), 166.65 (C=O). IR (cm^{-1}): 3035.96 (C-H aromatic), 2851–2918 (C-H aliphatic), 1737 (C=O), 1626 (CH=N), 1576 (C=N thiazole), 1537 (C=C aromatic); MS (m/z) 502[M⁺] (Fig. S1). Elemental Analysis: (Calcd) Found: C (69.29) 69.59; H (6.02) 6.03; N (5.57) 5.68.

4-[(6-Chlorobenzothiazolyl)imino]methyl}phenyl-4-(octylthio)benzoate (2): Chemical Formula: $\text{C}_{29}\text{H}_{29}\text{ClN}_2\text{O}_2\text{S}_2$; yellow solid; yield 65%; ^1H -NMR spectrum (CDCl_3 , 400 MHz): δ (ppm) 0.90 (t, $J = 6.8$ Hz, 3 H, H_a), 1.25–1.32 (m, 8 H, H_b, H_c, H_d, H_e), 1.47 (pent, $J = 7.4$ Hz, 2 H, H_f), 1.73 (pent, $J = 7.4$ Hz, 2 H, H_g), 3.04 (t, $J = 7.6$ Hz, 2 H, H_h), 7.35 (d, $J = 8.8$ Hz, 2 H, H_5, H_5'), 7.41 (d, $J = 8.4$ Hz, 2 H, H_7, H_7'), 7.45 (d, $J = 2.4$ Hz, 1 H, H_2), 7.83 (d, $J = 2.0$ Hz, 1 H, H_1), 7.88 (d, $J = 8.8$ Hz, 2 H, H_4, H_4'), 8.09 (t, $J = 9.2$ Hz, 3 H, H_3, H_6, H_6'), 9.08 (s, 1 H, H_k); ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 14.10 (C_a), 22.65 (C_b), 28.68 (C_c), 28.93 (C_d), 29.13 (C_e), 29.16 (C_f), 30.94 (C_g), 31.90 (C_h), 121.34, 122.60, 123.87, 125.05, 126.19, 127.32, 130.54, 130.90, 131.71, 132.22, 136.40, 154.92 for aromatic carbons, 165.22 (CH=N), 166.74 (C=O); IR (KBr, cm^{-1}):

3055 (C-H aromatic), 2853–2955 (C-H aliphatic), 1736 (C=O), 1595 (CH=N), 1574 (C=N thiazole), 1510 (C=C aromatic); MS (m/z) 537[M⁺]. (Fig. S1). Elemental Analysis (Calcd) Found: C (64.85) 65.07; H (5.44) 5.47; N (5.22) 5.35.

4-[(6-Chlorobenzothiazolyl)imino]methyl}phenyl-4-methoxybenzoate (3): Chemical Formula: $\text{C}_{22}\text{H}_{15}\text{ClN}_2\text{O}_3\text{S}$; yellow solid; yield 77%; ^1H -NMR spectrum (CDCl_3 , 400 MHz): δ (ppm) 3.91 (s, 3 H, H_a), 7.01 (d, $J = 12.0$ Hz, 2 H, H_7, H_7'), 7.40 (d, $J = 8.4$ Hz, 2 H, H_5, H_5'), 7.42 (d, $J = 2.4$ Hz, 1 H, H_2), 7.43 (d, $J = 2.0$ Hz, 1 H, H_1), 8.11 (d, $J = 8.4$ Hz, 2 H, H_4, H_4'), 8.17 (d, $J = 9.2$ Hz, 3 H, H_3, H_6, H_6'), 9.08 (s, 1 H, H_b); ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 55.59 (C_a), 114.00, 120.73, 122.62, 123.47, 126.74, 131.26, 132.47, 154.15 for Ar-carbons, 164.17 (CH=N), 167.05 (C=O). IR (cm^{-1}): 3055 (C-H aromatic), 2841–2968 (C-H aliphatic), 1732 (C=O), 1602 (CH=N), 1573 (C=N thiazole), 1512 (C=C aromatic). MS (m/z) 422[M⁺] (Fig. S1). Elemental Analysis (Calcd) Found: C (62.49) 62.74; H (3.58) 3.61; N (6.62) 6.70.

