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Synthesis and mesomorphic behavior of benzothiazole-based liquid crystals having terminal methoxyl group

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Abstract

A homologous series of benzothiazole derivatives, 6-methoxy-2-(4-alkanoyloxybenzylidenamino)benzothiazoles, were synthesized and characterized using FT-IR, ^{1}H and ^{13}C NMR, mass spectrometry and elemental analysis. Enantiotropic nematic phase was observed throughout the entire series. Smectic C phase only emerged from the decanoyloxy derivative onwards. The terminal methoxyl group and the ester linkage influenced the mesomorphic behavior of the present series.

Keywords: Benzothiazole; Schiff bases; Nematic; Smectic C; Liquid crystal

Liquid crystalline phase was first reported during the 19th century by the Austrian botanist Friedrich Reinitzer from his microscopic observation on the thermal behavior of molten cholesteryl benzoate [1]. This observation led to the discovery of a new and fascinating class of soft materials which combines extraordinary optical, elastic and viscous properties [2]. Selection of a mesogenic core, terminal groups and a suitable length of the flexible chains is the prerequisite in designing new thermotropic liquid crystals [3]. An earlier report has shown that the introduction of heterocycles as the central core greatly influenced the mesomorphic properties of the calamatic molecules owing to their unsaturation and/or their more polarizable nature [4–7]. It has been reported that benzothiazole-based liquid crystals possessed good hole-transporting properties with a low ionization potential, making them of potential interest as hole-transporting materials in organic light emitting devices (OLEDs) [8]. In our previous studies [9], a benzothiazole ring was incorporated as a mesogenic core in thermotropic liquid crystals which enabled them to exhibit good mesomorphic properties.

In order to further explore the benzothiazole as a mesogenic core in Schiff base liquid crystals, here, we reported a new homologous series of 6-methoxy-2-(4-alkanoyloxybenzylidenamino)benzothiazoles and their synthetic route is illustrated in Scheme 1. 2-Amino-6-methoxybenzothiazole was condensed with 4-hydroxybenzaldehyde upon refluxing in ethanol for 3 h following which the particular Schiff base intermediate was subjected to Steglich

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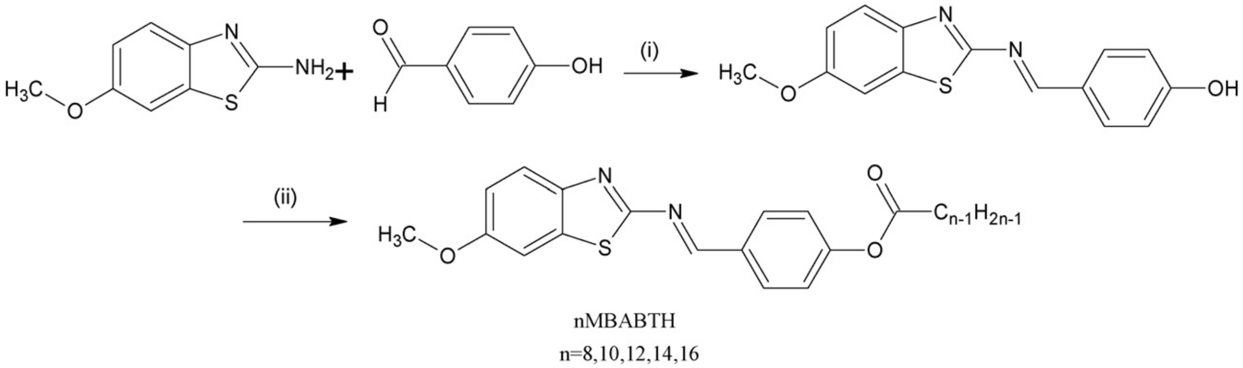

Scheme 1. Synthetic route for the target compounds. (i) C_2H_5OH and (ii) $C_{n-1}H_{2n-1}COOH$, DCC, DMAP, CH_2Cl_2, DMF. Yield of 8MBABTH (55%), 10MBABTH (48%), 12MBABTH (57%), 14MBABTH (52%), and 16MBABTH (63%).

esterification with the appropriate fatty acid in the presence of DCC and DMAP according to previously reported procedures [10–13]. All the crude products were purified upon repeated recrystallization using ethanol until constant melting points were obtained. The yield of the final products was between 48% and 63% (Scheme 1). Structural elucidation of the title compounds was carried out via elemental analysis, FT-IR, NMR and EI-MS spectroscopic techniques [14].

