

Mesogenic Schiff Base Ethers with Heterocyclic Benzothiazole Core: Synthesis and Phase Transitions Studies

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Abstract. A homologous series of new liquid crystals, 6-ethoxy-2-(4-alkyloxybenzylidenamino) benzothiazoles, consisting of benzothiazole core, Schiff base and ether linkers was synthesized. All the members can be differed by the number of carbon atoms at terminal alkyloxy chain. The molecular structure of title compound was confirmed with infrared and nuclear magnetic resonance spectroscopic techniques. Mesomorphic properties were studied using differential scanning calorimetry and polarizing optical microscopy. Enantiotropic liquid crystal phases were present throughout the series.

Keywords: Benzothiazole, Schiff Base, Ether Linker, Nematic, Smectic

1. Introduction

Liquid crystals have gained additional attention as new type of organic semiconductor exhibiting self organization, liquid crystal display, separation membrane materials, high yield strength polymers, photonic, thin films *etc* [1]. Heterocycles play a significant role as core units in calamitic liquid crystals owing to their capability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape and geometry [2]. Numerous mesomorphic compounds containing heterocyclic units have been reported, and interest in such structures is continuously growing [2,3]. However, only limited information can be found on the inclusion of benzothiazole core into liquid crystal system [4-6]. Funahashi and co-worker have reported the fast hole transport property of the photoconductive rod-like liquid crystal, 2-(4-heptyloxyphenyl)-6-dodecylthiobenzothiazole [7]. It was found that benzothiazole ring containing electron-rich sulphur atom can contribute to a low ionisation potential and also induce a smectic phase. The flat molecular shape with small interannular twisting in fused heterocyclic rings may also facilitate a high degree of overlapping molecular wavefunction for an efficient hopping mechanism of charge transport [8]. Benzothiazole unit was also reported in fluorescent compounds, which is useful in applications as a result of high fluorescence quantum yields in the presence of the rigid core structure [9]. Recently, benzothiazole derivatives have been continuously investigated for their applications in thin-film, organic field-effect transistors [10].

In order to further explore benzothiazole as a mesogenic core in heterocyclic liquid crystals, here, we reported a new homologous series of 6-ethoxy-2-(4-alkyloxybenzylidenamino)benzothiazoles, nOEtBTH. This homologous series consists of benzothiazole core, a Schiff base central linkage, a ether terminal linkage

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and a even number of carbon atoms of terminal alkyloxy chain ($C_{n-1}H_{2n-1}O-$, $n = 10, 12, 14, 16$). Ethoxyl group was introduced and served as terminal substituent while no lateral substituent is present in this series.

2. Experimental

2.1. Materials and Methods

2-Amino-6-ethoxybenzothiazole, 4-hydroxybenzaldehyde and anhydrous potassium carbonate were purchased from Merck (Germany). Bromoalkanes ($C_nH_{2n+1}Br$, where $n = 10, 12, 14, 16$) were purchased from Acros Organics (USA). All solvents and reagents were purchased commercially and used without any further purification.

IR spectra were recorded using Perkin-Elmer System 2000 FT-IR Spectrometer via KBr disc procedure. 1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ using Bruker Avance 400 MHz Spectrometer in the Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia.

Phase-transition temperatures and enthalpy changes were measured using Differential Scanning Calorimeter Mettler Toledo DSC823e at heating and cooling rates of $10\text{ }^\circ\text{C}/\text{min}$ and $-10\text{ }^\circ\text{C}/\text{min}$, respectively. A Carl Zeiss polarizing optical microscope (POM) equipped with Linkam heating stage was used for temperature dependent studies of the liquid crystal textures. Phase identification was made by comparing the observed textures with those reported in the literature [11,12].

2.2. Synthesis of Heterocyclic Liquid Crystals

nOEtBTH were prepared via modification of previously reported methods [13,14]. The synthetic route of nOEtBTH is shown in Fig. 1. Equivalent molar of 4-hydroxybenzaldehyde and 2-amino-6-ethoxybenzothiazole were stirred under reflux for three hours in appropriate amount of ethanol. A few drops of acetic acid served as catalyst was added into mixture before the condensation reaction. Schiff base formed, HOEtBTH was separated by suction filtration and washed with ethanol.