4-[(6-Chlorobenzothiazolyl)imino]methyl}phenyl-3,4,5-trimethoxybenzoate (4): Chemical Formula: $\text{C}_{24}\text{H}_{19}\text{ClN}_2\text{O}_5\text{S}$; yellow solid; yield 74%; ^1H -NMR spectrum (CDCl_3 , 400 MHz): δ (ppm) 3.95 (s, 3 H, H_a), 3.96 (s, 6 H, H_b, H_b'), 7.39 (d, $J = 8.4$ Hz, 2 H, H_6, H_6'), 7.44 (d, $J = 2.4$ Hz, 2 H, H_5, H_5'), 7.46 (s, 1 H, H_3), 7.83 (d, $J = 2$ Hz, 1 H, H_1), 7.89 (d, $J = 8.8$ Hz, 1 H, H_2), 8.13 (d, $J = 8.4$ Hz, 2 H, H_4, H_4'), 9.09 (s, 1 H, H_c); ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 56.37 (C_a), 61.05 ($C_{b+b'}$), 107.51, 120.61, 121.35, 122.63, 122.66, 123.88, 126.54,



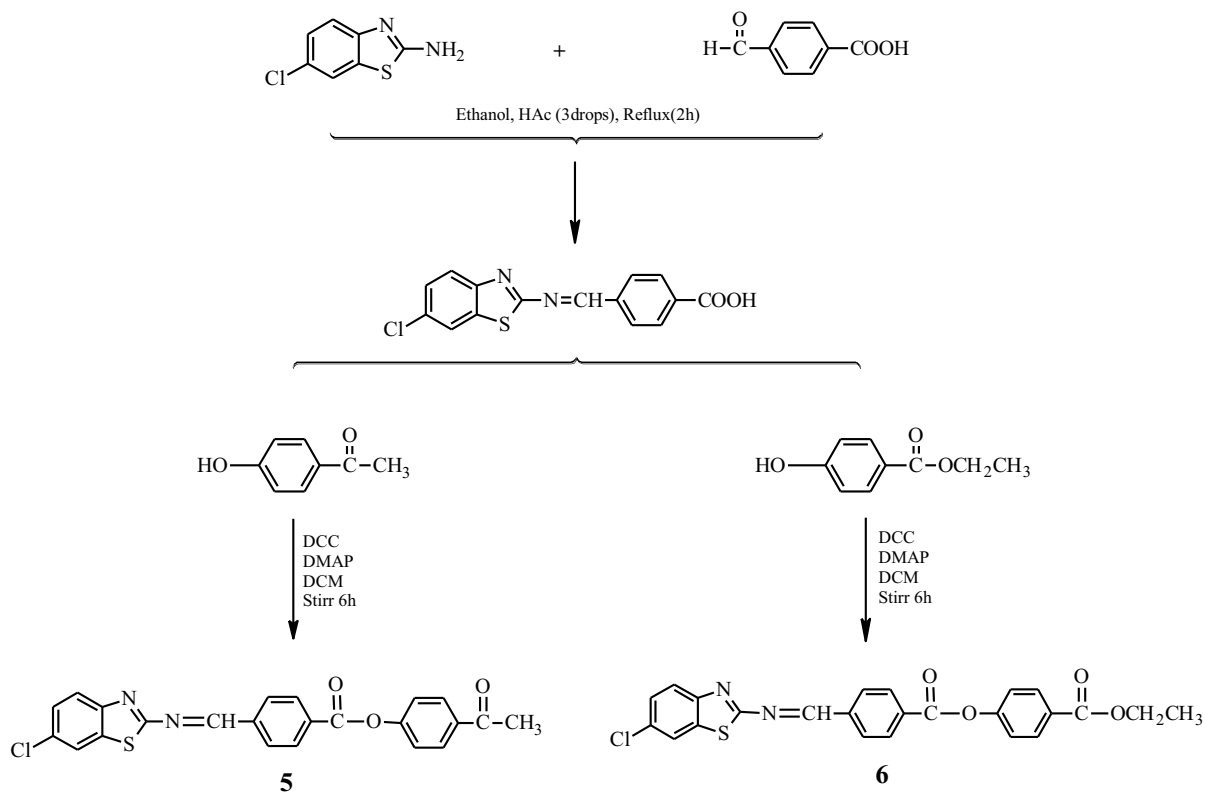
Scheme 2. Synthesis of compounds **3**, **4** and **9**.

