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Synthesis and Mesogenic Properties of New Schiff Bases Comprising Benzothiazole Moiety

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Abstract

A new homologous series of mesogen, 6-ethoxy-2-(4-alkanoyloxybenzylideneamino)benzothiazoles with even number of carbons (n = 6, 8, 10, 12, 14, 16, 18) at terminal ester chain have been successfully synthesized and isolated. The structure of the title compound was confirmed using elemental analysis and various spectroscopic techniques including FT-IR, ^{1}H NMR and ^{13}C NMR and EI-MS. Phase transition temperatures and thermal data were determined using differential scanning calorimetry. The textures of mesophases were observed under optical polarizing microscope attached with a Linkam hotstage. All the compounds are enantiotropic liquid crystals. While *n*-hexanoyloxy and *n*-octanoyloxy derivatives exhibited nematic, *n*-decanoyloxy to *n*-octadecanoyloxy derivatives showed smectic C and nematic phases.

Key words: Liquid crystal, Benzothiazole, Schiff bases, Nematic, Smectic C.

INTRODUCTION

Over the past few decades, liquid crystals comprising a Schiff base (or azomethine) linkage have received overwhelming attention since the discovery of the room temperature-liquid crystal, 4-methoxybenzylidene-4'-butylaniline (MBBA) [1]. Selection of a mesogenic core, terminal groups and a flexible chain are the essential criteria in designing new thermotropic liquid crystals [2]. A *para*-substituted phenyl ring ensures that the molecules have structural linearity and large molecular polarizability, which consequently enables them to exhibit liquid crystalline behavior [3].

Recently, there has been a continuing interest in the study of heterocyclic based liquid crystal compounds due to their unique properties [4-6]. Earlier report has shown that the introduction of heterocycles as the core has greatly influenced the mesomorphic properties of the calamatic molecules owing to their unsaturation and/or their more polarizable nature [7].

Here, we report in this paper the synthesis and the mesomorphic properties of a new homologous series of 6-ethoxy-2-(4-alkanoyloxybenzylidenamino)benzothiazoles with a Schiff base linkage and a sixth-position terminal ethoxyl group.