The liquid crystalline textures of the title compounds were observed under a polarizing optical microscope equipped with a hotstage and temperature regulator. Phase identification was made by comparing the observed textures with those reported in the literature [15,16]. Transition temperatures and corresponding enthalpy changes were determined using a differential scanning calorimeter.

The transition temperatures obtained from the DSC analysis are tabulated in Table 1 and it can be deduced that the enantiotropic nematic phase was observed throughout the series. Among all the members in the series, only the octanoyloxy derivative is pure nematogen. While a monotropic SmC phase was observed for the decanoyloxy derivative, an enantiotropic SmC was observed from the dodecanoyloxy to the hexadecanoyloxy derivatives. A monotropic mesophase is observed when the melting temperature is higher than the phase transition temperature [17]. Upon cooling of the isotropic liquid of 16MBABTH, the typical Schlieren texture (Fig. 1a) of a nematic phase was first observed. If the SmC phase is formed directly from a nematic mesophase, an appearance that is called striated texture can often be observed at the N–SmC transition [18]. This is also sometimes referred as transition bars texture [16]. Upon further cooling of the nematic phase of 16MBABTH, the transition bars texture (Fig. 1b) was observed at the transition of nematic to SmC phase. Appearance of SmC phase can also be further confirmed by the Schlieren texture.

Table 1
Phase transition and transition enthalpy changes for *n*-MBABTH upon heating and cooling.

Compound	Phase transition, °C (corresponding enthalpy changes, kJ mol^{-1})
8MBABTH	Cr 74.5 (28.97) N 120.5 (0.78) I *Cr 48.2 (35.62) N 118.9 (1.08) I*
10MBABTH	Cr 70.2 (28.97) N 117.8 (0.90) I *Cr 46.6 (25.24) SmC 56.3 (1.61) N 112.9 (1.16) I*
12MBABTH	Cr 65.6 (30.98) SmC 73.1 (0.37) N 114.3 (0.79) I *Cr 52.4 (29.08) SmC 69.1 (1.18) N 110.6 (0.94) I*
14MBABTH	Cr1 65.6 (10.18) Cr2 78.8 (22.92) SmC 79.7 (0.10) N 109.6 (1.47) I *Cr 59.0 (35.46) SmC 79.7 (1.12) N 107.9 (1.41) I*
16MBABTH	Cr 83.7 (26.01) SmC 88.3 (0.22) N 107.2 (1.49) I *Cr 65.7 (26.00) SmC 85.9 (0.51) N 105.2 (1.49) I*

Cr, crystal; N, nematic; SmC, smectic C; I, isotropic.
Phase transition: roman indicates heating, italic indicates cooling.

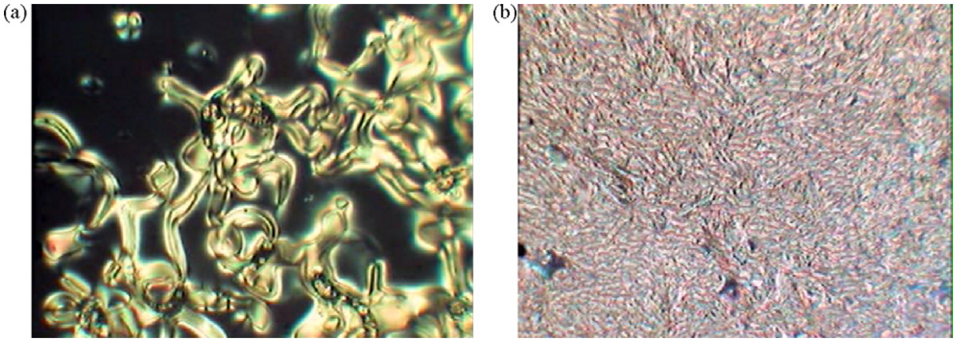

Fig. 1. Liquid crystal textures (100×) of 16MBABTH upon cooling. The nematic Schlieren texture (a) was observed followed by transition bars texture at the N–SmC transition (b) upon further cooling.

The occurrence of SmC phase in these compounds is in accordance with the previously reported benzothiazole liquid crystals [6].