127.35, 131.31, 131.74, 134.11, 154.25 for Ar-carbons, 164.21 (CH=N), 167.20 (C=O). IR (cm⁻¹): 3009 (C-H aromatic), 2839–2945 (C-H aliphatic), 1736 (C=O), 1618 (CH=N), 1589 (C=N thiazole), 1578 (C=C aromatic). MS (m/z) 482[M⁺] (Fig. S1). Elemental Analysis (Calcd) Found: C (59.69) 59.94; H (3.97) 4.06; N (5.80) 5.93.

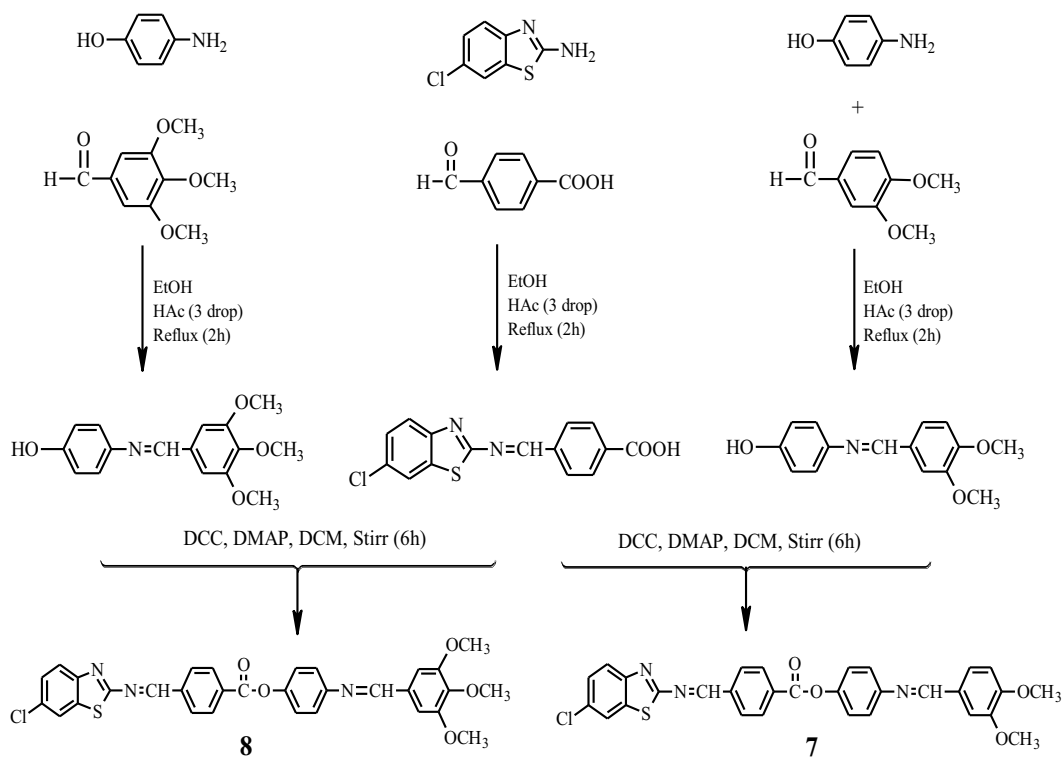
4-Acetylphenyl-4-[(6-chlorobenzothiazolyl)imino]methyl]benzoate (5): Chemical Formula: C₂₃H₁₅ClN₂O₃S; yellow solid; yield 75%; ¹H-NMR spectrum (CDCl₃, 400 MHz): δ (ppm) 2.64 (s, 3 H, H_a), 7.36 (d, J = 8.4 Hz, 2 H, H₁, H₂), 7.38 (d, J = 7.6 Hz, 2 H, H₆, H_{6'}), 8.05 (d, J = 8.0 Hz, 1 H, H₃), 8.08 (d, J = 8.0 Hz, 4 H, H₄, H_{4'}, H₇, H_{7'}), 8.35 (d, J = 8.4 Hz, 2 H, H₅, H_{5'}), 9.19 (s, 1 H, C_b); ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 26.67 (C_a), 121.44, 121.85, 124.16, 127.57, 130.12, 130.24, 130.82, 154.22 for aromatic carbons, 164.81 (CH=N), 168.85 (C=O ester), 197.99

(C=O ketone); IR (cm⁻¹): 3063 (C-H aromatic), 2908–2984 (C-H aliphatic), 1732 (C=O), 1684 (C=O ketone), 1597 (CH=N), 1562 (C=N thiazole), 1543 (C=C aromatic); MS (m/z) 434[M⁺] (Fig. S1). Elemental Analysis (Calcd) Found: C (63.52) 63.81; H (3.48) 3.52; N (6.44) 6.55.

