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Synthesis of new schiff base ester liquid crystals with a benzothiazole core

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A series of new calamitic liquid crystals, 6-methoxy-2-(4-alkanoyloxybenzylidenamino)benzothiazoles, comprising a benzothiazole core, terminal methoxy group and a Schiff base linkage were synthesised and characterised. This series comprises 12 members wherein members differ by the length of the alkanoyloxy chain ($C_{n-1}H_{2n-1}COO-$, where $n = 2-8, 10, 12, 14, 16, 18$). Their mesomorphic properties were studied by using differential scanning calorimetry, optical polarising microscopy and powder X-ray diffraction techniques. The short chain derivatives ($n = 2$ and 3) were non-mesogenic compounds, while an enantiotropic nematic phase was present throughout the remaining members of the series. The smectic C phase emerged from the decanoyloxy derivative onwards.

Keywords: 6-methoxy-2-(4-alkanoyloxybenzylidenamino)benzothiazole; Schiff bases; nematic; smectic C

1. Introduction

Anisometric rod-like (calamitic) or disc-like (discotic) molecules used to be a fundamental prerequisite for the formation of conventional thermotropic liquid crystals because steric packing considerations play an important role in this interesting state of soft matter [1]. Liquid-crystalline behaviour of a calamitic organic compound is basically dependent on its molecular architecture, in which a minor change in the molecular geometry may bring about substantial changes in its mesomorphic properties. Detailed studies by liquid crystal researchers have led to empirical rules, one of which includes the effect of the chemical constitution in the formation of nematic and smectic mesophases [2]. Most of these studies focused largely on Schiff's bases since the discovery of 4-methoxybenzylidene-4'-butylaniline, which exhibited a nematic phase at room temperature [3].

A great number of mesomorphic compounds containing heterocyclic units have been synthesised, and interest in such structures is constantly growing [4–6]. This is not only because of the greater possibilities with heterocyclics in the design of new mesogenic molecules, but also because the insertion of heteroatoms strongly influences the formation of mesomorphic phases. The effect of heteroatoms (S, O and N) can change considerably the polarity, polarisability and sometimes, the geometric shape of the molecule, thereby influencing the type of mesophase, the phase

transition temperatures, and the dielectric and other properties of the mesogens [7]. The incorporation of heterocyclic rings such as pyridine [8], thiophene [6, 9] and 1,3,4-thiadiazole [10] as the core in liquid-crystalline materials has been widely reported.

However, only scant information on the incorporation of benzothiazole as a core in liquid-crystalline compounds is available [11–18]. Benzothiazole derivatives have been studied as photoconductive materials [19–21]. Funahashi and Hanna [22] have reported the fast hole transport property of the photoconductive calamitic liquid crystal, 2-(4-heptyloxyphenyl)-6-dodecylthiobenzothiazole. A benzothiazole ring containing the electron-rich sulphur atom can contribute to a low ionisation potential and also induce a smectic phase. The flat molecular shape with little inter-annular twisting in fused heterocyclic rings may also facilitate a high degree of overlapping molecular wave function for an efficient hopping mechanism of charge transport [16]. A benzothiazole core was also found in fluorescent compounds, which is useful in applications as a result of high fluorescence quantum yields in the presence of the rigid core structure [23]. Lately, benzothiazole derivatives have been continuously investigated for application in thin-film, organic field-effect transistors [24].

The growing scientific interest in the synthesis of heterocyclic-based liquid crystals has prompted us to synthesise a series of 6-methoxy benzothiazole-based

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liquid crystals. The polar methoxy terminal group can facilitate the formation of the nematic phase [13] and widen the mesophase range [25]. The 2,6-disubstituted pattern of a benzothiazole core is also well known to be more linear than the 2,5-disubstituted pattern [17]. The substitution at the sixth position was thermally more stable compared with that at the fifth position on the benzothiazole ring [11]. In this continuing work, we describe the synthesis and mesomorphic properties of a homologous series of Schiff base esters, 6-methoxy-2-(4-alkanoyloxybenzylidenamino)benzothiazoles (*n*MBABTH), where the length of the mesogenic groups varied ($n = 2-8, 10, 12, 14, 16, 18$) as shown in Scheme 1. This work represents an extension of our previous works in this field [26–29].