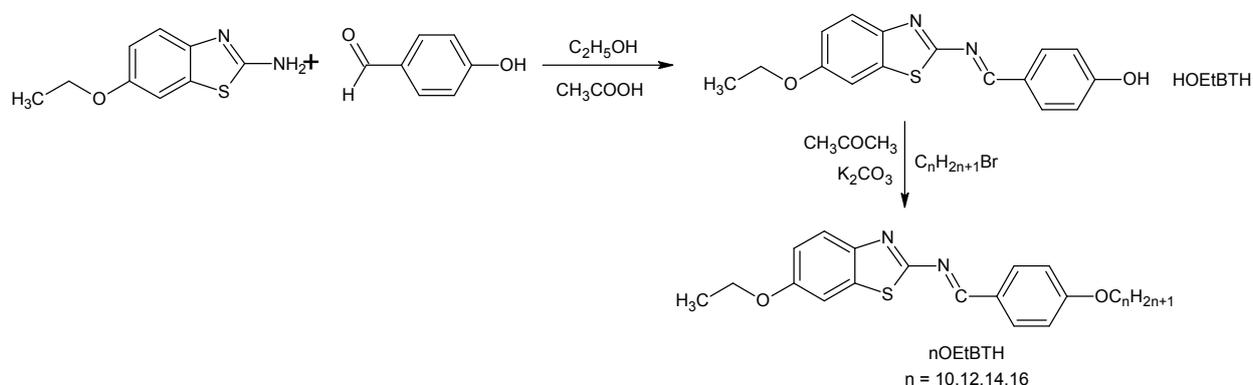


Fig. 1: Synthetic route of nOEtBTH

Then, HOEtBTH was subjected to Williamson etherification with the appropriate bromoalkanes in the presence of anhydrous potassium carbonate. The crude products were recrystallized several times with ethanol whereupon pure compound was isolated. The FTIR, 1H and ^{13}C NMR spectral data for the representative compound, 12OEtBTH, are summarized as follows.

IR ν_{max} (KBr, cm^{-1}): 3064 (C-H aromatic), 2917, 2847 (C-H aliphatic), 1594 (C=N Schiff base), 1563 (C=N thiazole), 1253 (C-O aromatic ether); 1H NMR (400MHz, $CDCl_3$, δ ppm) : 0.90 (t, 3H, CH_3-), 1.27-1.40 (m, 18H, $CH_3-(CH_2)_9-$), 1.48 (t, 3H, Ar- OCH_2CH_3), 1.83 (p, 2H, $-CH_2CH_2O-$), 4.06 (t, 2H, $-CH_2CH_2O-$), 4.11 (q, 2H, Ar- OCH_2CH_3), 7.01 (d, 2H, Ar-H), 7.06 (dd, 1H, Ar-H), 7.29 (d, 1H, Ar-H), 7.85 (d, 1H, Ar-H), 7.97 (d, 2H, Ar-H), 8.92 (s, 1H $-N=CH-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.84 (CH=N), 164.34, 163.41, 156.88, 146.11, 135.57, 132.12, 127.63, 123.46, 115.85, 114.98, 105.25 for aromatic carbons, 68.38 ($-CH_2CH_2O-$), 64.12 (Ar- OCH_2CH_3), 31.91 ($-CH_2CH_2O-$), 29.64, 29.62, 29.58, 29.55, 29.34, 29.11, 25.98, 22.67 for methylene carbons [$CH_3(CH_2)_9-O$], 14.84 (Ar- OCH_2CH_3), 14.09 (CH_3)

3. Results and Discussion

3.1. Synthesis and Spectral Studies

Structure elucidation of compounds 12OEtBTH was ascertained by using IR and NMR spectroscopic methods. Infrared spectral studies suggested the presence of diagnostic bands for aromatic ether, C=N of benzothiazole, C=N of Schiff base and aliphatic chain.

The ^1H NMR spectrum of 12OEtBTH further supported its structure. Two triplets at $\delta = 0.90$ and 4.06 ppm, are respectively ascribed to the methyl and methylene protons which attached to aromatic ether ($-\text{CH}_2\text{O-Ar}$), while the multiplet signal between $\delta = 1.27$ and 1.40 ppm is assigned to the methylene protons of the long alkyl chain $\{\text{CH}_3-(\text{CH}_2)_9-\}$. Two distinct doublets at the respective chemical shift of $\delta = 7.01$ and 7.97 ppm are attributed to four aromatic protons. Another three signals appeared at $\delta = 7.06$, 7.29, 7.85 ppm confirmed the presence of fused aromatic protons. The presence of terminal ethoxyl group attached to the benzothiazole is confirmed with the occurrence of quartet and triplet signals at $\delta = 4.11$ and 1.48 ppm, respectively. The singlet observed at the most downfield region, $\delta = 8.94$ ppm, supported the presence of the imine linking group [15].

