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Synthesis and mesomorphic behaviours of a homologous series of 2-(4-alkyloxybenzylidenamino)benzothiazoles

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The synthesis and characterisation of a series of new rod-shaped liquid crystal (LC), 2-(4-alkyloxybenzylidenamino)benzothiazoles possessing even number of carbon atoms at the alkyloxy chain ($C_nH_{2n+1}O-$, $n = 2, 4, 6, 8, 10, 12, 14, 16, 18$) are reported. The molecular structures of title compounds were elucidated using FTIR and nuclear magnetic resonance spectroscopic techniques. The phase behaviour of these new compounds was characterised and studied by differential scanning calorimetry and polarising optical microscopy. Lower members ($n = 2, 4$ and 6) did not exhibit mesophase. Octyloxy derivative was monotropic LC. Enantiotropic smectic A phase was observed from n-decyloxy derivatives onward to the last homologous synthesised.

Keywords: 2-(4-alkyloxybenzylidenamino)benzothiazoles; Schiff bases; smectic A; liquid crystals; enantiotropic

1. Introduction

Liquid crystals (LCs) are fluid phases of matter where the constituent molecules are sufficiently disordered to be classified as a liquid, and generate flow properties, yet retain varying degrees of ordering depending on the actual type of LC phase. Hence, LCs are anisotropic fluid, where the unique combination of flow and molecular ordering confers some exciting optical, dielectric and visco-electric properties.[1] LCs have many useful applications in scientific and technological areas, in particular as display devices, organic light emitting diodes, anisotropic networks, photoconductors and semiconductor materials.[2–4] High demand of new LCs for applications has led to the preparation and study of numerous mesogens, in particular thermotropic LCs.[5,6]

Over many years, a large number of thermotropic LCs containing heterocyclic units have been synthesised. This research field has grown even more in recent years because of improvements in synthesised methodologies. The incorporation of heterocyclic moieties as core units in thermotropic LC can result in large changes in their mesophases and physical properties, because they possess more polarisable heteroatoms than carbon, such as nitrogen, oxygen and sulphur atoms.[7] Many mesogenic compounds containing heterocyclic ring such as pyridine, pyrimidine, furyl, thiazole, thiophene, oxadiazole, benzothiazole and benzothiadiazole have been reported in the literature.[8–19] Heterocyclic rings fused with benzene

rings are also becoming popular mesogenic cores to be incorporated into the molecular structure.

In our previous work, we have reported the mesomorphic (smectic A) properties of heterocyclic LCs, 2-(4-alkanoyloxybenzylideneamino)benzothiazoles.[20] In our continuing effort on finding new benzothiazole LCs, we modify the existing system by introducing alkyloxy ether chain instead of alkanoyloxy chain in the previous work. This paper describes the synthesis and mesomorphic properties of a new homologous series of 2-(4-alkyloxybenzylidenamino)benzothiazoles possessing an even number of carbon atoms at the alkyloxy chain ($C_nH_{2n+1}O-$, $n = 2$ to 18). FT-IR, 1H and ^{13}C nuclear magnetic resonance (NMR) and Electron ionisation mass spectrum (EI-MS) analyses were employed to elucidate the molecular structure of the title compounds whereas the LC properties were determined by differential scanning calorimeter (DSC) and polarising optical microscopy (POM) analyses. The mesomorphic behaviours of the homologous compounds are rationalised based on the varying lengths of the alkyl chain. In addition, the relationship between the molecular structure and LC properties is also discussed in this paper.

2. Experimental

2.1 Materials & instrumentals

2-Aminobenzothiazole, 4-hydroxybenzaldehyde, 1-bromoalkanes ($C_nH_{2n+1}Br$, $n = 2, 4, 6, 8, 10, 12,$

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14, 16 and 18) and potassium carbonate were purchased from Merck (Germany). All solvents and reagents were used without further purification.

EI-MS was recorded using a Finnigan MAT95XL-T mass spectrometer operating at 70 eV ionising energy. Samples were introduced using a direct inject system with a source temperature of 200°C. FT-IR data were acquired with a Perkin Elmer 2000-FTIR spectrophotometer in the frequency range of 4000–400 cm^{-1} with samples embedded in KBr pellets. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 using a Bruker Advance 300 MHz NMR Spectrometer with TMS as the internal standard. Thin-layer chromatography analyses were carried out using aluminium backed silica gel plates (Merck 60 F₂₅₄) and were examined under shortwave UV light.

