



## Synthesis and mesomorphic properties of non-symmetric liquid crystal dimers stabilized by benzothiazole and substituted aromatic imines



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### Abstract

Two new homologous series of non-symmetric liquid crystal dimers *N*-(4-(*n*-(4-(benzothiazol-2-yl)phenoxy)alkyloxy)benzylidene)-4-bromoanilines and *N*-(4-(*n*-(4-(benzothiazol-2-yl)phenoxy)alkyloxy)benzylidene)-4-methoxyanilines in which the methylene spacer of C<sub>n</sub>H<sub>2n</sub> with even parity of *n* ranging from 4 to 12 and the substituents of bromo and methoxy attached to respective aniline fragments have successfully been synthesized and characterized. The salient feature of these series can be attributed to the conversion of non-mesogenic units of benzothiazole and aromatic imine units to mesogens through the formation of dimers. All the title compounds exhibit enantiotropic nematic phases. The smectogenic properties also prevail among the series containing Br entity wherein the spacers are C<sub>8</sub>H<sub>16</sub>, C<sub>10</sub>H<sub>20</sub> and C<sub>12</sub>H<sub>24</sub>. In general, the isotropization temperatures for both series were seen to descend with the increase in the spacer length. Comparison among the compounds possessing Br and OCH<sub>3</sub> substituents shows that the anisotropic properties are governed partially by the presence of substituent residing in the aniline unit.

**Keywords:** non-symmetric dimers; benzothiazole; aromatic imine; enantiotropic nematic; smectic.

### 1. Introduction

Liquid crystals play an important role in today's world of science and technology. One of the reasons can be attributed to their technological applications, particularly as optical imaging, liquid crystal displays, organic light emitting diodes (OLEDs), anisotropic networks and semiconductor materials [1–3]. Liquid crystals incorporating a benzothiazole fragment have been used to display positive hole-transporting character owing to its low ionization potential. As such, they could serve as hole-transporting materials in organic light-emitting

devices [4–7].

Dimers possessing identical mesogenic units are referred to as symmetric dimers. In contrary the dimers consisting two different mesogenic groups are named as non-symmetric dimers [8–18]. Most of the dimers which have hitherto been reported are symmetric in nature. However, non-symmetric dimers receive more attention as these compounds exhibit liquid crystalline behaviour, not commonly found on the symmetric dimers, such as intercalated and interdigitated phases [9]. In addition, the non-symmetric dimers exhibit interesting polymorphic properties and stabilize a wide range of chiral

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nematic (N\*) and smectic A (SmA) phases [15, 16, 19, 20].

Another notable feature related to the liquid crystal dimers can be ascribed to the incorporation of the heterocyclic ring which had made remarkable contribution toward stabilizing the mesophases [7,21,22]. The incorporation of benzothiazole ring, for instance, can enhance the hole-transporting properties with a low ionization potential which is essential in organic light-emitting devices (OLEDs) [23-25]. Knowing the importance of benzothiazole-based compounds has prompted us to carry out synthesis and characterization of some novel mesogens in recent years [26-31].

In the present study, two homologous series of non-symmetric liquid crystal dimers derived from 2-(4-hydroxyphenyl)benzothiazole and *N*-(4-hydroxybenzylidene)-4-substituted-aniline moieties bridged by a methylene spacer will be highlighted wherein the mesomorphic behaviour due to the variation of the spacer length and the terminal substituent effect will be discussed. Actually, this work has focused on the conversion of non-mesogenic units to mesogenic dimers. This conversion has been conceptualized based on the stability of the electronic delocalization and conjugation systems within respective benzothiazole and aromatic imine. The members of these homologous series possess the generalized formula of PBTH-*n*-X in which PBTH denotes the 2-(4-hydroxyphenyl)benzothiazole, *n* the number of carbon in the methylene spacer and X denotes the substituent (Br or OCH<sub>3</sub>) attached to the 4-position of the benzylidene-4-substituted anilines.

## 2. Experimental

The starting materials of 2-aminothiophenol, 4-hydroxybenzaldehyde, 4-bromoaniline, 4-methoxyaniline and dibromoalkane (C<sub>n</sub>H<sub>2n</sub>Br<sub>2</sub>; where *n* = 4, 6, 8, 10 and 12) were purchased from Acros Organics (New Jersey, USA) and Merck (Darmstadt, Germany). All solvents and reagents were purchased commercially and used without further purification.

The molecular structures of all intermediary and title compounds were elucidated via spectroscopic methods. The FT-IR technique was carried out on a Perkin Elmer 2000 FTIR spectrophotometer. The samples were prepared in the form of KBr pellets and analyzed at frequency range of 4000-

400 cm<sup>-1</sup>. The investigation by <sup>1</sup>H-NMR was performed on a Bruker Avance 300 and 400 MHz Ultrashield<sup>TM</sup> spectrometers. Deuterated chloroform (CDCl<sub>3</sub>) and dimethylsulphoxide (DMSO-d<sub>6</sub>) were used as solvents and TMS as internal standard. CHN microanalyses were conducted using a Perkin Elmer 2400 LS Series CHNS/O Analyser. TLC was carried out on aluminium-backed silica gel plates (Merck 60F254) and visualized under short-wave UV light. The optical textures of the phases shown by the dimers were observed using a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Linkam TMS94 temperature controller and an LTS350 hot-stage. In order to determine the phase transition temperatures, associated enthalpies and entropy changes for the phase transition, differential scanning calorimetry was carried out using a Seiko DSC6200R calorimeter with the heating and cooling rate of ±5°C min<sup>-1</sup> at Tokyo Institute of Technology, Japan.