2. Experimental details

2.1 Characterisation

Fourier transform infrared spectroscopy (FTIR) analyses were performed on a Perkin-Elmer System 2000 FTIR spectrometer. All compounds were analysed using KBr discs with a measurement range of 400–4000 cm^{-1} . ^1H nuclear magnetic resonance (NMR) (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in CDCl_3 using a JEOL LA-400 MHz NMR spectrometer with tetramethylsilane as the internal standard. EI-MS (70 eV) were measured with a mass spectrometer Finnigan MAT 95 XL-T at a source temperature of 200°C. Elemental analyses were carried out on a Perkin Elmer 2400 LS Series CHNS/O analyser.

Phase-transition temperatures and enthalpy changes were measured using a differential scanning calorimeter (DSC) Mettler Toledo DSC823e at heating and cooling rates of 10 and $-10^\circ\text{C min}^{-1}$, respectively. A polarising optical microscope (POM) (Carl Zeiss) equipped with a Linkam heating stage was used for temperature-dependent studies of the textures of liquid crystals. A video camera (Video Master coomo 20P) installed on the POM was coupled to a video capture card (Video Master coomo 600), allowing real-time video capture and image saving. Textures exhibited by the compounds were observed using polarised light with crossed polarisers. Samples were prepared as thin films sandwiched between a glass slide and a cover slip. Phase identification was made by comparing the observed textures with those reported in the literature [18, 19].

Synchrotron powder X-ray diffraction (XRD) measurements were performed at beamline BL17A of the National Synchrotron Radiation Research Center in Taiwan, where the X-ray wavelength used was 1.32633 Å. The XRD data were collected using imaging plates (area = $20 \times 40 \text{ cm}^2$ with a pixel resolution

of 100) curved with a radius equivalent to a sample-to-image plate distance of 280 mm, and the diffraction signals were accumulated for 3 min. The powder samples were packed into a capillary tube and heated by a heat gun, where the temperature controller was programmed by a PC with a PID feedback system. The scattering angle θ was calibrated by a mixture of silver behenate and silicon.

2.2 Synthesis

All solvents and reagents were purchased commercially and used without any further purification. 4-Dimethylaminopyridine (DMAP) and fatty acids ($\text{C}_{n-1}\text{H}_{2n-1}\text{COOH}$ where $n = 2, 4, 6, 7, 12, 14, 16, 18$) were obtained from Merck (Darmstadt, Germany). 2-Amino-6-methoxybenzothiazole, 4-hydroxybenzaldehyde, propanoic acid, pentanoic acid, octanoic acid, decanoic acid and *N,N'*-dicyclohexylcarbodiimide (DCC) were purchased from Acros Organics (USA).

2.2.1 Synthesis of benzothiazole 1

2-Amino-6-methoxybenzothiazole (40 mmol, 7.21 g) and 4-hydroxybenzaldehyde (40 mmol, 4.88 g) were refluxed for 3 h in an ethanol solution (60 ml) upon the addition of two drops of acetic acid. The reaction mixture was then filtered and the filtrate was left to evaporate at room temperature in the fume hood. The yellow solid that was obtained (benzothiazole **1**) was recrystallised from ethanol before being used for further reaction.

6-Methoxy-2-(4-hydroxybenzylidenamino)benzothiazole Yellow. Yield: 86%. Melting point: 237°C. IR (KBr) $\nu_{\text{max}} \text{ cm}^{-1}$ 1600 (C=N, thiazole), 1465 (C=C of aromatic). ^1H NMR (400 MHz, DMSO): δ/ppm 3.6 (s, 3H, CH_3O -), 6.7 (d, $J = 8.1 \text{ Hz}$, 2H, Ar-H), 6.8 (dd, $J = 2.1, 8.7 \text{ Hz}$, 1H, Ar-H), 7.3 (d, $J = 2.4 \text{ Hz}$, 1H, Ar-H), 7.5 (d, $J = 8.6 \text{ Hz}$, 1H, Ar-H), 7.7 (d, $J = 8.4 \text{ Hz}$, 2H, Ar-H), 8.7 (s, 1H, CH=N), 10.3 (s, broad, OH). ^{13}C NMR (100 MHz, DMSO): δ/ppm 164.96 (C=N), 160.33, 158.14, 152.55, 141.07, 130.60, 128.90, 127.04, 121.46, 119.45, 112.72, 99.68 for aromatic carbons, 52.16 (CH_3O -). EI-MS m/z (rel. int. %): 284(100) (M) $^+$.