2.2 LC study

The phase transition temperatures were measured using a Mettler Toledo DSC823 DSC at a scanning rate of 10°C min^{-1} . Liquid crystalline properties were investigated by POM using a Carl Zeiss Polarising Optical Microscope (POM) attached to a Linkam Hotstage. The texture of the compounds was observed using polarised light with crossed polarisers, the sample being prepared as a thin film sandwiched between a glass slide and a cover. A video camera (Video Master coomo20P) was installed on the polarising microscope and coupled to a video capture card (Video master coomo600), allowing real-time video capture and image saving. Mesophase identification was made by comparing the observed textures with the literature.[21,22]

The synthetic route of 2-(4-alkyloxybenzylidena-amino)benzothiazoles, nHBZT is illustrated in Figure 1. The intermediate and title compounds were prepared according to previously reported methods.[23,24]

2.2.1 Synthesis of 2-(4-hydroxybenzylidena-amino)benzothiazole (OHBZT)

Equal amounts (10 mmol) of 4-hydroxybenzaldehyde and 2-aminobenzothiazole, along with 30 mL of ethanol, were refluxed for 3 hours in the presence of acetic acid (two drops). The precipitate formed was separated by filtration. The yellow product was recrystallised with ethanol.

2.2.2 Synthesis of 2-(4-alkyloxybenzylidena-amino)benzothiazoles (nOBZT)

Firstly, OHBZT was dissolved in minimum amount of *N,N'*-dimethylformamide solution prior to the

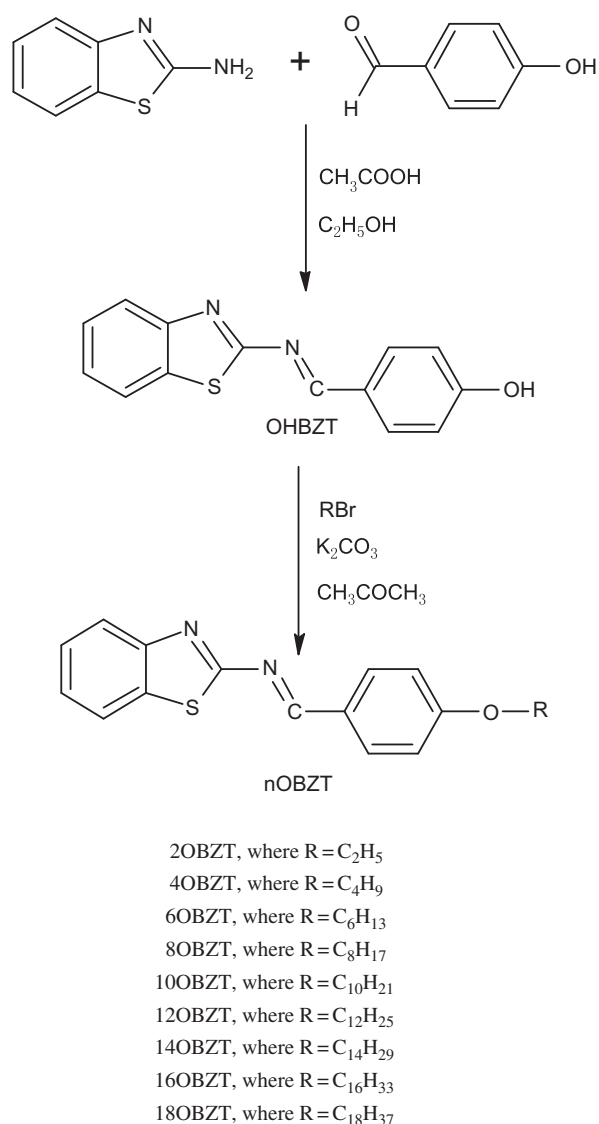


Figure 1. Synthetic route toward the formation of liquid crystal nOBZT.