### 2.1 Synthesis of 2-(4-hydroxyphenyl)benzothiazole (1)

It was prepared according to the reported method [32].

### 2.2. Synthesis of 2-(4-(*n*-bromoalkoxy)phenyl)benzothiazole (2a-2e)

They were prepared according to the reported method [32].

### 2.3 Synthesis of *N*-(4-hydroxybenzylidene)-4-substituted-anilines (3a, 3b)

They were prepared according to the reported method [33].

### 2.4. Synthesis of *N*-(4-(*n*-(4-(benzothiazol-2yl)phenoxy)alkoxy)benzylidene)-4-substituted-anilines 4a-j (PBTH-*n*-X)

To a solution of **2a-2e** (0.84 mmol) in 20 mL DMF, K<sub>2</sub>CO<sub>3</sub> (0.7g, 5 mmol) was added and the solution was stirred for 30 min. **3a** or **3b** (0.7 mmol) in 30 ml acetone, in the presence of a catalytic amount of potassium iodide, was then added dropwise to this solution. The resulting mixture was heated with stirring under nitrogen atmosphere for 24 h. The reaction mixture was poured into ice-water (60 ml) to afford products as a white coloured solid of **PBTH-*n*-X**. Elemental analysis, IR and <sup>1</sup>H-NMR

data for **4a-j (PBTH-*n*-X)** are summarized as follows:

**PBTH-4-Br:** Yield: 73 %. Elemental analysis: Calculated for C<sub>30</sub>H<sub>25</sub>BrN<sub>2</sub>O<sub>2</sub>S (557.50): C,

64.63; H, 4.52; N, 5.02 %. Found: C, 64.43; H, 4.35; N, 4.97 %. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2936-

2854 (C-H aliphatic), 1622 (C=N), 1608 (C=N, thiazole), 1253 (C-O). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 2.02-2.10 (m, 4H, CH<sub>2</sub>), 4.11-4.19 (m, 4H, -OCH<sub>2</sub>), 6.98-7.03 (m, 4H, Ar-H),

7.10 (d, 2H, Ar-H), 7.39 (t, 1H, Ar-H), 7.47-7.52 (m, 3H, Ar-H), 7.85 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.01-8.09 (m, 3H, Ar-H), 8.36 (s, 1H, CH=N).

**PBTH-6-Br:** Yield: 77 %. Elemental analysis: Calculated for C<sub>32</sub>H<sub>29</sub>BrN<sub>2</sub>O<sub>2</sub>S (585.55): C,

65.64; H, 4.99; N, 4.78 %. Found: C, 65.76; H, 5.08; N, 4.82 %. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2935-

2852 (C-H aliphatic), 1620 (C=N), 1605 (C=N, thiazole), 1255 (C-O). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 1.52-1.60 (m, 4H, CH<sub>2</sub>), 1.84-1.92 (m, 4H, CH<sub>2</sub>), 4.05-4.10 (m, 4H, -OCH<sub>2</sub>),

6.97-7.04 (m, 4H, Ar-H), 7.09 (d, 2H, Ar-H), 7.38 (t, 1H, Ar-H), 7.46-7.53 (m, 3H, Ar-H), 7.84 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.02-8.07 (m, 3H, Ar-H), 8.36 (s, 1H, CH=N).

**PBTH-8-Br:** Yield: 75 %. Elemental analysis: Calculated for C<sub>34</sub>H<sub>33</sub>BrN<sub>2</sub>O<sub>2</sub>S (613.61): C,

66.55; H, 5.42; N, 4.57 %. Found: C, 66.39; H, 5.28; N, 4.49 %. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2938-

2847 (C-H aliphatic), 1623 (C=N), 1608 (C=N, thiazole), 1251 (C-O). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 1.35-1.58 (m, 8H, CH<sub>2</sub>), 1.80-1.90 (m, 4H, CH<sub>2</sub>), 4.02-4.09 (m, 4H, -OCH<sub>2</sub>),

6.97-7.02 (m, 4H, Ar-H), 7.00 (d, 2H, Ar-H), 7.39 (t, 1H, Ar-H), 7.48-7.51 (m, 3H, Ar-H),

7.84 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.00-8.08 (m, 3H, Ar-H), 8.36 (s, 1H, CH=N)

**PBTH-10-Br:** Yield: 72 %. Elemental analysis: Calculated for C<sub>36</sub>H<sub>37</sub>BrN<sub>2</sub>O<sub>2</sub>S (641.66): C,

67.39; H, 5.81; N, 4.37 %. Found: C, 67.30; H, 5.97; N, 4.29 %. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2935-

2851 (C-H aliphatic), 1620 (C=N), 1606 (C=N, thiazole), 1250 (C-O). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>) / ppm: 1.31-1.57 (m, 12H, CH<sub>2</sub>), 1.80-1.89 (m, 4H, CH<sub>2</sub>), 4.01-4.09 (m, 4H, -OCH<sub>2</sub>),

6.98-7.02 (m, 4H, Ar-H), 7.10 (d, 2H, Ar-H), 7.40 (t, 1H, Ar-H), 7.47.55 (m, 3H, Ar-H), 7.85 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.02-8.08 (m, 3H, Ar-H), 8.36 (s, 1H, CH=N).