EXPERIMENTAL

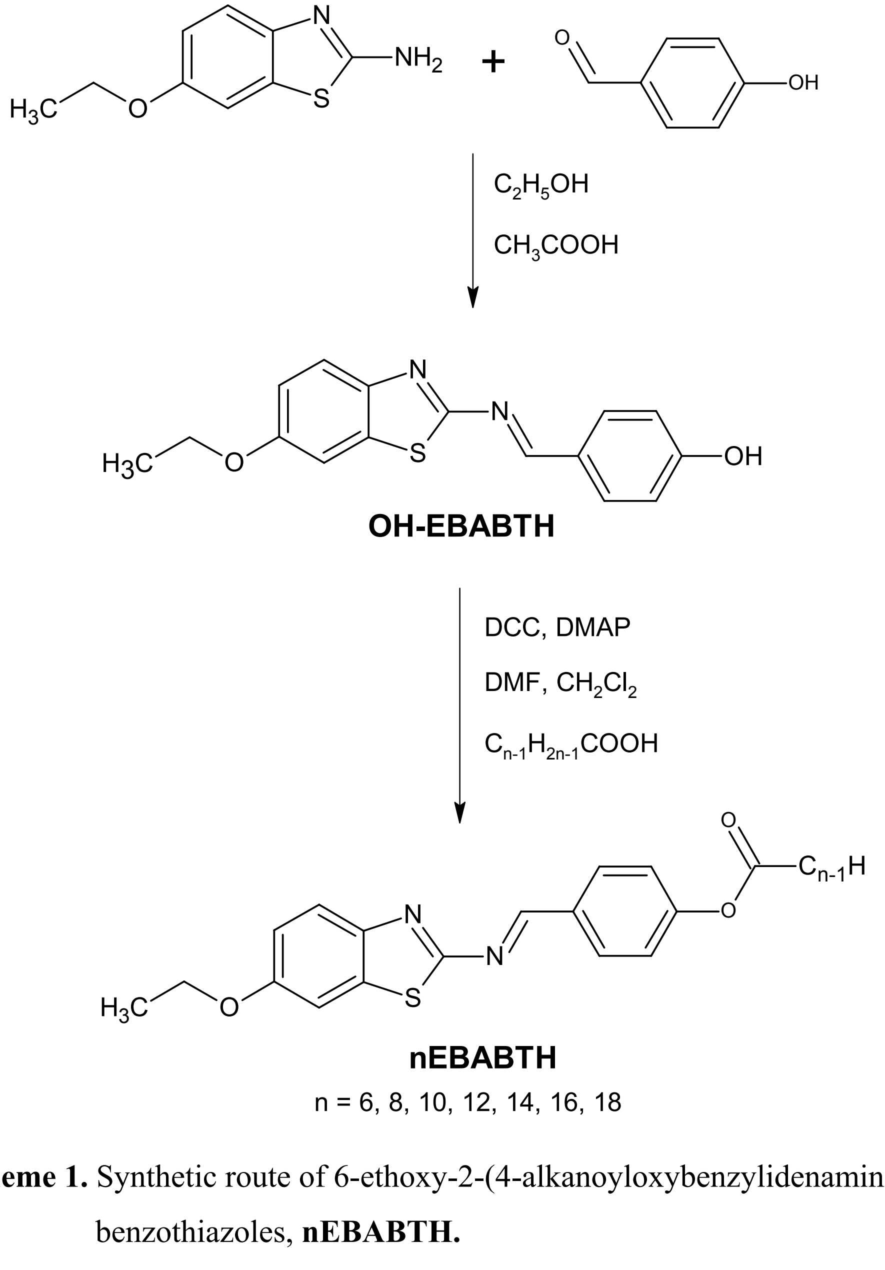
The title compounds were synthesized according to a previously reported method [8]. The synthetic route is depicted in Scheme 1. The synthetic route is depicted in Scheme 1. A solution of 2-amino-6-ethoxybenzothiazole and 4-hydroxybenzaldehyde in absolute ethanol was heated under reflux for 3 hours in the presence of acetic acid. The Schiff base formed, **OH-EBABTH**, was recrystallized from absolute ethanol.

The schiff base **OH-EBABTH** appropriate fatty acid and DMAP were dissolved in a mixture of dichloromethane and DMF and stirred in an ice bath. To this solution, DCC dissolved in dichloromethane was added drop wise upon stirring in the ice bath for an hour. The resulting mixture was subsequently stirred at room temperature for another three hours. The reaction mixture was then filtered and the excess solvent was removed from the filtrate by evaporation. The yellow solid obtained was recrystallized several times using ethanol. The structure of the products was confirmed using elemental analysis, IR, NMR and EI-MS spectroscopic techniques

The IR, NMR (^{1}H and ^{13}C) and mass spectral data for the representative compound, **16EBABTH**, are summarized as follows.

6-Ethoxy-2-(4-hexadecanoyloxybenzylidenamino)benzothiazole (16EBABTH). Yield 60%. IR (KBr) $\nu_{\max}$ cm^{-1} 3047 (C-H aromatic), 2922, 2849 (C-H aliphatic), 1755 (C=O ester), 1597 (C=N thiazole), 1450 (C=C aromatic). ^{1}H NMR (400 MHz, CDCl$_3$): δ/ppm