addition of potassium carbonate anhydrous. A solution of appropriate 1-bromoalkanes in 40 mL acetone was added to the mixture and subsequently refluxed for 5 hours. The resulting mixture was left to cool at room temperature. The precipitate formed was then filtered off, dried and recrystallised from ethanol twice to yield the pure yellow solid. Percentage yields of all compounds are given as follows: 2OBZT (27%), 4OBZT (35%), 6OBZT (48%), 8OBZT (56%), 10OBZT (64%), 12OBZT (69%), 14OBZT (66%), 16OBZT (75%) and 18OBZT (78%). IR, NMR (^1H and ^{13}C) and mass spectral data of representative compound, 12OBZT, are summarised as follows:

12OBZT: EI-MS m/z (rel. int. %): 422.3 (91) [M^+], 253.0 (100). IR (KBr) ν_{max} cm^{-1} 3056

(C–H aromatic), 2918 and 2847 (C–H aliphatic), 1601 (C=N), 1255 (C–O ether). ^1H NMR (400 MHz, CDCl_3 , δ ppm): 0.90 (t, 3H, CH_3 -), 1.29 (m, 18H, $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{CH}_2\text{O}$ -), 1.84 (quint, 2H, $-\text{CH}_2\text{CH}_2\text{O}$ -), 4.06 (t, 2H, CH_2O -Ar-), 7.02 (d, 2H, Ar-H), 7.37 (d, 1H, Ar-H), 7.49 (t, 1H, Ar-H), 7.84 (t, 1H, Ar-H), 7.97 (d, 1H, Ar-H), 7.99 (d, 2H, Ar-H), 8.99 (s, 1H $-\text{N}=\text{CH}$ -). ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 172.34 (C=N thiazole), 165.37 (C=N), 163.63, 151.85, 134.47, 132.36, 127.50, 126.30, 124.77, 122.83, 121.60, 115.20 for aromatic and benzothiazole carbons, 68.41 (Ar- OCH_2 -), 31.91 (Ar- OCH_2CH_2 -), 29.64, 29.57, 29.54, 29.33, 29.10, 25.98, 22.67 for methylene carbons [$\text{CH}_3(\text{CH}_2)_9$], 14.09 (CH_3).

3. Results and discussion

Structural identification of nOBZT was carried out by employing a combination of spectroscopic techniques (FT-IR, ^1H & ^{13}C NMR and EI-MS). Molecular ion peak at m/z 422 suggested molecular formula of $\text{C}_{26}\text{H}_{34}\text{N}_2\text{OS}$, which supported the proposed structure of 12OBZT.

3.1 FTIR, ^1H NMR and ^{13}C NMR spectral studies

Based on FT-IR spectrum of 12HBZT, It is clearly shown that the terminal phenolic hydroxy group ($-\text{OH}$) attached at one end of the intermediate was substituted by alkyloxy long chain ($-\text{OC}_n\text{H}_{2n+1}$). The presence of these alkyl groups can be supported by the appearance of two strong bands at the frequencies of 2918 and 2847 cm^{-1} . The band with strong intensity observed at 1601 cm^{-1} can be assigned to the C=N bond of Schiff base. This absorption band overlapped with the band arising from the C=N of the benzothiazole ring, resulting in a sharp and strong absorption band.[20] A very strong band occurred at 1255 cm^{-1} can be ascribed to the stretching of ether, C–O–C bond.

In the ^1H NMR spectrum, two triplets at $\delta = 0.90$ ppm and $\delta = 4.06$ ppm were, respectively, ascribed to the methyl and methylene protons ($-\text{CH}_2\text{O}$ -Ar), while the multiplet at $\delta = 1.29$ ppm was assigned to the methylene protons of the long alkyl chain $\{-(\text{CH}_2)_9-$. The appearance of signals in between $\delta = 7.02$ –7.99 ppm are owing to the exhibition of benzothiazole and aromatic protons. The singlet observed at the most downfield region, $\delta = 8.99$ ppm, supported the presence of the imine linking group.[25] The molecular structure of 12HBZT was further verified using ^{13}C NMR spectroscopy. The peak at $\delta = 14.09$ ppm was attributed to the methyl carbon while the peaks between $\delta = 22.67$ –68.41 ppm represented the methylene