**PBTH-12-Br:** Yield: 70 %. Elemental analysis: Calculated for C<sub>38</sub>H<sub>41</sub>BrN<sub>2</sub>O<sub>2</sub>S (669.71): C,

68.15; H, 6.17; N, 4.18 %. Found: C, 67.99; H, 6.20; N, 4.13 %. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2931-

2855 (C-H aliphatic), 1621 (C=N), 1606 (C=N, thiazole), 1252 (C-O). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 1.22-1.54 (m, 16H, CH<sub>2</sub>), 1.81-1.89 (m, 4H, CH<sub>2</sub>), 4.01-4.09 (m, 4H, -OCH<sub>2</sub>),

6.98-7.04 (m, 4H, Ar-H), 7.09 (d, 2H, Ar-H), 7.39 (t, 1H, Ar-H), 7.47-7.55 (m, 3H, Ar-H),

7.82 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.01-8.08 (m, 3H, Ar-H), 8.36 (s, 1H, CH=N).

**PBTH-4-OCH<sub>3</sub>:** Yield: 80 %. Elemental analysis: Calculated for C<sub>31</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>S (508.63): C,

73.20; H, 5.55; N, 5.51 %. Found: C, 73.31; H, 5.48; N, 5.62 %. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2935-

2852 (C-H aliphatic), 1626 (C=N), 1610 (C=N, thiazole), 1253 (C-O). <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 2.02-2.10 (m, 4H, CH<sub>2</sub>), ), 3.85 (s, 3H, -OCH<sub>3</sub>), 4.13-4.20 (m, 4H, -OCH<sub>2</sub>),

6.92-7.05 (m, 6H, Ar-H), 7.22 (d, 2H, Ar-H), 7.38 (t, 1H, Ar-H), 7.50 (t, 1H, Ar-H), 7.85 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.01-8.09 (m, 3H, Ar-H), 8.42 (s, 1H, CH=N).

**PBTH-6-OCH<sub>3</sub>:** Yield: 77 %. Elemental analysis: Calculated for C<sub>33</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>S (536.68): C,

73.85; H, 6.01; N, 5.22 %. Found: C, 74.02; H, 6.10; N, 5.30 %. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2934-

2851 (C-H aliphatic), 1623 (C=N), 1607 (C=N, thiazole), 1251 (C-O). <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 1.51-1.62 (m, 4H, CH<sub>2</sub>), 1.82-1.95 (m, 4H, CH<sub>2</sub>), 3.84 (s, 3H, -OCH<sub>3</sub>), 4.03-

4.10 (m, 4H, -OCH<sub>2</sub>), 6.90-7.05 (m, 6H, Ar-H), 7.21 (d, 2H, Ar-H), 7.39 (t, 1H, Ar-H), 7.50 (t, 1H, Ar-H), 7.81 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.00-8.09 (m, 3H, Ar-H), 8.41 (s, 1H, CH=N).

**PBTH-8-OCH<sub>3</sub>:** Yield: 74 %. Elemental analysis: Calculated for C<sub>35</sub>H<sub>36</sub>N<sub>2</sub>O<sub>3</sub>S (564.74): C,

74.44; H, 6.43; N, 4.96 %. Found: C, 74.29; H, 6.31; N, 5.01 %. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2938-

2849 (C-H aliphatic), 1621 (C=N), 1606 (C=N,

thiazole), 1250 (C-O).  $^1\text{H-NMR}$  (300MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 1.41-1.59 (m, 8H,  $\text{CH}_2$ ), 1.80-1.90 (m, 4H,  $\text{CH}_2$ ), 3.84 (s, 3H,  $-\text{OCH}_3$ ), 4.01-4.09 (m, 4H,  $-\text{OCH}_2$ ), 6.91-7.04 (m, 6H, Ar-H), 7.22 (d, 2H, Ar-H), 7.37 (t, 1H, Ar-H), 7.49 (t, 1H, Ar-H), 7.84 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.01-8.08 (m, 3H, Ar-H), 8.41 (s, 1H,  $\text{CH}=\text{N}$ ).

**PBTH-10-OCH<sub>3</sub>**: Yield: 87 %. Elemental analysis: Calculated for  $\text{C}_{37}\text{H}_{40}\text{N}_2\text{O}_3\text{S}$  (592.79): C,

74.97; H, 6.80; N, 4.73 %. Found: C, 75.03; H, 6.77; N, 4.68 %. IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2936-

2851 (C-H aliphatic), 1620 (C=N), 1606 (C=N, thiazole), 1248 (C-O).  $^1\text{H-NMR}$  (300MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 1.30-1.58 (m, 12H,  $\text{CH}_2$ ), 1.79-1.90 (m, 4H,  $\text{CH}_2$ ), 3.84 (s, 3H,  $-\text{OCH}_3$ ), 4.00-

4.10 (m, 4H,  $-\text{OCH}_2$ ), 6.90-7.02 (m, 6H, Ar-H), 7.21 (d, 2H, Ar-H), 7.40 (t, 1H, Ar-H), 7.50 (t, 1H, Ar-H), 7.82 (d, 2H, Ar-H), 7.69 (d, 1H, Ar-H), 8.00-8.10 (m, 3H, Ar-H), 8.41 (s, 1H,  $\text{CH}=\text{N}$ ).