The molecular structure of 12OEtBTH was further verified by using ^{13}C NMR spectroscopy. The peak at $\delta = 14.09$ ppm was attributed to the methyl carbon while the peaks between $\delta = 22.67$ -31.91 ppm represented the methylene carbons of the long alkyl chain. Signals attributed to the benzothiazole and aromatic carbons were resonated between $\delta = 105.25$ -164.34 ppm. The peak at $\delta = 169.84$ ppm confirmed the presence of the azomethine carbon in the molecule.

3.2. Phase Transition Behavior and Liquid Crystallinity

All compounds exhibited interesting thermotropic properties and its melting behavior was carefully monitored by POM during both heating and cooling scans. Optical photomicrographs of 12OEtBTH are shown in Fig. 2 as the representative illustration. The results from the POM observation were verified by the DSC measurements. The transition temperatures, enthalpy changes, and phase sequences are summarized in Table 1. Mesophase identification was based on the optical textures, and the magnitude of isotropization on enthalpies is consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus [16] and Gray and Goodby [17]. A plot of phase transition temperature against number of carbon atom (n) in alkyloxy chains during heating scan is shown in Fig. 3.

Table 1. Phase transition temperatures and enthalpy changes of nOEtBTH

Compound	Phase transition temperature, °C (enthalpy change, kJ mol ⁻¹)
10OEtBTH	Cr 88.7 (45.52) SmC 95.6 (0.25) N 131.2 (1.58) I <i>Cr 57.0 (19.34) SmC 93.9 (0.21) N 129.5 (1.76) I</i>
12OEtBTH	Cr 90.3 (50.00) SmC 97.7 (2.07) SmA 109.1 (1.26) N 126.9 (1.87) I <i>Cr 65.9 (45.38) SmC 92.0* SmA 107.66 (1.02) N 125.4 (2.22) I</i>
14OEtBTH	Cr 91.3 (51.43) SmA 113.2 (1.65) N 121.8 (1.67) I <i>Cr 69.4 (46.98) SmA 111.6 (1.39) N 120.3 (1.86) I</i>
16OEtBTH	Cr 96.5 (62.28) SmA 116.1 (1.46) N 120.1 (1.40) I <i>Cr 67.2 (53.60) SmA 114.5 (1.31) N 118.5 (1.63) I</i>

Note: Cr= crystal; SmA= smectic A; N = nematic; I= isotropic. *POM data
Cooling data is presented in *italics*.

Low member of the series, 10OEtBTH displayed enantiotropic nematic and smectic C properties. DSC thermogram of 10OEtBTH showed endotherms characteristic of the crystal-to-smectic C, smectic C-to-nematic and nematic-to-isotropic transitions at temperatures greater than melting temperature. Under POM, it is therefore confirmed the existence of two mesophases in 10OEtBTH. An increase of two carbons at the alkyloxy chain in 12OEtBTH has shown an interesting phenomenon wherein a third mesophase was observed. This additional phase with fan-shaped texture assigned as smectic A (SmA) phase (Fig. 2c) was observed after the formation of the nematic droplets (Fig. 2a) and disclination lines (Fig. 2b) on the cooling run. Further cooling of SmA phase led to the appearance of gray texture (Fig. 2d) identified as smectic C phase. Higher members of the series displayed only nematic and SmA phases.