4-(Ethoxycarbonyl)phenyl-4-[(6-chlorobenzothiazolyl)imino]methyl]benzoate (6): Chemical Formula: C₂₄H₁₇ClN₂O₄S; yellow solid; yield 68%; ¹H-NMR spectrum (CDCl₃, 400 MHz): δ (ppm) 1.41 (t, J = 6.8 Hz, 3 H, H_a), 4.40 (q, J = 7.0 Hz, 2 H, H_b), 7.33 (d, J = 7.6 Hz, 2 H, H₆, H_{6'}), 7.48 (d, J = 8.8, 1 H, H₂), 7.85 (s, 1 H, H₃), 7.92 (d, J = 8.8 Hz, 1 H, H₁), 8.15 (d, J = 7.3 Hz, 2 H, H₄, H_{4'}), 8.18 (d, J = 7.5 Hz, 2 H, H₇, H_{7'}), 8.34 (d, J = 7.6 Hz, 2 H, H₅, H_{5'}), 9.18 (s, 1 H, H_c); ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 14.35 (C_a), 61.18 (C_b), 121.43, 121.60, 124.16, 127.56, 128.43, 130.23, 130.79, 131.29, 132.94, 133.15, 135.18, 135.35,



Scheme 3. Synthesis of compounds 5 and 6.



Scheme 4. Synthesis of compound 7 and 8.

136.85, 139.04, 154.21 for Ar-carbons, 164.73 (CH=N), 168.74 (C=O, C_c), 168.97 (C=O, C_d). IR (cm⁻¹): 3051 (C-H aromatic), 2907–2980 (C-H aliphatic), 1739 (C=O), 1716 (C=O), 1598 (CH=N), 1562 (C=N thiazole), 1502 (C=C aromatic); MS (m/z) 464[M⁺] (Fig. S1). Elemental Analysis (Calcd) Found: C (62.00) 62.19; H (3.69) 3.74; N (6.03) 6.14.

4-[(3,4-Dimethoxybenzylidene)amino]phenyl-4-[[6-(6-chlorobenzothiazolyl)imino] methyl] benzoate (7): Chemical Formula: C₃₀H₂₂ClN₃O₄S; yellow solid; yield 61%; ¹H-NMR spectrum (CDCl₃, 400 MHz): δ (ppm) 3.97 (s, 3 H, H_a), 4.00 (s, 3 H, H_b), 6.95 (d, *J* = 8.0 Hz, 1 H, H₁₀), 7.28 (d, *J* = 2.0 Hz, 2 H, H₆, H_{6'}), 7.33 (d, *J* = 2.0 Hz, 2 H, H₇, H_{7'}), 7.46 (d, *J* = 2.0 Hz, 1 H, H₈), 7.48 (d, *J* = 2.0 Hz, 1 H, H₉), 7.63 (d, *J* = 2.0 Hz, 1 H, H₂), 7.86 (d, *J* = 2 Hz, 1 H, H₁), 7.92 (d, *J* = 8.8 Hz, 2 H, H₄, H_{4'}), 8.18 (d, *J* = 8.4 Hz, 1 H, H₃), 8.36 (d, *J* = 8.0 Hz, 2 H, H₅, H_{5'}), 8.40 (s, 1 H, H_c), 9.18 (s, 1 H, H_d); ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 56.05 (C_{a+a'}), 108.98, 110.53, 121.42, 121.91, 122.17, 124.14, 124.60, 127.54, 129.45, 130.20, 130.74, 154.23 for Ar-carbons, 160.22 (CH=N, C_b), 164.97 (CH=N, C_d), 167.12 (C=O). IR (cm⁻¹): 3063 (C-H aromatic), 2849–2918 (C-H aliphatic), 1736 (C=O), 1624 (CH=N), 1579 (C=N thiazole), 1512 (C=C aromatic); MS (m/z) 556 [M⁺] (Fig. S1). Elemental Analysis (Calcd) Found: C (64.80) 65.06; H (3.99) 4.05; N (7.56) 7.69.