**PBTH-12-OCH<sub>3</sub>**: Yield: 85 %. Elemental analysis: Calculated for  $\text{C}_{39}\text{H}_{44}\text{N}_2\text{O}_3\text{S}$  (620.84): C,

75.45; H, 7.14; N, 4.51 %. Found: C, 75.34; H, 7.05; N, 4.58 %. IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2939-

2852 (C-H aliphatic), 1623 (C=N), 1603 (C=N, thiazole), 1255 (C-O).  $^1\text{H-NMR}$  (300MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 1.28-1.52 (m, 16H,  $\text{CH}_2$ ), 1.80-1.90 (m, 4H,  $\text{CH}_2$ ), 3.85 (s, 3H,  $-\text{OCH}_3$ ), 4.09-

4.10 (m, 4H,  $-\text{OCH}_2$ ), 6.90-7.00 (m, 6H, Ar-H), 7.22 (d, 2H, Ar-H), 7.38 (t, 1H, Ar-H), 7.50 (t, 1H, Ar-H), 7.83 (d, 2H, Ar-H), 7.90 (d, 1H, Ar-H), 8.01-8.09 (m, 3H, Ar-H), 8.42 (s, 1H,  $\text{CH}=\text{N}$ ).

### 3. Results and Discussion

#### 3.1. Synthesis

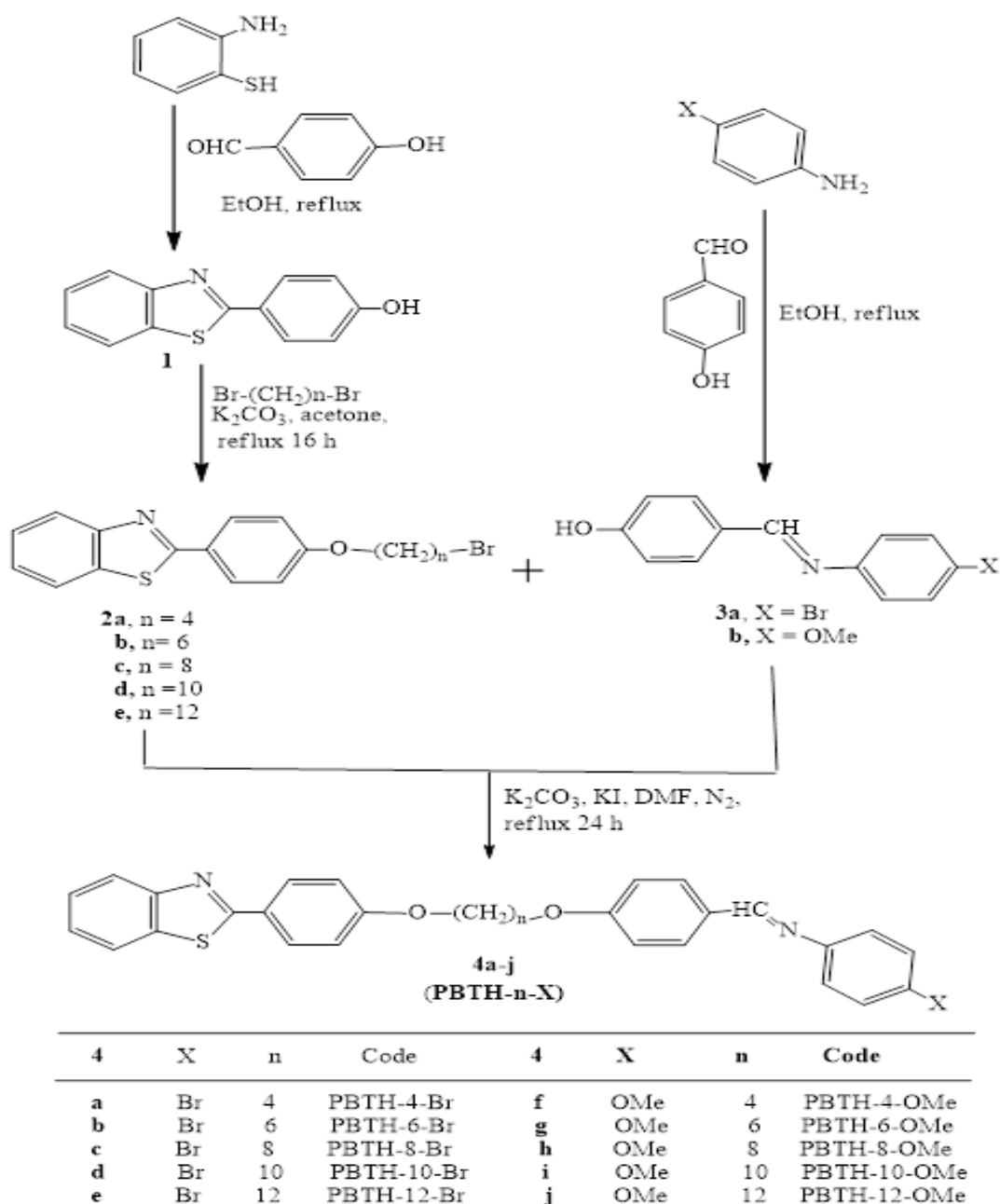
The synthetic routes toward the formation of intermediates **1**, **2a-2e**, **3a**, **3b** and the target compounds **4a-j** (coded by **PBTH-n-X**) are shown in Scheme 1. Thus, condensation of 2-aminothiophenol with 4-hydroxybenzaldehyde gave the Schiff base **1** which was reacted with equimolar ratios of some polymethene of terminal dibormide by refluxing in acetone containing anhydrous potassium carbonate afforded the bomoinated thioethers **2a-e**. Also, reaction of 4-hydroxybenzaldehyde with 4-bromo or 4-methoxyaniline produced the corresponding azomethine compounds **3a** or **3b** respectively.