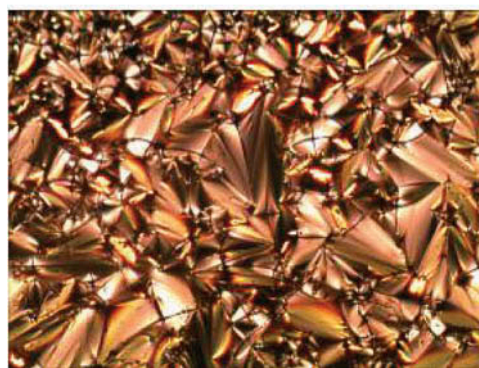
carbons of the long alkyl chain. Ten aromatic and benzothiazole carbons are resonated between $\delta = 115.20$ –163.63 ppm. The peaks at $\delta = 172.34$ and 165.37 ppm confirmed the presence of the C=N of thiazole ring and Schiff base group in the molecule.

3.2 Mesomorphic properties

nOBZT exhibited interesting thermotropic properties and its melting behaviour was carefully monitored by POM during both heating and cooling scans. Optical photomicrographs of 8OBZT and 14OBZT are shown in Figure 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 summarised in Table 1. Phase identification was based on the optical textures, and the magnitude of isotropisation on enthalpies is consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus,[26] and Gray and Goodby.[27]



(a)



(b)

Figure 2. (colour online) Optical photomicrograph of 8OBZT exhibiting fan-shaped textures of SmA phase. (b) Optical photomicrograph of 14OBZT displaying fan-shaped textures of SmA phase.

Table 1. Transition temperatures and associated enthalpy changes of nOBZT upon heating and cooling scans.

Compound	Melting point (°C)	Transition temperature (°C) (ΔH , kJ mol ⁻¹)	Heating
			Cooling
2OBZT	85.0	Cr 85.0 (26.23) I Cr 20.3 (16.78) I	
4OBZT	86.5	Cr 86.5 (24.29) I Cr 56.5 (19.98) I	
6OBZT	90.7	Cr ₁ 74.2 (1.10) Cr ₂ 90.7 (41.74) I Cr 61.2 (32.83) I	
8OBZT	79.6	Cr 79.6 (46.75) I Cr 58.7 (32.74) SmA 76.3 (6.74) I	
10OBZT	82.5	Cr 82.5 (35.80) SmA 84.6 (5.60) I Cr 38.4 (22.94) SmA 80.6 (6.16) I	
12OBZT	81.9	Cr 81.9 (45.42) SmA 90.1 (7.60) I Cr 46.3 (36.84) SmA 86.1 (7.79) I	
14OBZT	77.7	Cr 77.7 (45.60) SmA 91.9 (8.85) I Cr 47.6 (36.09) SmA 89.0 (8.60) I	
16OBZT	84.7	Cr 84.7 (48.08) SmA 90.8 (6.28) I Cr 61.3 (43.91) SmA 87.8 (9.89) I	
18OBZT	83.8	Cr 83.8 (37.79) SmA 90.4 (5.57) I Cr 61.2 (51.72) SmA 87.4 (9.87) I	

Note: Cr = Crystal; SmA = smectic A; I = Isotropic.

Under POM, *bâtonnets* textures of a smectic A (SmA) phase were observed during the cooling cycle. When further cooled, the *bâtonnets* coalesced to produce fan-shaped textures (Figure 2a and 2b). This phase is identified as a SmA phase.

3.3 Influence of Alkyl chain length on mesomorphic properties

Representative DSC thermograms for 8OBZT and 16OBZT upon heating and cooling scans are depicted in Figure 3. A plot of the transition temperatures against the number of carbons in the alkyloxy chain during the heating cycle is shown in Figure 4.

Based on the plot, it can be deduced that mesomorphic behaviour of nOBZT was greatly influenced by length of the terminal alkyloxy chain. Out of the nine compounds, the first three members ($n = 2, 4$ and 6) did not possess mesomorphic properties. These molecules with short alkyloxy chains are too rigid and therefore have high melting points, thus impeding their LC properties.[28] Once the length of the terminal chain is increased, the molecule becomes more flexible, hence promoting a monotropic (less stable) mesophase in a particular compound. Therefore, member with $n = 8$ is monotropic smectogen whereby mesophase (SmA) was only observed during the cooling scan. In monotropic mesogens, the melting points were always equal to or higher than the clearing points, hence exhibiting supercooling properties. It can therefore be proposed that in order to generate

the smectic phase in the analogous substituted 2-(benzylidenamino)benzothiazole, the number of carbons in the alkyloxy chain ($C_nH_{2n+1}O-$) must be at least 8 ($n \geq 8$). In addition, the formation of smectic A phase can be driven by molecular inhomogeneity wherein the mesogenic groups and the alkyl chains form chemical distinct regions (separate microdomains). The difference in the strengths of the various interactions between these regions should, therefore, give rise to microphase separation and hence a smectic molecular arrangement.[29]