0.9 (t, 3H, $C\underline{H}_3$-), 1.2-1.4 (m, 24H, CH_3-$(C\underline{H}_2)_{12}$-CH_2-CH_2-COO-), 1.5 (t, 3H, $C\underline{H}_3$-CH_2-O-), 1.8 (m, 2H, -$C\underline{H}_2$-CH_2-COO-), 2.6 (t, 2H, -$C\underline{H}_2$-COO-), 4.1 (m, 2H, CH_3-$C\underline{H}_2$-O-), 7.0 (d, 1H, Ar-H), 7.2 (d, 2H, Ar-H), 7.3 (s, 1H, Ar-H), 7.8 (d, 1H, Ar-H), 8.0 (d, 2H, Ar-H), 9.0 (s, 1H, -N=C$\underline{H}$-). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 171.60 (COO), 168.95 (C=N), 163.53, 157.02, 154.34, 145.90, 135.77, 132.30, 131.19, 123.66, 122.19, 116.04, 104.96 for aromatic carbons, 63.64 (-O-$\underline{C}H_2$-CH_3), 34.33, 31.86, 29.63, 29.61, 29.58, 29.53, 29.38, 29.29, 29.18, 29.01, 24.77, 24.62 for methylene carbons [CH_3-$(\underline{C}H_2)_{14}$-COO-], 14.75 (-O-CH_2-$\underline{C}H_3$), 14.05 [$\underline{C}H_3$-$(\underline{C}H_2)_{14}$-COO-]. EI-MS m/z (rel. int. %): 536(42) $(M)^+$, 298(100).



Scheme 1. Synthetic route of 6-ethoxy-2-(4-alkanoyloxybenzylidenamino)-benzothiazoles, **nEBABTH.**

RESULTS AND DISCUSSION

Thermal studies and liquid crystallinity of nEBABTH

Observation under POM revealed the schlieren and marble textures typical of a nematic mesophase (Fig. 1), as reported in the literature [9,10]. As the length of the terminal chain increases, the smectic phase emerges. Whilst **6EBABTH** and **8EBABTH** were purely nematogenic, the higher members**, nEBABTH** (n = 10, 12, 14, 16 and 18) exhibited both nematic and tilted smectic C phases. Fig. 2 depicts the representative optical photomicrographs of **10EBABTH** during the cooling run. The smectic C phase was identified on the basis of its characteristic schlieren texture (Fig. 2b) and by the appearance of the familiar fingerprint texture (Fig. 2a) during the N-to-SmC transition [11].

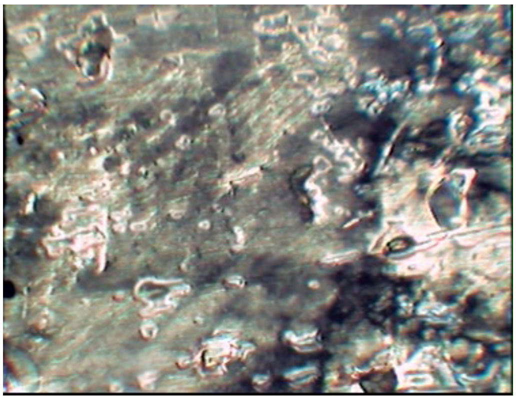
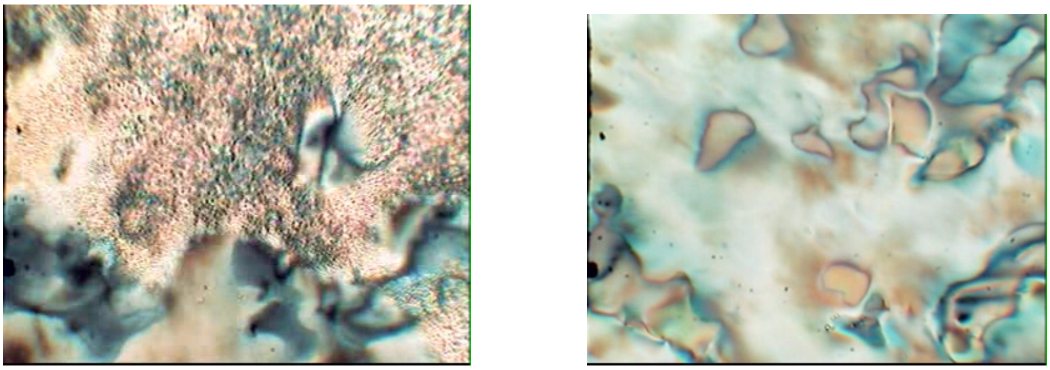


Fig.1 Optical photomicrograph of **8EBABTH** .