2.2.2 Synthesis of benzothiazole 2

Benzothiazole **1** (20 mmol, 5.69 g), the appropriate fatty acid (20 mmol) and DMAP (4 mmol, 0.49 g) were dissolved in a 50 ml mixture of dichloromethane (DCM) and dimethylformamide and stirred at 0°C. DCC (20 mmol, 4.13g) dissolved in 10 ml of DCM was added dropwise into the mixture and continuously stirred for 1 hour at 0°C. The mixture was then stirred at room temperature for another 3 h. Finally, the

mixture was filtered and the solvent was removed by slow evaporation. The yellow solid that was formed was recrystallised several times with ethanol whereupon the pure compound was obtained. The purity of all compounds was checked by thin layer chromatography (Merck 60 F₂₅₄) and visualised under short-wave UV light.

The IR, NMR (¹H and ¹³C) and mass spectral data for the representative compound, **16MBABTH**, are summarised as follows.

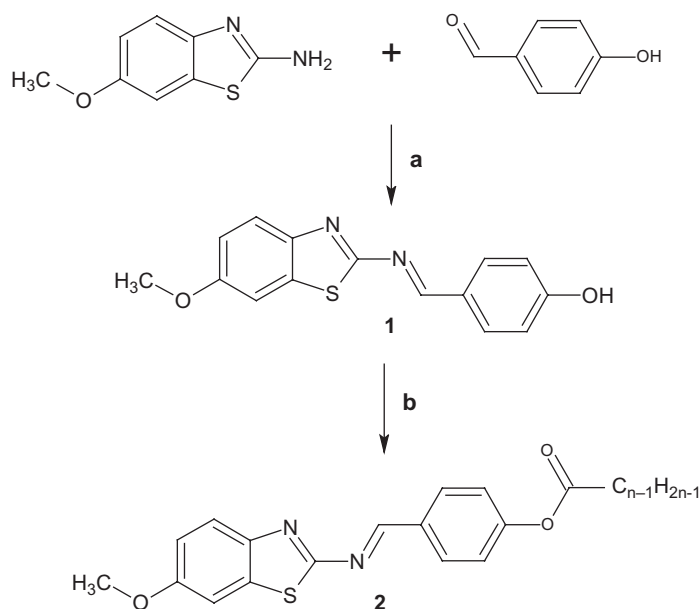
6-Methoxy-2-(4-hexadecanoyloxybenzylidenamino)-benzothiazole (16MBABTH) IR (KBr) ν_{\max} cm⁻¹: 3064 (C-H aromatic), 2916, 2849 (C-H aliphatic), 1752 (C=O ester), 1600 (C=N, thiazole). ¹H NMR (400 MHz, CDCl₃): δ /ppm 0.9 (t, J = 6.6 Hz, 3H, CH₃-), 1.3 (m, 24H, CH₃-(CH₂)₁₂-), 1.8 (quint, J = 7.4 Hz, 2H, -CH₂-CH₂-COO-), 2.6 (t, J = 7.4 Hz, 2H, -CH₂-COO-), 3.8 (s, 3H, CH₃O-), 7.1 (d, J = 9.0 Hz, 1H, Ar-H), 7.2 (d, J = 8.5 Hz, 2H, Ar-H), 7.3 (s, 1H, Ar-H), 7.9 (d, J = 9.1 Hz, 1H, Ar-H), 8.0 (d, J = 8.8 Hz, 2H, Ar-H), 9.0 (s, 1H, -CH=N-). ¹³C NMR (100 MHz, CDCl₃): δ /ppm 171.74 (-COO-), 169.17 (C=N), 163.75, 157.73, 154.44, 146.07, 135.87, 132.37, 131.31, 123.76, 122.30, 115.69, 104.41 for aromatic carbons, 55.79 (CH₃O-), 34.43, 31.91, 29.68, 29.66, 29.65, 29.63, 29.58, 29.44, 29.35, 29.23, 29.08, 24.85, 22.68 for methylene carbons (two aliphatic signals missing due to the accidental equivalence), 14.10 [CH₃]. EI-MS m/z (rel. int. %): 522(18) (M)⁺, 284(100).