Further lengthening of the alkyloxy chain from $n = 10$ to $n = 18$ (medium to high members) has led to the formation of enantiotropic (more stable) SmA mesophase during both heating and cooling processes. This is due to enhancement of flexibility resulted by longer terminal alkyloxy, which contributed to the suitable balancing of rigidity and flexibility of these compounds and subsequently promoted the exhibition of enantiotropic smectic A phase.[30]

It has been reported that melting point within a homologous series varies depending on molecular mass wherein the molecule with a lower mass possesses a lower melting point in comparison to a member with a higher mass.[31] Melting point increases when polarisability of the compounds within the same series increases. However, the current trend was not in accordance with this common rule. Whilst the highest melting point of this series is attributed to 6OBZT (90.7°C), the lowest melting point is due to 14OBZT (77.7°C).

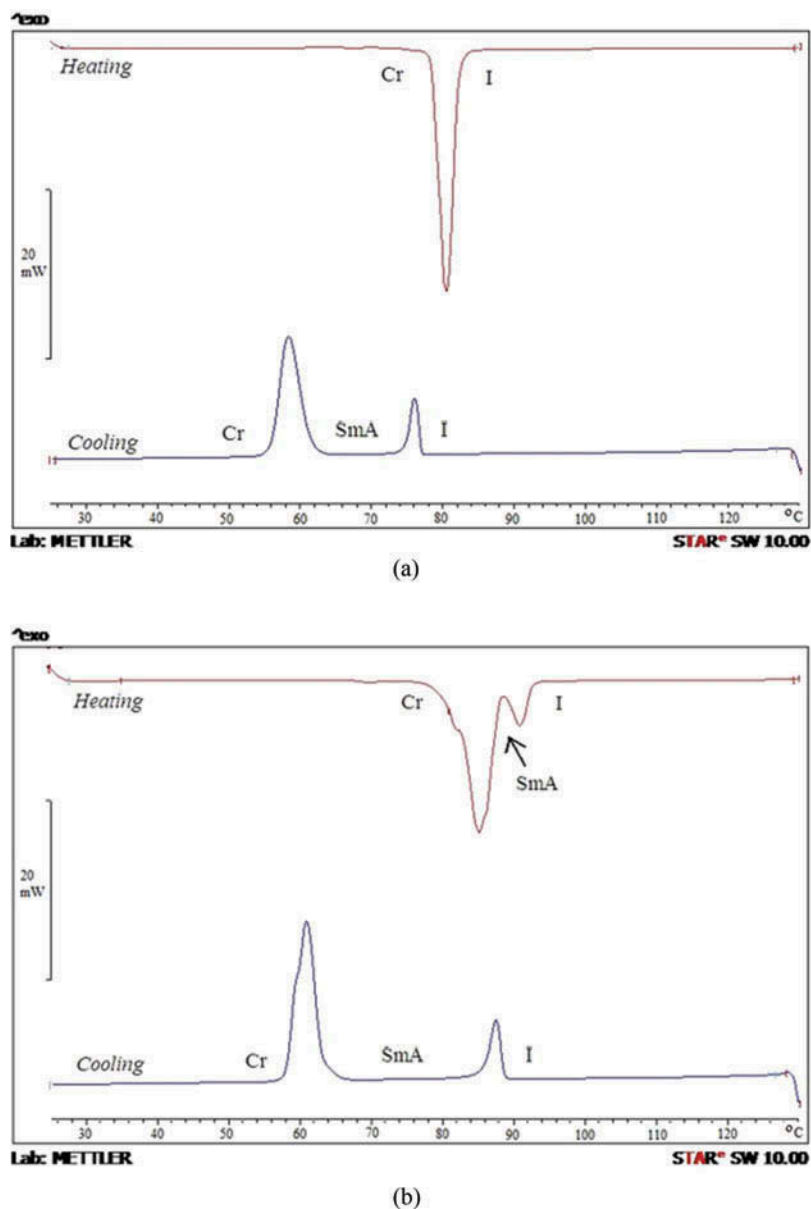


Figure 3. (colour online) DSC thermograms of (a) 8OBZT and (b) 16OBZT during heating and cooling scans.