4-[(3,4,5-Trimethoxybenzylidene)amino]phenyl-4-[[6-(6-chlorobenzothiazolyl) imino] methyl]benzoate (8): Chemical Formula: C₃₁H₂₄ClN₃O₅S; yellow solid; yield 74%; ¹H-NMR spectrum (CDCl₃, 400 MHz): δ (ppm) 3.93 (s, 3 H, H_a), 3.96 (s, 6 H, H_b, H_{b'}), 7.18 (d, *J* = 8.6 Hz, 2 H, H₈, H_{8'}), 7.46 (d, *J* = 2 Hz, 2 H, H₆, H_{6'}), 7.48 (d, *J* = 2 Hz, 2 H, H₇, H_{7'}), 7.91 (d, *J* = 2 Hz, 1 H, H₃), 7.93 (d, *J* = 8.8 Hz, 2 H, H₁, H₂), 8.17 (d, *J* = 8.4 Hz, 2 H, H₄, H_{4'}), 8.36 (d, *J* = 8.4 Hz, 2 H, H₅, H_{5'}), 8.39 (s, 1 H, H_c), 9.18 (s, 1 H, H_d); ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 56.31 (C_a), 61.04 (C_{b+b'}), 106.75, 108.97, 111.45, 121.43, 122.17, 122.92, 124.13, 124.61, 127.53, 129.74, 130.20, 131.24, 154.18 for Ar-carbons, 160.21 (CH=N, C_c), 164.96 (CH=N, C_e), 167.07 (C=O). IR (cm⁻¹): 3067 (C-H aromatic), 2839–2997 (C-H aliphatic), 1726 (C=O), 1618 (CH=N), 1579 (C=N thiazole), 1504 (C=C aromatic). MS (m/z) 586[M⁺] (Fig. S1). Elemental Analysis (Calcd) Found: C (63.53) 63.83; H (4.13) 4.17; N (7.17) 7.40.

4-[[6-(6-Chlorobenzothiazolyl)imino]methyl]phenyldecanoate (9): Chemical Formula: C₂₄H₂₇ClN₂O₂ S; Yellow solid; Yield 71%; ¹H-NMR spectrum (CDCl₃, 400 MHz): δ (ppm) 0.89 (t, *J* = 7.0 Hz, 3 H, H_a), 1.25–1.42 (m, 12 H, H_b, H_c, H_d, H_e, H_f, H_g), 1.77 (pent, *J* = 7.4 Hz, 2 H, H_h), 2.59 (t, *J* = 7.4 Hz, 2 H, H_n),

7.28 (d, *J* = 8.8 Hz, 2 H, H₅, H_{5'}), 7.45 (d, *J* = 8.8 Hz, 1 H, H₂), 7.82 (d, *J* = 2.0 Hz, 1 H, H₁), 7.89 (dd, *J* = 4.8 Hz, 12.2 Hz, 2 H, H₄, H_{4'}), 8.05 (d, *J* = 8.8 Hz, 1 H, H₃), 9.05 (s, 1 H, H_k); ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 14.12 (C_a), 22.68 (C_b), 24.83 (C_c), 29.08 (C_d), 29.26 (C_e), 29.41 (C_f), 30.95 (C_g), 31.86 (C_h), 34.41 (C_m), 121.34, 122.37, 123.90, 125.05, 126.19, 127.32, 130.54, 131.22, 131.71, 132.22, 154.91 for Ar-carbons, 165.24 (CH=N), 166.99 (C=O). IR (cm⁻¹): 3052 (C-H aromatic), 2851–2953 (C-H aliphatic), 1755 (C=O), 1599 (CH=N), 1576 (C=N thiazole), 1506 (C=C aromatic); MS (m/z) 443[M⁺] (Fig. S1). Elemental Analysis (Calcd) Found: C (65.07) 65.34; H (6.14) 6.22; N (6.32) 6.41.

Result and discussion

The new compounds **1–9** were essentially synthesised via a two-step procedure depicted in Schemes 1–4 (i) Schiff base synthesis (ii) ester formation. The structures of the synthesised compounds were confirmed by elemental analysis, ¹H- and ¹³C-NMR, FT-IR and mass spectrometry (Fig. S1 - Supplementary file). Furthermore, the thermal mesomorphic properties of the liquid crystalline compounds were analysed by hot stage polarising microscopy (POM) and differential scanning calorimeters (DSC). The results obtained confirm the liquid crystal behaviour as well as their transition temperatures.