3. Results and discussion

The synthetic route used for the preparation of **nMBABTH** is shown in Scheme 1. All compounds were characterised by elemental analysis, NMR and IR spectroscopy. The percentage yields and analytical data of each compound in the series are tabulated in Table 1. The percentages of C, H and N from the elemental analysis were in good agreement with the calculated values for compounds **nMBABTH**. The prominent molecular ion peak at 522 m/z in the mass spectrum of **16MBABTH** established its molecular formula as C₃₁H₄₂N₂O₃S, supporting the proposed structure.

3.1 Mesomorphic behaviour

The mesophases of all the compounds were observed under a POM during heating and cooling cycles. Observation of **10MBABTH** under the POM upon cooling from its isotropic liquid phase showed the presence of two mesophases. The optical photomicrographs of **10MBABTH** are depicted in Figure 1 as a representative illustration. Upon cooling the isotropic liquid of **10MBABTH**, nematic droplets (Figure 1(a)) appeared and coalesced to form the typical schlieren texture with disclination lines (Figure 1(b)). Upon further cooling of the nematic phase, the emergence of the smectic C phase was observed. All the observed liquid-crystalline textures were typical according to the literature [30, 31].



Scheme 1. Reagents and reaction conditions: (a) ethanol, acetic acid reflux for 3 h; (b) dichloromethane, dimethylformamide, *N,N'*-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, C_{n-1}H_{2n-1}COOH (where $n=2-8, 10, 12, 14, 16, 18$), stirred at 0°C for 1 h, stirred at room temperature for 3 h.

Table 1. Percentage yields and analytical data of *n*MBABTH.

Compound	Yield (%)	Formula	% Found (% calculated)		
			C	H	N
2MBABTH	33	C ₁₇ H ₁₄ N ₂ O ₃ S	62.66 (62.56)	4.25 (4.32)	8.49 (8.58)
3MBABTH	28	C ₁₈ H ₁₆ N ₂ O ₃ S	63.57 (63.51)	4.66 (4.74)	8.18 (8.23)
4MBABTH	39	C ₁₉ H ₁₈ N ₂ O ₃ S	64.51 (64.39)	5.04 (5.12)	7.82 (7.90)
5MBABTH	36	C ₂₀ H ₂₀ N ₂ O ₃ S	65.11 (65.20)	5.53 (5.47)	7.66 (7.60)
6MBABTH	41	C ₂₁ H ₂₂ N ₂ O ₃ S	65.83 (65.95)	5.89 (5.80)	7.34 (7.32)
7MBABTH	45	C ₂₂ H ₂₄ N ₂ O ₃ S	66.58 (66.64)	6.08 (6.10)	7.15 (7.07)
8MBABTH	55	C ₂₃ H ₂₆ N ₂ O ₃ S	67.38 (67.29)	6.30 (6.38)	6.78 (6.82)
10MBABTH	48	C ₂₅ H ₃₀ N ₂ O ₃ S	68.57 (68.46)	6.90 (6.89)	6.27 (6.39)
12MBABTH	57	C ₂₇ H ₃₄ N ₂ O ₃ S	69.58 (69.50)	7.28 (7.34)	6.05 (6.00)
14MBABTH	52	C ₂₉ H ₃₈ N ₂ O ₃ S	70.51 (70.41)	7.69 (7.74)	5.74 (5.66)
16MBABTH	63	C ₃₁ H ₄₂ N ₂ O ₃ S	71.12 (71.23)	8.14 (8.10)	5.27 (5.36)
18MBABTH	68	C ₃₃ H ₄₆ N ₂ O ₃ S	72.05 (71.96)	8.34 (8.42)	5.01 (5.06)