According to the plot (Figure 4), the SmA-to-I transition temperatures started to increase from the members with $n = 8$ to $n = 14$ and then it is followed a descending order when moving from $n = 16$ to $n = 18$. The shape of the SmA-to-I transition temperature curve is a typical pattern for a low clearing point series.[32] The sharp rise of the initial curve may be attributed to the pronounced effect on the molecules with increasing alkyl chain length.[33] The terminal intermolecular attractions play a role in determining the SmA-I transition temperatures, i.e., the destruction of the smectic molecular order is determined by the fact that the terminal attractions become weaker, allowing partial interpenetration of the layers to occur

more easily as the alkyloxy chains grow longer ($n = 16$ to $n = 18$), in turn depressing the SmA-to-I transition temperatures.[34,35] It is important to point out that the enthalpy change of SmA-I for 16OBZT and 18OBZT during heating cycle is smaller than the respective enthalpy values in the cooling cycle. This could be due to the small difference between transition temperature of Cr-SmA and SmA-I, which led to overlapped peaks in the heating cycle. Among all the members, tetradecyloxy derivative is the most stable LC because it has the widest SmA phase range ($\Delta\text{SmA} = 14.2^\circ\text{C}$). Therefore, compromise in chain length is required for low melting point (14OBZT) and wide phase range (14OBZT),

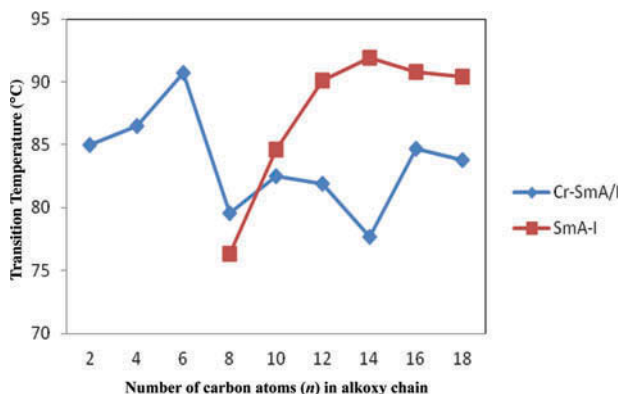


Figure 4. (colour online) Plot of transition temperature against number of carbon atoms (n) in alkoxy chain of n OBZT.

which is in agreement with those reported for alkylcyanobiphenyl homologues.[31]

3.4 Structure–mesomorphic property relationships

Molecular structure of organic compounds and their liquid crystalline properties are closely related. Table 2 shows the comparison of transition temperatures, mesophase range and molecular structures of the representative compounds 12OBZT with other structurally related compounds A,[35] B,[36] C,[37] D,[38] E,[20] F,[20] and G,[39] reported in the literatures. Reference to molecular structure indicates that all compounds have different substituents at the sixth position of benzothiazole moiety except for compound D having naphthalene fragment. Compound 12OBZT did not possess a terminal lateral group, whereas compound A has nitro group at the sixth position of the benzothiazole moiety. The higher smectic thermal stability of compound A could be due to the greater polarisability of the nitro group compared to the hydrogen atom, which is responsible for the higher transition temperatures and greater mesophase range.[40] Gray has explained that the dipole moment is an important factor as far as relative thermal stability of smectic phase is concerned, and the size effect is not prominent in such cases.[34]

The smectic phase range and thermal stability (refer to clearing point, T_C) of compound B are higher by 83.8 and 81.9°C compared to compound 12OBZT. These may be due to the presence of the more polar chloro substituent at the sixth position in compound B compared to the less polar hydrogen substituent at the same position in compound 12OBZT.[40] Polar chloro group increases the molecular polarisability of compound B compared to 12OBZT.