The results revealed that only compound **1** showed enantiotropic SmA and nematic phases. While compounds **3**, **5–7** showed an enantiotropic nematic phase only, compounds **2** and **9** showed SmA phase only. On the other hand, no liquid crystalline properties were present in compounds **4** and **8**.

All compounds possess a dipole moment across the longitudinal axis of the molecule due to the presence of an ester group. This dipole moment strengthens the lateral attraction forces in these compounds, which in turn enhances the appearance of the SmA phase [9,11]. However, the presence of a Schiff base mesogenic core in these systems plays a significant role in the mesomorphic properties [35].

The presence of the fused-ring system, i.e. benzothiazole, adds a molecular width or contributes to increase the molecular breadth, causing a thickening effect which disrupts the liquid crystalline packing [27,36,37]. This effect is clearly noticed in the examples of molecules bearing benzothiazole (a non-mesogenic compound) compared to molecules having a benzene ring where the SmA phase appeared in the latter compound.

The benzothiazole ring increases the overall polarisability of the molecule and increases the width of the molecule, which either causes the crystalline properties

to decrease or causes a decrease in the thermal range of both phases (SmA and nematic) in the liquid crystalline bases [38–40]. On the other hand, the presence of aromatic rings in the scaffold of the molecules leads to an increase in the polarisation of the molecule, causing it to adopt a more planar conformation, which in turn develops the appearance of liquid crystalline phases with a higher thermal range [37].

With the exception of compound **1**, all the synthesised compounds (**2–9**) possess polarity as a result of the polar chloride atom at position 6 of the aromatic moiety in the benzothiazole scaffold, which provides a polar group at the one terminal end of these molecules [41]. In addition to the above points, there is an electronic resonance along the longitudinal axis of the molecule that leads to an increase in the polarisation and thus enhances the liquid crystalline properties [41].

Compound **9** was synthesised to study the effect of the aliphatic terminal chain on its liquid crystalline properties compared with compounds (**2–8**).

It is also known that the presence of short alkyl chains in liquid crystalline compounds promotes the emergence of the nematic phase [42–45]. This result is in agreement with the results of a previous study on the effect of the length of the terminal alkoxy chain in benzothiazole compounds [46]. The phase change enthalpies of liquid crystals show that these compounds display many thermal transitions. The largest enthalpy change arises on conversion of the solid to a nematic or SmA phase.

The thermodynamic data for the phase transition temperatures (K) of compounds **1–9** and their associated (ΔH) and (ΔS) are presented in Table 1.

The enthalpy values (ΔH) for the transition from the solid state to the SmA phase for compounds **1**, **2** and **9** were measured as 25.16°C, 26.33°C and 23.74°C, respectively (Table 1). These values are less than the enthalpy

values for the transition to the nematic phase for compounds **3**, **5**, **6** and **7** being 27.53°C, 28.17°C, 30.78°C and 35.60°C, respectively. This is due to the SmA phase being more uniform than the nematic phase [47].

Compound **1** showed both nematic and SmA phases with thermal values of 19.77°C and 43.25°C, respectively (Table 1). This indicates that the difference between the terminal and lateral attractive forces is not large and therefore the two phases appeared in compound **1**. This is in agreement with the finding that arises from liquid crystalline compounds, which display a SmA and/or nematic phase depending on the differences between the terminal and lateral attractions [48].

It is interesting to note that the nematic–isotropic transition entropy shown by compound **1** is particularly low. This may be attributed to the reduction in structural anisotropy, specifically, an increase in molecular biaxiality, arising from the absence of a terminal group [49,50].

The presence of a nematic phase only is due to the higher attraction force of the terminal chain compared to the lateral attraction force, which in turn makes them more thermally stable. In general, liquid crystalline compounds display a SmA or nematic phase depending on the extent of the differences between the terminal and lateral attractions. The SmA phase usually appears when the lateral/terminal ratio is high, while the nematic phase is found when the opposite is true [51,52].

Table 1 illustrates that the entropy values (ΔS) for the transition from the solid state to the nematic phase in compounds **3**, **5**, **6** and **7** are 66.62, 66.66, 70.02 and 70.89, respectively. These values are higher than the values for the transition from the solid state to the SmA phase in compounds **1**, **2** and **9** viz. 65.77, 63.59 and 65.73, respectively. This is due to the difference in the regularity between the two phases. The arrangement of the crystals in nematic phase are randomly arranged

Table 1. Transition temperatures, enthalpy and entropy for compounds **1–9**.