Finally, condensation of compounds **2a-e** with **3a,b** produced the target compounds **4a-j** (coded by **PBTH-n-X** in this paper) (Scheme 1).

#### 3.2. Characterization

The percentages of C, H and N from the elemental analysis conform to the calculated values for all members in both series. From the FT-IR spectrum of compound **PBTH-10-Br**, the absorption bands at 2851-2935  $\text{cm}^{-1}$  are assigned to the C-H stretching of the decamethylene spacers. The azomethine group gives rise to a band with medium intensity at 1620  $\text{cm}^{-1}$ . The absorption band at 1606  $\text{cm}^{-1}$  can be attributed to thiazole C=N. The strongest band is observed in the fingerprint region of 1248-1251  $\text{cm}^{-1}$  which can be attributed to the presence of two ether ( $\text{O-CH}_2$ ) groups in each dimeric structure. All the remaining compounds from both series of **PBTH-n-X** (where X = Br and  $\text{OCH}_3$ ) exhibit similar characteristic bands as discussed for **PBTH-10-Br**.

From the  $^1\text{H-NMR}$  data for compound **PBTH-10-Br**, it shows a multiplet attributed to the decamethylene protons of  $\text{O-CH}_2\text{-CH}_2\text{-(CH}_2\text{)}_6\text{-CH}_2\text{-CH}_2\text{-O-}$  at  $\delta = 1.31\text{-}1.57$  ppm whilst the resonances in relation to two other methylene protons in the same spacer ( $-\text{O-CH}_2\text{-CH}_2\text{-(CH}_2\text{)}_6\text{-CH}_2\text{-CH}_2\text{-O-}$ ) appear as multiplets at  $\delta = 1.80\text{-}1.89$  ppm. Two overlapping triplets at  $\delta = 4.01\text{-}4.09$  ppm attributed to the remaining two methylene protons adjacent to the O atom in the fragment of  $-\text{O-CH}_2\text{-CH}_2\text{-(CH}_2\text{)}_6\text{-CH}_2\text{-CH}_2\text{-O-}$ . The fact that two overlapping triplets are observed instead of one triplet suggests that the molecule is non-symmetric. Sixteen aromatic protons are observed within the chemical shift range of 6.98-8.08 ppm. The singlet arising from the azomethine proton was observed at  $\delta = 8.36$  ppm. In terms of splitting and chemical shift, the spectra of compounds **PBTH-n-X** are almost similar to that of compound **PBTH-10-Br**. However, it is important to note that in the spectra of compounds **PBTH-n-OCH<sub>3</sub>**, an additional singlet is observed at  $\delta = 3.84$  ppm which can be ascribed to the presence of methoxy group.



**Scheme 1.** Synthetic route toward the formation of compounds **4a-j (PBTH-n-X)**

### 3.3. The thermal and optical properties

Phase transition temperatures and corresponding enthalpy changes for both series of **PBTH-n-Br** and **PBTH-n-OCH<sub>3</sub>** obtained from the DSC analysis are listed in Table 1. Table 1 shows the absence of any relation and influence between the different substituents on the transition temperature for series **PBTH-n-Br** and **PBTH-n-OCH<sub>3</sub>**. It can clearly be inferred from Table 1 that each of the members in **PBTH-n-Br** and **PBTH-n-**

**OCH<sub>3</sub>** exhibit enantiotropic liquid crystal phases. All the dimers **PBTH-n-Br** containing Br exhibit nematic (N) phase in which the members with longer methylene chain (**PBTH-8-Br**, **PBTH-10-Br** and **PBTH-12-Br**) also show SmA phases. The results suggest explicitly that the emergence of SmA phase occurs at lower temperature in comparison to the N phase owing to the higher order in the former case [34, 35]. However, the present study shows that for all the **PBTH-n-OCH<sub>3</sub>** members in which the substituent is methoxy (OCH<sub>3</sub>) only nematic phase

is observed under the polarized light.

The representative DSC thermogram for compound **PBTH-10-Br** (Figure 1(a)) shows distinctively three endotherms indicative of Cr-SmA, SmA-N and N-I transitions upon heating and vice-versa when the similar compound is cooled down from isotropic phase. Similar characteristics as inferred from DSC support the phase sequence of Cr-SmA-N-I for this series except **PBTH-10-OCH<sub>3</sub>** of which the presence of enantiotropic SmA phase is only observable under polarizing microscope.

The enantiotropic nematic phases in **PBTH-*n*-OCH<sub>3</sub>** series can well be substantiated by the phase transition detectable by DSC except **PBTH-10-OCH<sub>3</sub>** in which the nematogenic behaviour can only be observed by polarizing microscope. This phenomenon can be resulted from very small endothermic energy as observed previously for non-symmetric dimer [9]. The representative DSC thermograms for **PBTH-6-OCH<sub>3</sub>** upon heating and cooling cycles are shown in Figure 1(b) which is characteristic of enantiotropic nematic phase [36].