Compound C exhibited smectic C and nematic phases. A layered smectic order is favoured, which is

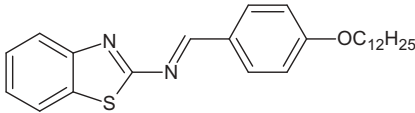
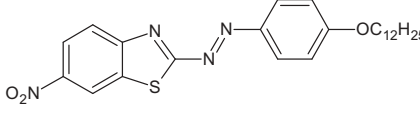
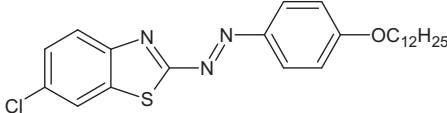
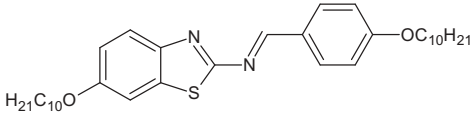
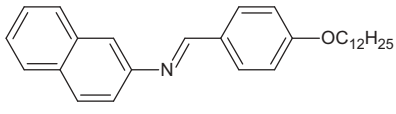
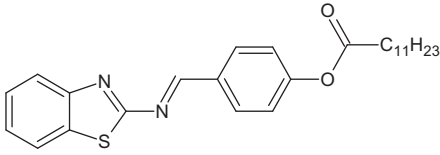
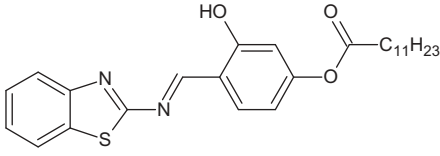
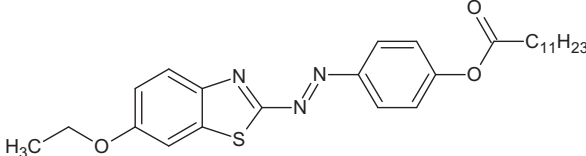
fully compatible with a molecular arrangement resulting from the intermolecular hydrogen bonding that develops in the tilt direction and thus stabilises the tilt of the smectic C phase.[37] The alkoxy chain ($-\text{OC}_{10}\text{H}_{21}$) at the sixth position of benzothiazole moiety has also caused the smectic phase range and thermal stability of compound C to be higher by 32.1 and 32.6°C, respectively, than 12OBZT. Decyloxy chain at the sixth position of benzothiazole moiety tends to encourage the intermolecular interactions and gives rise to a tilted arrangement of the molecule in the smectic layers.[37]

Table 2 shows that compound D exhibited monotropic SmA and nematic phases. Reference to molecular structure shows that compound D and 12OBZT differ only at the core system. Core system for 12OBZT is benzothiazole ring while compound D consists of naphthalene core group. The presence of benzothiazole ring increases the overall polarisability of the molecule (12OBZT) while lowering the symmetry of the molecule (12OBZT) as compared to phenyl/naphthyl derivatives. Therefore, benzothiazole LCs (12OBZT) exhibit higher transition temperatures than naphthalene LCs (compound D).[40]

Difference in the linking groups (ether group in 12OBZT and ester group in compound E) between the phenyl ring and the alkyl chain can also cause change in the mesomorphic properties. The ether linking group provides greater linearity to molecules rather than the ester group, thus resulting in the wider phase range of SmA phase being observed in 12OBZT ($\Delta\text{SmA} = 8.2^\circ\text{C}$) when compared to compound E ($\Delta\text{SmA} = 4.8^\circ\text{C}$). In addition, 12OBZT possessed higher thermal stability ($T_C = 90.1^\circ\text{C}$) compared to compound E ($T_C = 85.6^\circ\text{C}$). This indicated that the ether linkage is more conducive to mesomorphism than the ester linkage. Similar behaviour was also reported when comparing the properties of 4-alkoxybenzylidene-4'-bromoanilines (ether derivatives) and 4-alkanoyloxybenzylidene-4'-bromoanilines (ester derivatives).[41,42] It is interesting to note that a different trend is seen for the clearing temperatures of two series of dimer LCs wherein the general trend is the ester-linked materials $\{\alpha,\omega\text{-bis}(4\text{-cyanobiphenyl-4'-yl})\text{alkanedioates}\}$ possessed high clearing points than the ether-linked materials $\{\alpha,\omega\text{-bis}(4,4'\text{-cyanobiphenyloxy})\text{alkanes}\}$. [43] This could be due to the difference in molecular geometry between low molar mass mesogens (present compounds) and non-conventional dimer LCs.