(a) (b)

Fig.2 Optical photomicrograph of **10EBABTH**.

According to the plot of transition temperatures against the number of carbons in the alkanoyloxy chain (Fig. 3), the crystal-mesophase (Cr-M) transition temperatures initially decreased when the length of terminal chain of the derivatives increased from C6 to C10, and later exhibited an increase from the C10 to C18 derivatives. The unusual features shown by C6 to C10 members could be explained in terms of the rigidity of the long molecular axis which will often be reduced owing to the increase in the flexibility of the terminal alkanoyloxy chains which suppresses the anisotropy of the molecules [12]. As for compounds **nEBABTH** (where n=12,14,16,18) with longer chains, the Cr-M transition increased due the increase of the L/W ratio where the molecules are closely packed owing to the *van der Waals* intermolecular forces of attraction [13].

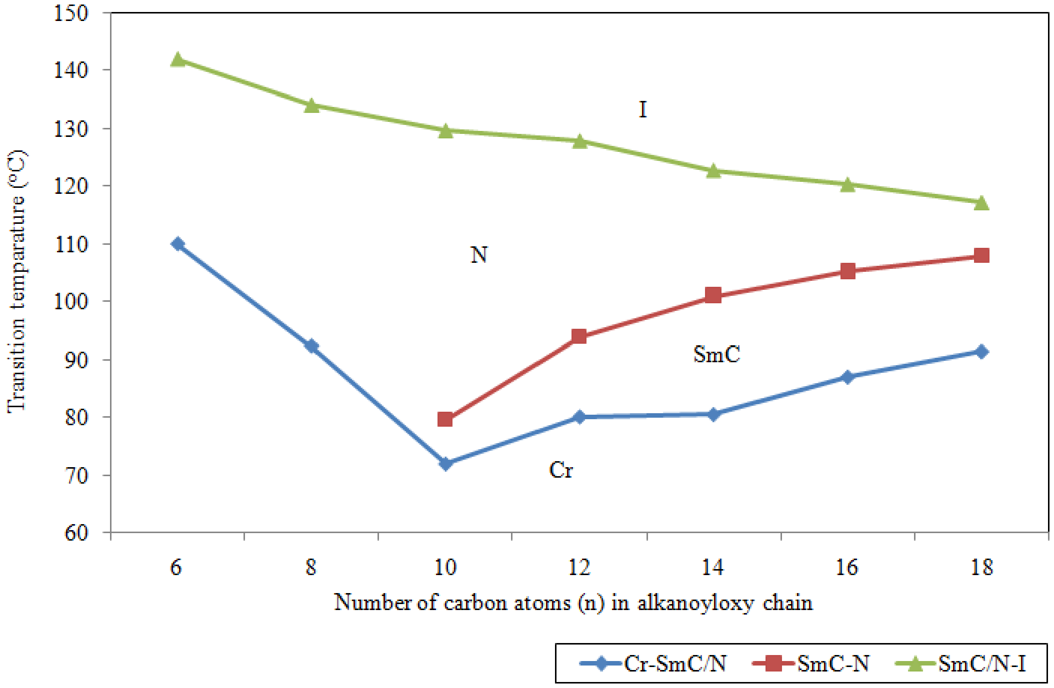


Fig.3 Plot of transition temperatures versus the number of carbons (n) in the alkanoyloxy chain of **nEBABTH** during heating cycle.

As for the clearing (N/SmC-I) points, the descending trend observed from C6 to C18 derivatives. It is common that the longest chain possessed the lowest thermal stability indicating that the long molecular axis is no longer fully extended resulting in the molecule becoming nonlinear when the length of the terminal chain increases [14]. Furthermore, the nematic phase range was found to decrease while the SmC phase range was enhanced as the length of the carbon chain increased. This is due to attraction between the long alkanoyloxy chains leading to their intertwining, facilitating the lamellar packing which is essential for the occurrence of the smectic phase [5].

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