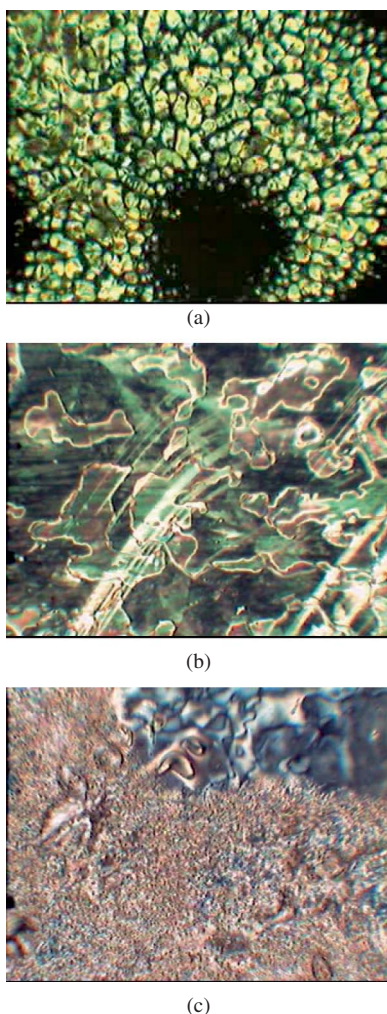


Figure 1. Optical photomicrographs of **10MBABTH** taken during the cooling cycle. Upon cooling from the isotropic liquid, nematic droplets (a) appeared and coalesced to form the typical schlieren texture (b). On further cooling, transition of nematic (top right corner) to smectic C (bottom left) phase was observed (c) (colour version online).

The phase transition temperatures and corresponding enthalpy changes of compounds *n*MBABTH were determined using a DSC. The data obtained from the DSC analysis are summarised in Table 2. Due to the partial decomposition at high temperature, only data from the heating scans were available for the propanoyloxy, butanoyloxy and pentanoyloxy derivatives in which traces of these compounds showed no distinct exothermic peaks during the cooling cycle. This phenomenon was also encountered in azine-type liquid crystals [32].

The short-chain derivatives are non-mesogenic compounds. Mesophases only started to appear beginning from the butanoyloxy derivative. The nematic phase was the only phase observed from the C4 to the C8 derivatives. A further increase in the length of the alkanoyloxy chain from C10 to C18 resulted in both nematic and smectic C phases being observed for those derivatives. The DSC thermograms of **7MBABTH** and **18MBABTH** during their heating and cooling scans are depicted in Figures 2 and 3, respectively. Based on Figure 2, **7MBABTH** is a nematogen as only the transition to the nematic phase was detected. However, in Figure 3, an additional phase transition was found for **18MBABTH**. Subsequently, three phase transitions were detected in its DSC thermogram, Cr-SmC, SmC-N and N-I.

3.2 Structure-mesomorphic property relationships

The plotting of the graph of phase-transition temperatures against the number of carbons in the alkanoyloxy chain enabled the effects of the terminal chain on the mesomorphic properties to be established (Figure 4). The adequate geometric anisotropy (ratio between length and width of the molecule) is an

Table 2. Transition temperatures and associated enthalpy changes of *n*MBABTH upon heating and cooling.

Compound	Transition temperatures (°C) (ΔH , kJ mol ⁻¹)
2MBABTH	Cr 136.6 (31.89) I <i>Cr 112.2 (28.28) I</i>
3MBABTH*	Cr 110.6 (30.89) I
4MBABTH*	Cr 104.3 (44.99) N 152.1 [‡] I
5MBABTH*	Cr 80.5 (29.92) N 121.7 (0.50) I
6MBABTH	Cr ₁ 71.0 (10.77) Cr ₂ 82.0 (18.29) N 116.8 (0.83) I <i>Cr 30.3 (21.18) N 114.5 (0.60) I</i>
7MBABTH	Cr 90.6 (40.72) N 119.9 (0.66) I <i>Cr 52.8 (29.06) N 118.4 (0.85) I</i>
8MBABTH	Cr 74.5 (28.97) N 120.5 (0.78) I <i>Cr 48.2 (35.62) N 118.9 (1.08) I</i>
10MBABTH	Cr 70.2 (28.97) N 117.8 (0.90) I <i>Cr 46.6 (25.24) SmC 56.3 (1.61) N 112.9 (1.16) I</i>
12MBABTH	Cr 65.6 (30.98) SmC 73.1 (0.37) N 114.3 (0.79) I <i>Cr 52.4 (29.08) SmC 69.1 (1.18) N 110.6 (0.94) I</i>
14MBABTH	Cr ₁ 65.6 (10.18) Cr ₂ 78.8 (22.92) SmC 79.7 (0.10) N 109.6 (1.47) I <i>Cr 59.0 (35.46) SmC 79.7 (1.12) N 107.9 (1.41) I</i>
16MBABTH	Cr 83.7 (26.01) SmC 88.3 (0.22) N 107.2 (1.49) I <i>Cr 65.7 (26.00) SmC 85.9 (0.51) N 105.2 (1.49) I</i>
18MBABTH	Cr 90.5 (43.17) SmC 99.7 (0.19) N 112.6 (2.70) I <i>Cr 76.1 (40.67) SmC 98.6 (0.29) N 111.2 (2.34) I</i>