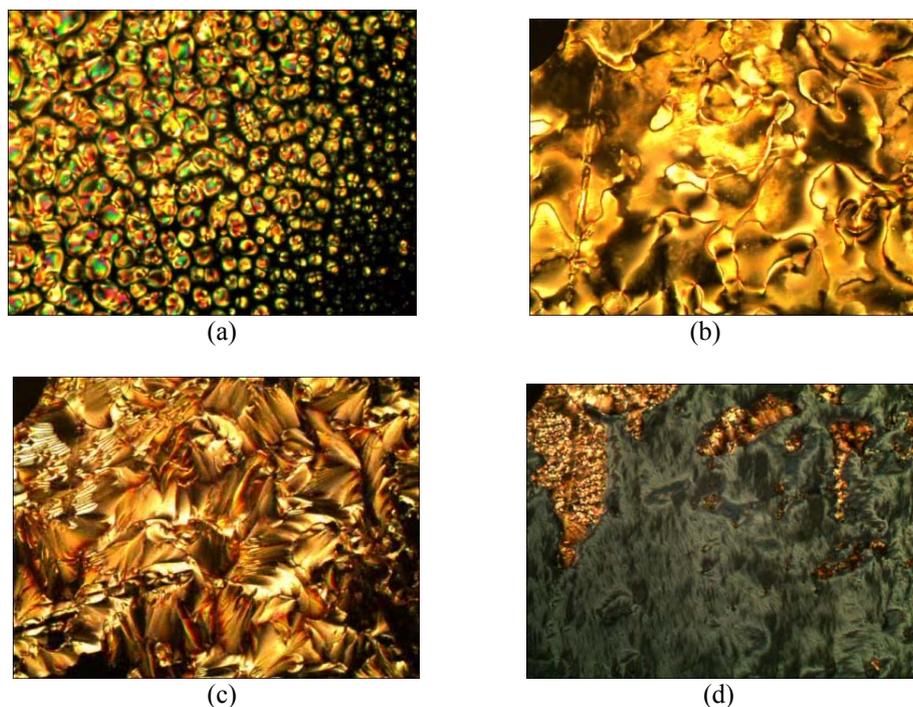


Fig. 2: Liquid crystals textures (100x) of 12OEtBTH upon cooling. Optical photomicrographs exhibiting (a) nematic droplets (b) nematic phase with disclination lines, (c) smectic A phase with fan-shaped texture (d) smectic C phase with gray texture.

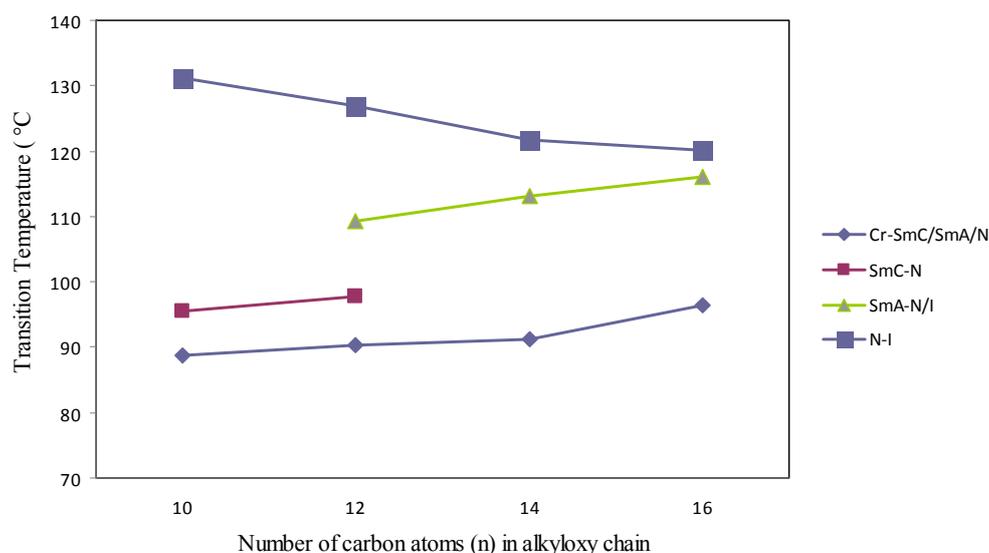


Fig. 3: Plot of transition temperatures versus the number of carbons (n) in the alkyloxy chain of nOEtBTH during heating cycle.

Based on the plot (Fig. 3), it can be deduced that the mesomorphic properties were significantly influenced by the length of terminal alkyloxy chain. The smooth falling trend in clearing temperature can be ascribed to the dilution of mesogenic core [19]. Similar trend was also reflected on the homologous series of *N,N'*-bis(3-methoxy-4-alkoxybenzylidene)-1,4-phenyldiamine [19]. The nematic phase range was found to be decreased as the chain length ascended from C10 (35.6 °C) to C16 (4.0 °C) member. The suppression of nematic phase range was accompanied by the uplifting of smectic phase range. For example, smectic phase range increased from C10 (6.9 °C) to C16 (19.6 °C) members. This may due to the attractions between the long alkyloxy chains leading to their intertwining and facilitates the lamellar packing which is essential for the occurrence of the smectic phase [15]. Increasing Van der Waals forces not only raised the melting temperatures but also enhanced the smectic phase stability whereby the smectic phase stability increased from 95.6 °C (C10) to 116.1 °C (C16).

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5. References

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