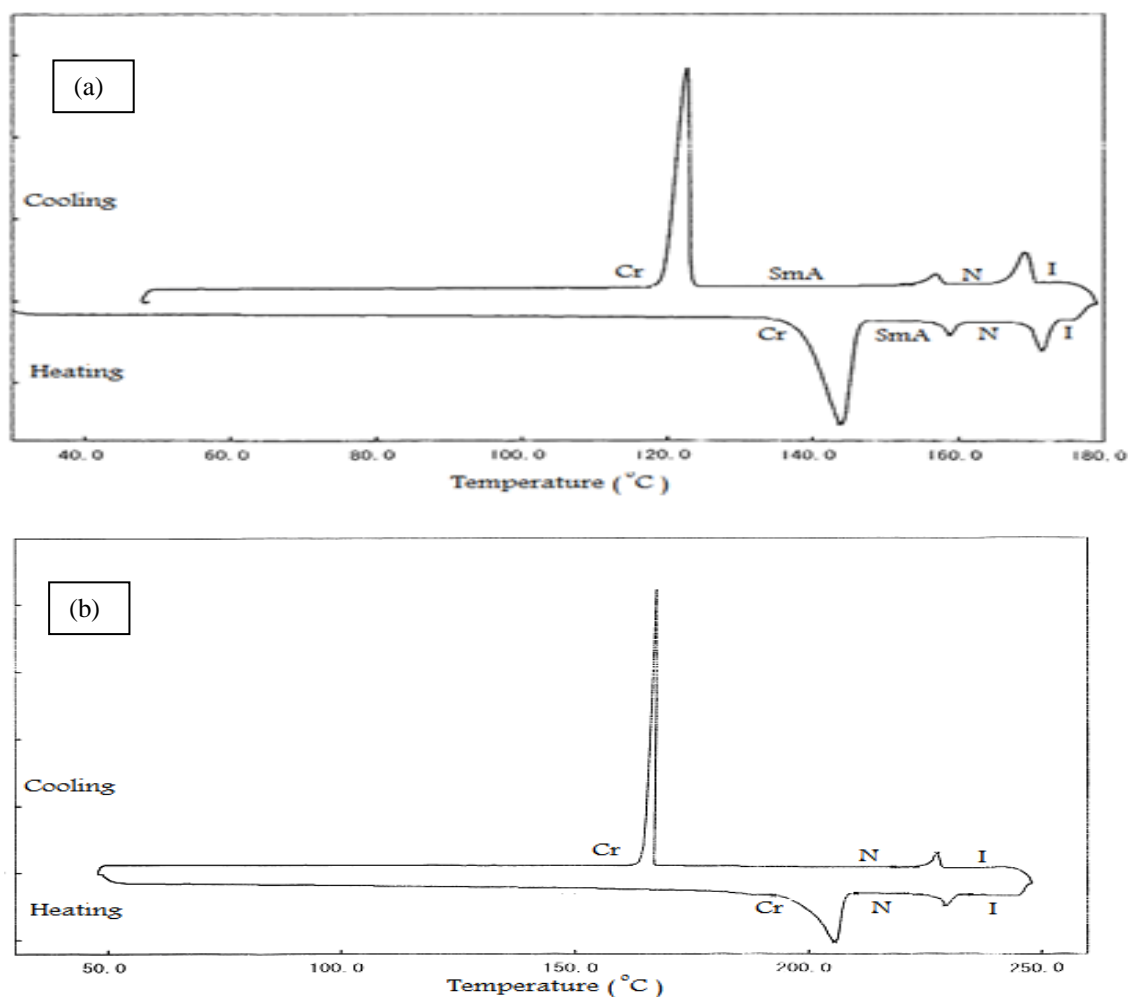
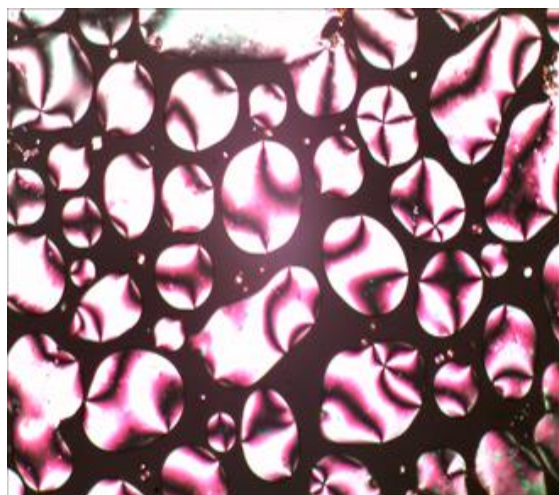


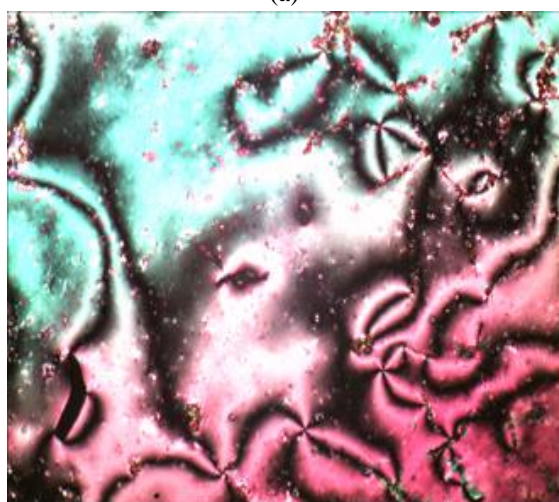
Figure 1. The DSC traces of (a) **PBTH-10-Br** and (b) **PBTH-6-OCH<sub>3</sub>** on heating and cooling cycles at the rate of  $\pm 5^\circ\text{C min}^{-1}$

Observation by polarizing optical microscopy has further substantiated that all the compounds show enantiotropic nematic phase. The representative optical photomicrographs of compound **PBTH-6-OCH<sub>3</sub>** is illustrated in Figure 2. On cooling from the isotropic phase, nematic droplets (Figure 2a) are seen

forming and gradually fused together to form the Schlieren defects with twofold and fourfold brushes (Figure 2b). Further evidence in relation to the nematic phase in **PBTH-6-OCH<sub>3</sub>** can also be derived exclusively from the fact that it appears to have high mobility with flashes when this compound is subjected to mechanical stress [37].