Notes: The values in italics were taken during the cooling cycle.

*No cooling data provided due to partial decomposition.

[‡]Polarising optical microscopy data.

Cr = crystal; I = isotropic liquid; N = nematic; SmC = smectic C.

important point. Based on Figure 4, the odd-even effect on the mesomorphic properties was not obvious but was still noticeable when moving from the C5 to the C7 derivatives. The short-chain derivatives ($n = 2$ and 3) are non-mesogenic compounds.

The high melting points of the early series may be partially responsible for the lack of mesophase formation. Since the terminal chains of the C4, C5, C6, C7 and C8 derivatives are long enough to promote mesophase formation, a nematic phase was observed for each of these derivatives [22]. As the length of the carbon chain increased, a monotropic (metastable) smectic C phase was observed for the C10 derivative. Similarly, once the carbon chain reached a certain length ($n \geq 12$), the enantiotropic (stable) smectic C phase, which accompanied the nematic phase at a higher temperature, was induced.

The melting points showed a descending trend from the C2 to C5 members and then gradually increased from the C5 to C7 members. As the alkyl chain gets longer, the melting point continued to decrease from C7 to C12 members. Due to the excessive Van der Waals attractive forces between the long alkyl chains, the melting temperatures increased obviously from the C12 to C18 members [33]. Likewise, the clearing temperatures dropped from the C4 to C6 members and a slight increment to the C8 member was observed. Clearing points then descended with the increase in length of the carbon chain due to the dilution of the mesogenic core resulting from the flexibility provided by the terminal alkanoyloxy chain (for C8 to C16 members) [34]. A clear increment was observed when moving to the longest chain member (C18).

By referring to the graph, the nematic phase range (Δ_N) apparently decreased by the increase in the length of the terminal chain resulting from the long carbon chain being attracted and intertwined, which in turn facilitates the lamellar packing causing a decrease in the nematic phase range [27]. However,

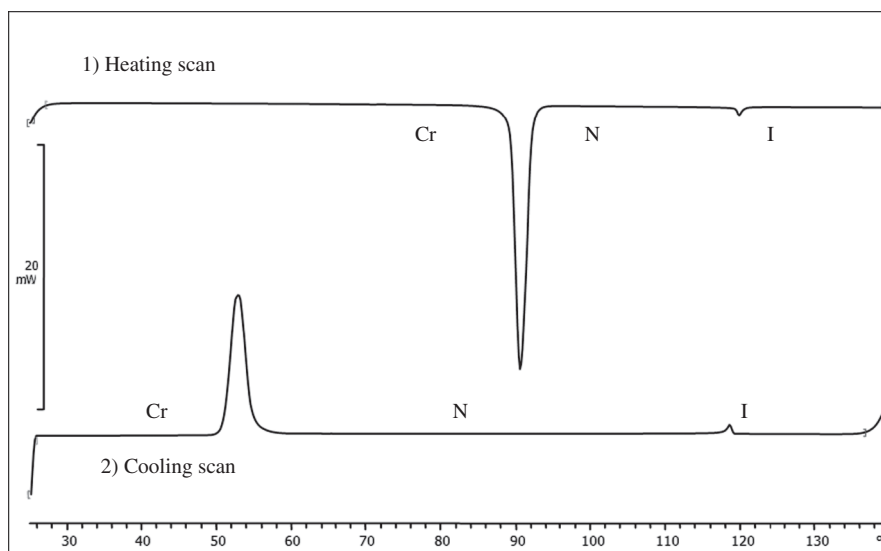


Figure 2. Differential scanning calorimetry thermogram of 7MBABTH during heating and cooling scans.