Incorporation of substituent at the lateral position shows strong influence on mesomorphic properties. Non-mesogenic compound F had an extra hydroxyl group at the lateral (*ortho*) position compared to mesogenic 12OBZT. The *ortho*-hydroxyl group exerts

Table 2. Comparison of mesomorphic behaviour of 12OBZT with structurally related compounds.

Compound	Molecular structure and phase transition (°C)	Mesophase range (°C)	
		Sm	N
12OBZT (Present study)	 <p>Cr 81.9 SmA 90.1 I</p>	8.2	-
Compound A [26]	 <p>Cr 156.0 SmA 194.0 I</p>	38.0	-
Compound B [27]	 <p>Cr 80.0 SmA 172.0 I</p>	92.0	-
Compound C [28]	 <p>Cr 81.3 SmC 121.6 N 122.7 I</p>	40.3	1.1
Compound D [29]	 <p>Cr (76.0) SmA (79.0) N 92.0 I</p>	3.0	13.0
Compound E [18]	 <p>Cr 80.8 SmA 85.6 I</p>	4.8	-
Compound F [18]	 <p>Cr 99.9 I</p>	-	-
Compound G [30]	 <p>Cr 106.5 N 132.5 I</p>	-	26

Note: () Monotropic phase transition.

a molecular broadening influence, reducing the lateral intermolecular force of attraction and thus impeding LC formation in compound F.[44] Compound with the *ortho*-hydroxyl group (compound F; $T_C = 99.9^\circ\text{C}$) possesses higher clearing temperature than compound without the *ortho*-hydroxyl group (12OBZT; $T_C = 90.1^\circ\text{C}$). There are also compounds in which the lateral substituents are shielded, so that they are less effective in molecular broadening.[45] Compound F may give rise to shielding effects owing to the presence of intramolecular association [46] and hence the polarisability along the long axis of molecule will be larger in such compounds than in unsubstituted analogue.[47] This results in higher clearing temperatures than the corresponding compound without an *ortho*-hydroxy group.

The main structural differences between 12OBZT and compound G are at the linking group and the lateral substituent. Lateral ethoxyl group at the sixth position of benzothiazole moiety has caused the mesophase range and thermal stability of compound G to become higher by 17.8°C and 42.4°C , respectively, than 12OBZT. This trend is supported by our earlier observation in this work whereby lateral substituents ($-\text{NO}_2$, $-\text{Cl}$, $-\text{OC}_{10}\text{H}_{21}$) in compounds A, B and C also showed higher mesophase range and thermal stability than compound without lateral substituent, 12OBZT. Another reason for the differing anisotropic properties between 12OBZT and compound G is the variation in dipole moment. It has been well known that the $\text{C}=\text{N}$ group is more polar than the $\text{N}=\text{N}$ moiety due to the presence of the effective charge between C and N while the dipole moment for the azo group is zero.[48] This has also been concurred by Gray that the dipole moment is an important factor as far as the relative thermal stability of the smectic phase is concerned.[34] The greater dipole moment led to enhanced polarisability and increase in intermolecular cohesive forces. Hence, it helps stabilise the smectic phase in 12OBZT but not for compound G since it only exhibited the nematic phase.

Existence of nematic behaviour in compounds C, D and G is rather surprising. This may imply that the unsubstituted compounds are forming anti-parallel molecular dimer arrangement, which would further stabilise interdigitated structures in 12OBZT and compound E. The smectic phase in compounds C, D and G may belong to monolayer smectic phase and this increases the possibility of exhibiting a nematic phase in these compounds. Another notable feature is the slight difference of SmA-to-I transition temperatures between 12OBZT and compound E may be dipolar in origin, especially if it appeared as the interdigitated phase.

4. Conclusion

In this paper, we report a homologous series of 2-(4-alkyloxybenzylideneamino)benzothiazoles (*n*HBZT). The short-chain derivatives ($n = 2, 4$ and 6) are non-mesogenic compounds. Smectic A phase started to emerge from *n*-octyloxy derivative as the monotropic mesophase and the remaining compounds ($n = 10, 12, 14, 16$ and 18) exhibited a smectic A phase until the last derivative of the series. Comparison of the present series with other structurally related compounds revealed that benzothiazole is a good building block for LCs.

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