Compounds	Transition temperature (°C)	ΔH KJ/mol	ΔS J/mol.K	ΔT_N	ΔT_S	
1	C → SmA	110.02	25.19	65.77	19.7	43.3
	SmA → N	153.27	0.81	1.91		
	N → I	173.01	0.53	1.19		
2	C → SmA	141.10	26.33	63.59	–	123.9
	SmA → I	265.01	8.32	8.3		
3	C → N	195.23	31.19	66.62	74.9	–
	N → I	270.14	2.40	4.43		
4*	C → I	220–223	–	–	–	–
5	C → N	209.24	32.14	66.66	38.9	–
	N → I	248.10	1.54	2.96		
6	C → N	208.56	33.72	70.02	56.6	–
	N → I	265.11	1.63	3.04		
7	C → N	229.11	35.60	70.89	51.1	–
	N → I	280.23	2.20	3.97		
8*	C → I	288–290	–	–	–	–
9	C → SmA	88.13	23.74	65.73	–	61.4
	SmA → I	149.52	3.37	7.98		

with their long axes pointing to the same direction. On the other hand, arrangement of the crystals in the SmA phase is more constrained to parallel planes [53].

The molecular structure of compound **2** is similar to that of compound **1**, with the exception that it has a chloride atom in position 6 of the aromatic ring of the benzothiazole molecule. This compound shows the SmA phase only with a thermal range of 124°C. This could be explained by the fact that the lateral forces of attraction in this compound are higher than the terminal attraction forces. This difference in the attraction forces is due to the existence of a polar substituent at position-6 in compound **2** compared to compound **1** where a less polar hydrogen substituent exists at the same position [53,54]. Polar chloro groups have the tendency to increase the molecular polarisability of compound **2** compared to that of compound **1** [42,43]. In addition, the chloro group possesses a dipole moment along the axis of the molecule, which enhances the appearance of a SmA phase. These molecules are expected to be tilted at an angle to the layer interfaces. When the molecules are tilted, the positive and negative charges of the C-Cl dipoles will be separated and as a result the positive charge of one dipole will become closer to the negative centre of an adjacent dipole. This arrangement enhances the lateral attraction forces and the appearance of a SmA phase in compound **2** [40,42–44].

Similar observations have been reported for cases in which a hydrogen atom has been replaced by a methyl group. It thus suggests that this reflects a subtle change in shape rather than a significant increase in shape anisotropy [55].

This result is in agreement with previous studies, which showed that liquid crystals with a terminal chloro group attached to an aromatic ring support the emergence of the SmA phase [14,39].

Compound **3** showed the nematic phase with a thermal range of 74.91°C. This compound contains a methoxy group attached to the terminal aromatic ring that provides a dipolar moment across the axis of the molecule in addition to being a short terminal chain, which enhances the appearance of nematic phase. It should be noted that compound **4** differs from compound **3** in that the terminal aromatic ring of the former is substituted with three methoxy groups at the *para* and *meta* positions. The increased number of methoxy groups in the terminal aromatic ring results in an increase in the molecular width and a decrease in the length-to-width ratio of the compound, and as a result, the liquid crystalline properties of the compound **4** disappeared [56].

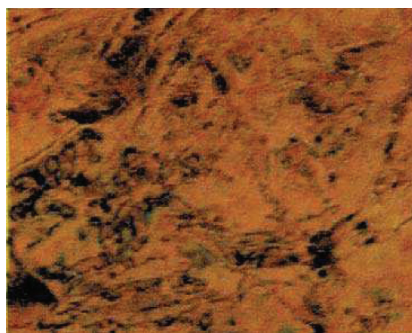
The molecular structure of compound **5** contains an acetyl terminal group (COCH₃), which has a polarity less than compound **6** in which the substituted terminal group is an ester (COOEt). Therefore, the ratio of the lateral attraction forces to the terminal attraction forces in compound **6** is higher than in compound **5**, which enhances the appearance of the nematic phases in compound **6** with a thermal range of 56.23°C, while the comparable thermal range for compound **5** is 38.81°C [57,58].