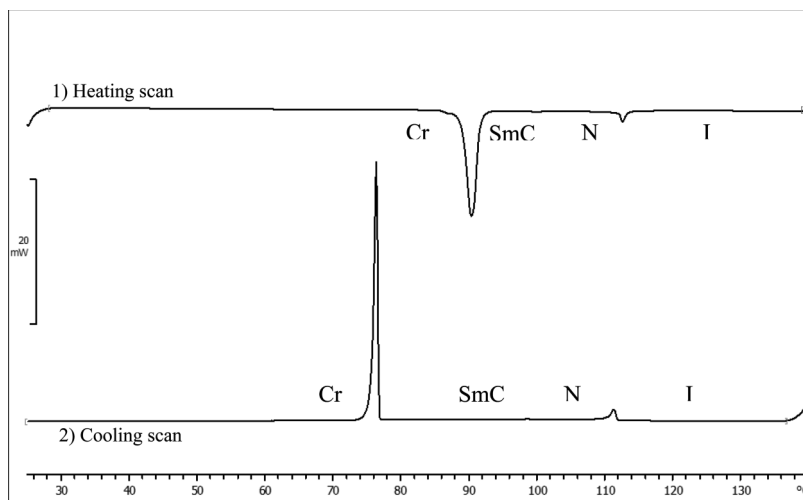


Figure 3. Differential scanning calorimetry thermogram of **18MBABTH** during heating and cooling scans.

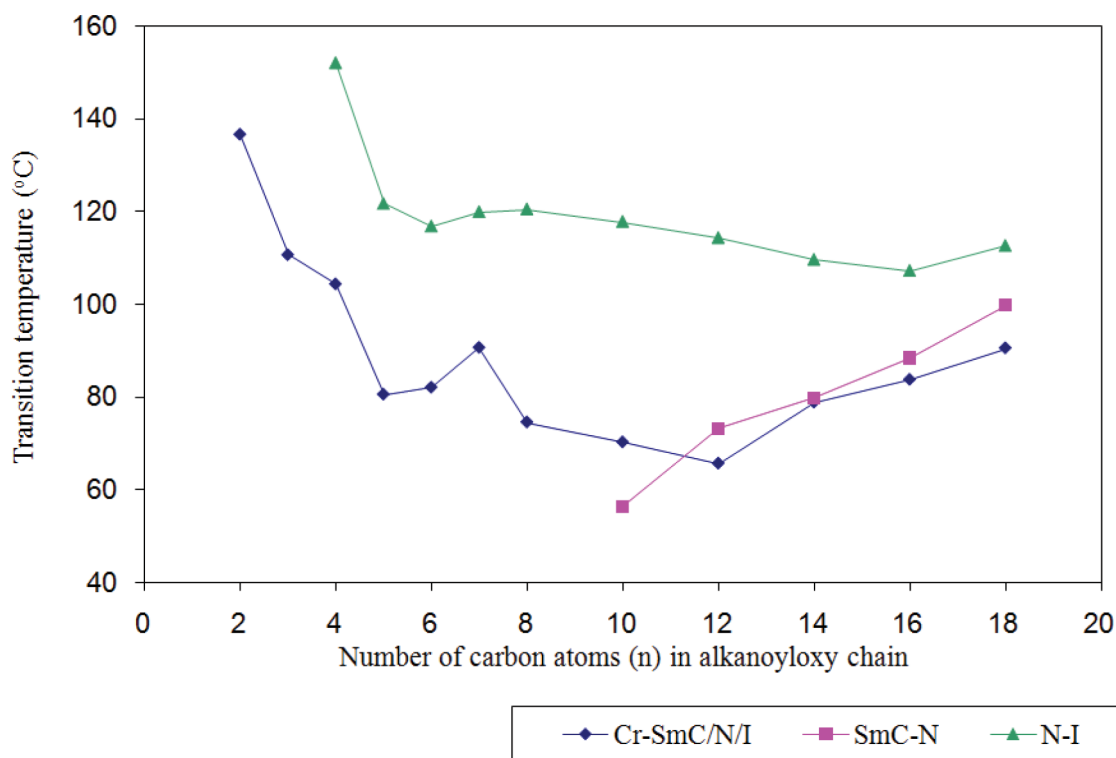


Figure 4. Plot of transition temperatures versus the number of carbons (n) in the alkanoyloxy chain of n **MBABTH** during the heating cycle.