By referring to the chemical constitution of the present series, the nematic phase which was observed could have resulted from the terminal methoxyl group which disrupted the lamellar arrangement of the smectic phase. The similar phenomenon was also reported for a homologous series of azo liquid crystals with a benzothiazole core [19]. Furthermore, the azomethine (CH=N) linkage which conferred a step like structure resulted in the thickening effect which in turn enhanced the nematic phase stability [20]. The presence of the SmC phase however was influenced by two factors: (i) a longer alkyl chain and (ii) an ester linking group. Generally, a smectic phase is observed for higher members of a series as the longer alkyl chain is able to intertwine and facilitate the smectic phase formation [21]. In addition, the greater dipole–dipole interaction provided by the ester linking group also influenced the lateral packing hence generating the smectic phase.

A plot of the transition temperatures against the number of carbons in the alkanoyloxy chain during the heating scan is depicted in Fig. 2. The melting temperatures (T_{Cr-N}) initially decreased from the C_8 to the C_{12} members and then increased from the C_{12} to the C_{16} members. However, the clearing temperatures exhibited a descending trend throughout the series due to the dilution of the mesogenic core resulting from the long carbon chain [22,23]. From the graph, it is apparent that the nematic phase range decreased while the smectic phase stability increased due to the lengthening of the carbon chain. Hence, the increase in the length of the terminal chain causes the nematic properties to decrease, in turn leading to the enhancement of the smectic properties.

In conclusion, all the title compounds exhibited a nematic phase whereby the SmC phase emerged from the C_{10} derivatives onwards. While the terminal methoxyl group and the azomethine linkage facilitated the nematic phase formation, the long alkanoyloxy chain favoured the lamellar arrangement which resulted in the smectic phase formation.

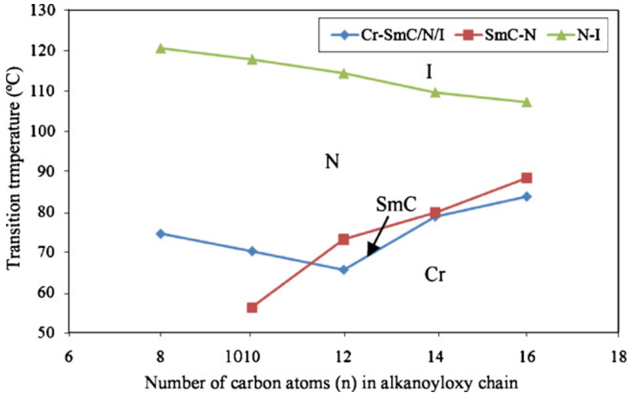

Fig. 2. Phase behavior of *n*MBABTH.

Acknowledgments

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[14] Analytical and spectroscopic data for the representative compound 16MBABTH: yield 63%, EI-MS *m/z* (rel. int.%): 522 (18) [M+], 284 (100), IR ν_{max} (KBr, cm^{-1}): 3064 (C–H aromatic); 2916, 2849 (C–H aliphatic); 1752 (C═O ester); 1600 (C═N thiazole), ^{1}H NMR (400 MHz, $CDCl_3$, δppm): 0.9 (t, 3H, J = 6.6 Hz, CH_3–), 1.3 (m, 24H, CH_3–$(CH_2)_{12}$–CH_2–CH_2–COO–), 1.8 (q, 2H, J = 7.4 Hz, –CH_2–CH_2–COO–), 2.6 (t, 2H, J = 7.4 Hz, –CH_2–COO–), 3.8 (s, 3H, CH_3O–), 7.1 (d, 1H, J = 9.0 Hz, 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, –N═CH–), ^{13}C NMR (100 MHz, $CDCl_3$, δppm): 14.10 (CH_3–), 22.68, 24.85, 29.08, 29.23, 29.35, 29.44, 29.58, 29.63, 29.65, 29.66, 29.68 for methylene carbons (CH_3–$(CH_2)_{12}$–), 31.91 (–CH_2CH_2COO–), 34.43 (–CH_2COO–), 55.79 (–OCH_3), 104.41, 115.69, 122.30, 123.76, 131.31, 132.37, 135.87, 146.07, 154.44, 157.73, 163.75 for aromatic carbons, 169.17 (–CH═N–), 171.74 (–COO–), anal. calcd. for $C_{31}H_{42}N_2O_3S$: C, 71.23%, H, 8.10%, N, 5.36%; found: C, 71.20%, H, 8.12%, N, 5.33%.
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