(a)



(b)

Figure 2. Optical photomicrographs of **PBTH-6-OCH<sub>3</sub>** upon cooling from isotropic liquid; (a) nematic droplets coalesce at 195.8°C and (b) texture of Schlieren defects with twofold and fourfold brushes at 196.9°C.

It is also an undeniable fact that all the observed liquid crystalline textures in **PBTH-*n*-Br** and **PBTH-*n*-OCH<sub>3</sub>** can be concluded through comparison with those reported in the literature [38]. In compounds **PBTH-*n*-Br**, the SmA phase for higher members ( $n= 8, 10$  and  $12$ ) can be identified on the basis of its fan-shaped textures as reported previously for liquid crystals including symmetric liquid crystal dimers [39]. A representative photomicrograph of compound **PBTH-8-Br** is depicted in Figure 3 for clarity.

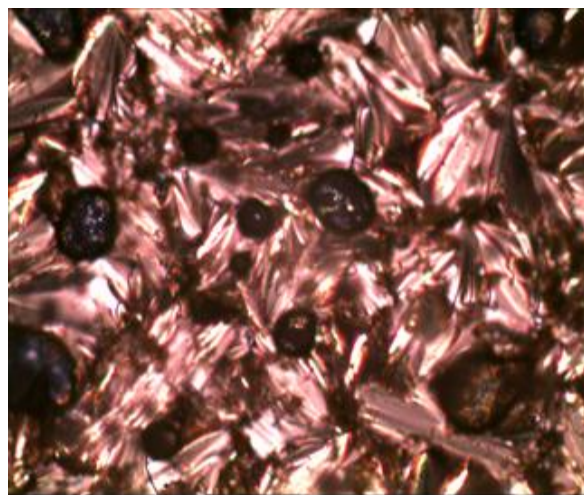


Figure 3. Optical photomicrograph of **PBTH-8-Br** exhibiting fan-shaped textures of SmA phase at 163.6°C.

### 3.4. Effect of the spacer length and substituent on mesogenic properties

The correlations between the phase transition temperatures and the number of methylene units ( $n$ ) in **PBTH-*n*-Br** and **PBTH-*n*-OCH<sub>3</sub>** series are shown in Figures 4 and 5, respectively. In general, the clearing temperatures in both series of **PBTH-*n*-Br** and **PBTH-*n*-OCH<sub>3</sub>** exhibit a descending trend as the spacer length is increased. This can probably be due to the flexibility of spacer leading to the dilution of mesogenic cores [40].

For both series of **PBTH-*n*-Br** and **PBTH-*n*-OCH<sub>3</sub>**, the addition of more methylene units seems to result in the decrease of the N phase temperature range (Table 1). Apart from this, the domains associated with the smectic phase appear in the series of **PBTH-*n*-Br** when the lengths of the spacer increase from **PBTH-8-Br** to **PBTH-12-Br**.

It is also important to note that in the series of **PBTH-*n*-OCH<sub>3</sub>** which possess the methoxy group as substituent along the long molecular axis, all the members exhibit nematogenic properties only (Table 1). This phenomenon can probably be attributed to the steric hindrance effect of the OCH<sub>3</sub> group, which is greater than that of Br group. Moreover, the presence of the more electronic delocalization –OCH<sub>3</sub> group as seen in series **PBTH-*n*-OCH<sub>3</sub>** compared to the Br group at the same position in **PBTH-*n*-Br** series, which has prevented the layered molecular arrangement and hence explains the absence of smectogenic properties in

PBTH-*n*-OCH<sub>3</sub> series.

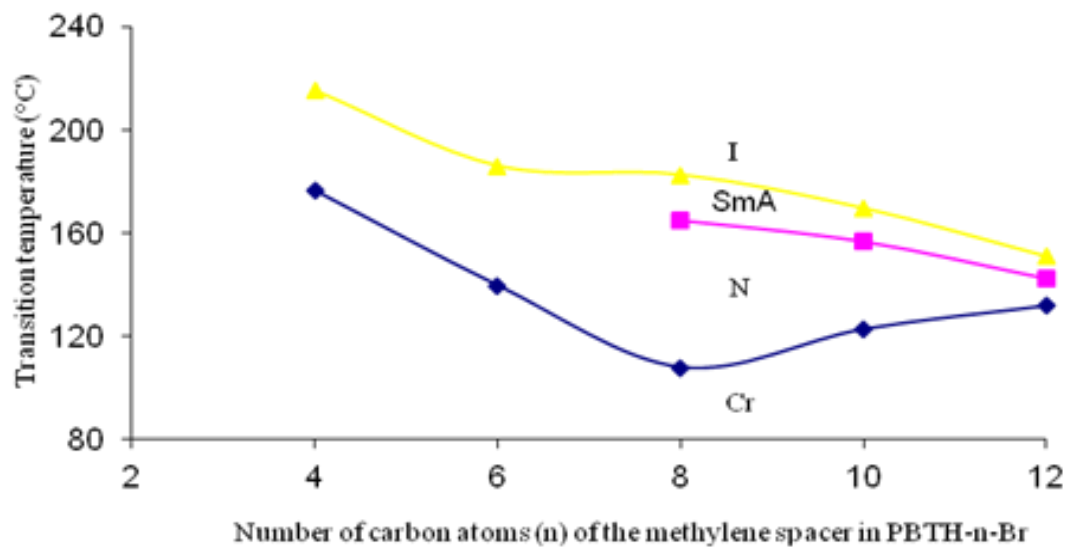


Figure 4. Plot of transition temperatures (T) versus the carbon number (n) of the methylene spacer in PBTH-*n*-Br.