by increasing the length of the carbon chain, the smectic C phase range (Δ_{SmC}) did not exhibit the usual trend whereby Δ_{SmC} should increase. The Δ_{SmC} was found to be 7.6°C for the C12 member, it decreased to 0.9°C for the C14 member, and

increased again to 4.6°C and 9.2°C for the C16 and C18 members, respectively. Although smectic phase stability was enhanced from the C12 to C18 members, the increasing melting temperatures caused the Δ_{SmC} to become insignificant.

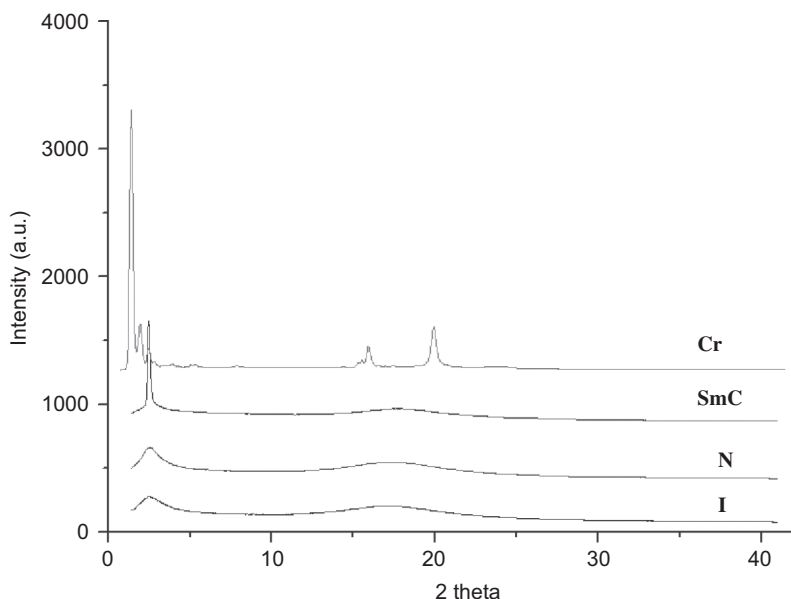


Figure 5. X-ray diffraction patterns of **12MBABTH** at different temperatures on cooling from the isotropic phase.

3.3 XRD analysis

In order to confirm the presence of the smectic C phase in the series, XRD analysis was performed. The XRD diffractogram of the representative compound **12MBABTH** is depicted in Figure 5. Its XRD pattern revealed a sharp and strong peak in low angle ($2\theta = 2.48^\circ$), indicating the presence of a lamellar structure (smectic-layered arrangement) together with a broad peak in wide angle ($2\theta \approx 17^\circ$). In general, for a smectic liquid-crystalline phase, a sharp and strong peak at low angle ($1^\circ < 2\theta < 4^\circ$) in a small-angle X-ray scattering curve and a broad peak associated with lateral packing at $2\theta \approx 20^\circ$ can be observed in wide-angle XRD curve. However, for the nematic phase, no peak appears at small angle and a broad peak at $2\theta \approx 20^\circ$ can be observed in the XRD diffractogram [35]. Upon combining the results from the POM and XRD analysis, the presence of the smectic C phase in this series was confirmed.

4. Conclusion

In this paper, we described the synthesis and mesomorphic behaviour of a homologous series of 6-methoxy-2-(4-alkanoyloxybenzylideneamino)benzothiazoles. Short-chain derivatives ($n = 2$ and 3) are non-mesogenic compounds. The nematic phase was observed from the *n*-butanoyloxy to *n*-octanoyloxy derivatives. Both nematic and smectic C phases were observed from *n*-decanoyloxy to *n*-octadecanoyloxy derivatives. The study also revealed that the length of the alkyl chain gives a significant effect to the mesomorphic properties

in which the smectic phase can only be observed for mid to long-chain derivatives ($n \geq 10$).

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