The terminal aromatic ring in compound **7** includes two methoxy groups attached to the aromatic ring at the *para* and *meta* positions. Each of these two methoxy groups provides a dipolar moment across the molecule axis that enhances the terminal attraction forces in the compound, which ultimately leads to the emergence of a nematic phase with a thermal range of 51.12°C. Although the methoxy group at the *meta* position causes an increase in the molecular width, this, however, does not negatively influence the liquid crystal properties.

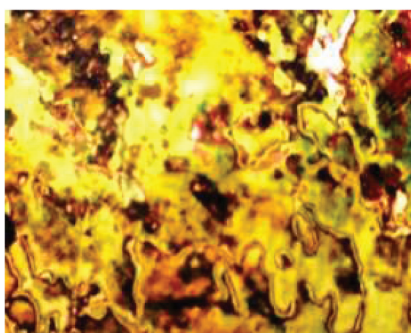
To study the effect of adding a third methoxy group substituted at the second *meta* position, compound **8** was synthesised. It was found that the additional methoxy group has a significant effect on the molecular width, which is evident by the disappearance of the liquid crystalline properties of compound **8** [58,59].

Compound **9** having an aliphatic long chain terminal group that effectively replaces the terminal aromatic ring was found to not enhance the terminal forces. Thus, the presence of an aliphatic long chain terminal group, in addition to the ester group, made the ratio of lateral attraction forces higher than the terminal attraction forces [40]. This leads to the appearance of the SmA phase only in compound **9** with a thermal range of 61.39°C. This is in agreement with the reported result where a substituted compound with the same terminal group showed only the SmA phase [56,60]. Consequently, the SmA phase appeared in compounds **2** and **9** only, but not in compounds **3,5–7** despite having a chloro terminal group. It is believed that this is due to the presence of the long-chain terminal aliphatic group at opposite ends of the molecule in addition to the chloro terminal group in compounds **2** and **9** that enhances the lateral attraction forces and leads to the emergence of the SmA phase. However, smectic behaviour tends to disappear if the terminal chain length exceeds that of the spacer [61].

Liquid crystalline texture shows a nematic phase in compounds **3,5–7** which is illustrated by a marbled texture on heating and Schlieren on cooling, whereas the SmA phase takes on the focal conic texture in compounds **2** and **9** on heating and cooling (Figure 2) [62].



a: Marbled texture in Nematic phase for compound **3** on heating



b: Schlieren texture in Nematic phase for compound **3** on cooling



c: Batonnets texture is S_A phase for compound **7** on cooling and after the clearing temperature,



d: Focal conc texture in S_A phase for compound **7** on cooling.

Figure 2. (colour online) (a) Marbled texture in Nematic phase for compound **3** on heating, (b) Schlieren texture in Nematic phase for compound **3** on heating, (c) batonnets texture is S_A phase for compound **9** on cooling and after the clearing temperature, (d) Focal conic texture in S_A phase for compound **9** on cooling.

Conclusions

A small library (**1–9**) of new rod-like benzothiazole-based compounds were synthesised. All these compounds display liquid crystal properties except compounds **4** and **8**. The synthesised compounds (**2–9**) possess polarity resulting from the polar chloride atom substituted at position-6 of the benzene ring of the benzothiazole moiety, which thus provides a polar group at the one terminal end of the molecules except compound **1**, where no chloride atom is attached. The effect of the terminal group depends on the strength of the dipole moment possessed by this group. A strong dipole moment enhances the terminal attraction forces and leads to the appearance of the nematic phase having a wide thermal range. The S_{MA} phase appears when the opposite occurs, i.e. it has a weak dipole moment. The effect of terminal groups in **1–9** on thermal stability of mesomorphic compounds was evaluated. Polarised Optical Microscope (POM) and differential scanning calorimetry measurements were performed to study the thermal transition temperature, isotropic phases including

the type of phase. The thermal transition temperatures and mesophase behaviour confirmed their liquid crystalline properties. Compound **1** showed enantiotropic S_{MA} and nematic phases, while compounds **3**, **5–7** showed an enantiotropic nematic phase. Compounds **2** and **9** showed a S_{MA} phase due to the presence of a long terminal chain in addition to a chloro terminal group, which enhanced the lateral attraction forces and lead to the emergence of the S_{MA} phase. No liquid crystalline properties were found in compounds **4** and **8**.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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