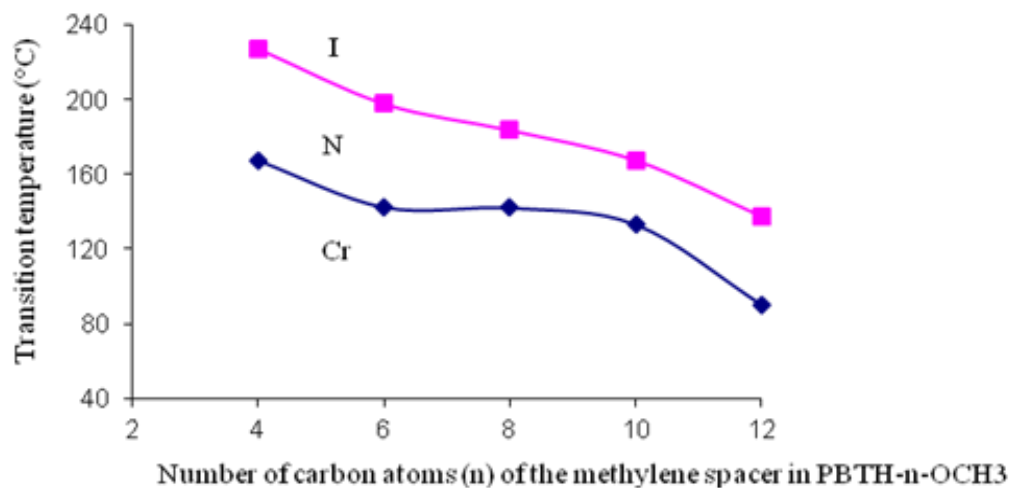


Figure 5. Plot of transition temperatures (T) versus the carbon (n) of the methylene spacer in PBTH-*n*-OCH<sub>3</sub>.



Table 1. Transition temperatures ( $^{\circ}\text{C}$ ) and associated enthalpies ( $\text{KJ mol}^{-1}$ ) for compounds **PBTH-*n*-X** upon heating and cooling.

Compound	Phase sequence with transition temperatures, $^{\circ}\text{C}$ ( $\Delta\text{H}$ , $\text{KJ mol}^{-1}$ )
<b>PBTH-4-Br</b>	Cr 198.3(26.09) N 216.6(2.85) I I 214.9(4.38) N 176.5(28.09) Cr
<b>PBTH-6-Br</b>	Cr 170.9(38.78) N 186.2(5.63) I I 185.8(5.40) N 139.6(39.23) Cr
<b>PBTH-8-Br</b>	Cr 152.6(25.49) SmA 167.8(1.45) N 184.6 (4.04) I I 182.4(4.42) N 165.0(1.44) SmA 107.8 (14.95) Cr
<b>PBTH-10-Br</b>	Cr 143.7(54.86) SmA 158.7(2.89) N 171.5 (7.17) I I 169.4(7.60) N 156.8(2.85) SmA 122.6 (52.53) Cr
<b>PBTH-12-Br</b>	Cr 150.5(39.01) N 156.0(1.02) I I 150.7(5.38) N 142.4(4.67) SmA 131.7(36.45) Cr
<b>PBTH-4-OCH<sub>3</sub></b>	Cr 205.5(36.25) N 228.9(4.33) I I 227.2(4.04) N 167.5(43.80) Cr
<b>PBTH-6-OCH<sub>3</sub></b>	Cr 192.9(52.77) N 200.1(3.49) I I 197.8(4.08) N 142.4(50.37) Cr
<b>PBTH-8-OCH<sub>3</sub></b>	Cr 173.4(44.84) N 185.3(3.94) I I 183.6(5.55) N 142.0(30.77) Cr
<b>PBTH-10-OCH<sub>3</sub></b>	Cr 176.6(78.02) I I 167.5(6.35) N 133.1(69.84) Cr
<b>PBTH-12-OCH<sub>3</sub></b>	Cr 116.3(32.74) N 145.0(3.21) I I 137.5(2.25) N 90.0(20.19) Cr

Cr = crystal; SmA = smectic A; N = nematic and I = isotropic

#### 4. Conclusions

Two series of novel non-symmetric liquid crystal dimers  $N$ -(4-(*n*-(4-(benzothiazol-2-yl)phenoxy)alkoxy)benzylidene)-4-bromoanilines

**PBTH-*n*-Br** and  $N$ -(4-(*n*-(4-(benzothiazol-2-yl)-phenoxy)alkoxy)benzylidene)-4-

methoxyanilines **PBTH-*n*-OCH<sub>3</sub>** were synthesized and characterized. The members with shorter methylene spacer in **PBTH-*n*-Br** (where *n*=4 and 6) are nematogenic but the compounds with the longer spacer lengths (**PBTH-8-Br**, **PBTH-10-Br** and **PBTH-12-Br**) show enantiotropic nematic and smectic phases. The present study also shows that the terminal substituent (Br or OCH<sub>3</sub>) affects the mesomorphic properties. The series with Br as terminal substituent favors the formation of the smectic phase; while the analogous compounds containing OCH<sub>3</sub> will only behave as nematogens. However, the clearing temperature for both series decreased when the lengths of spacer were increased.

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