



Original article

New mesomorphic benzothiazol derivatives: Synthesis and characterization

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ABSTRACT

In this paper, the synthesis of new mesomorphic benzothiazolyl derivatives, 6-ethoxy-2-[4-(4-alkyloxybenzoyloxy)benzylideneamino]benzothiazoles, is presented. The structures of the title compounds were elucidated using spectroscopic techniques, such as FT-IR, NMR (¹H and ¹³C), elemental analysis and EI-MS. The mesomorphic behaviours of these compounds were determined by differential scanning calorimetric and polarizing optical microscopic techniques. Compounds exhibited nematic and tilted smectic phases upon heating from crystal phase. An obvious odd-even effect was observed in this homologous series.

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1. Introduction

The electronic conducting behaviours of liquid crystals (LCs) have received tremendous attention since the discovery of high hole mobility in the hexagonal columnar phase of hexapenthyloxy-triphenylene [1–5]. Recently, calamitic LCs became another potential material for applications in electronic devices due to the presence of some ordered mesophases, such as SmA, SmC, SmB and SmE. The two-dimensional (2D) arrangement (layers) in smectics is more tolerant with regard to defects than the one-dimensional (1D) ordered discotic columns, thus resulting in an improved performance [6]. The electronic conducting behaviour of calamitic LCs was first examined in the SmA phase of 2-phenylbenzothiazole derivatives. Existence of a layer(ed) structure in all smectic LCs induces π - π stacking interactions which can facilitate the hopping of charge carrier mobility [7–9].

In our previous studies, we successfully synthesized and isolated a series of homologues of smectic LCs containing the benzothiazole moiety [10–13]. Incorporation of benzothiazole ring into calamitic LCs, as the mesogenic core, enabled them to easily exhibit mesophase transitions due to the more polarizable nature

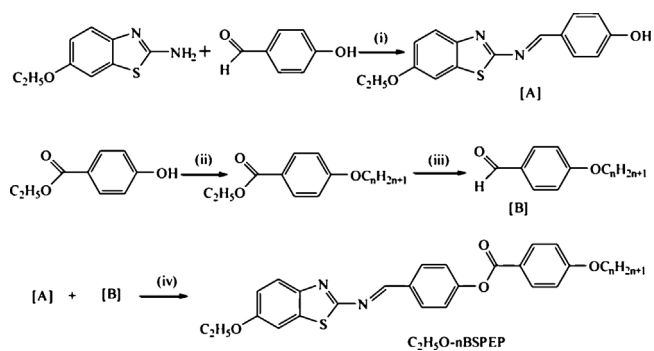
of the heteroatoms, sulfur and nitrogen [14]. In this paper, we report another new homologous series of benzothiazole liquid crystals (Scheme 1). Three core units (one benzothiazole and two phenyl rings) were connected via a Schiff base and ester linkers which can increase the molecular broadness and anisotropy.

2. Experimental

The synthetic protocol towards (producing/creating) the title compounds, 6-ethoxy-2-[4-(4-alkyloxybenzoyloxy)benzylideneamino]-benzothiazoles (C₂H₅O-nBSPEP, where n = 7, 8, 9, 10, 12, 14) is illustrated in Scheme 1. 2-Amino-6-ethoxybenzothiazole was condensed with 4-hydroxybenzaldehyde upon refluxing in ethanol for 3 h to yield intermediate A [11]. Etherification of ethyl-4-hydroxybenzoate in acetone with the appropriate 1-bromoalkane and acidification using concentrated HCl produced intermediate B [15]. Intermediates A and B were then subjected to Steglich esterification with the appropriate fatty acid in the presence of DCC and DMAP according to previously reported procedures [16] to yield title compounds C₂H₅O-nBSPEP. All the crude products were purified by repeated recrystallization using ethanol until constant melting points were obtained. The yields of the final products were between 29% and 55% (Scheme 1). Structural elucidation of the title compounds was carried out via elemental analysis, FT-IR, NMR, and EI-MS spectroscopic techniques [17].

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Scheme 1. Synthetic route for the target compounds. (i) EtOH, (ii) $C_nH_{2n+1}Br$, K_2CO_3 , CH_3COCH_3 , (iii) $H_2O:EtOH$ (1:1), KOH, conc. HCl, (iv) DCC, DMAP, DCM, DMF. Yield of C_2H_5O -7BSPEP (29%), C_2H_5O -8BSPEP (33%), C_2H_5O -9BSPEP (37%), C_2H_5O -10BSPEP (41%), C_2H_5O -12BSPEP (48%), and C_2H_5O -14BSPEP (55%).

3. Results and discussion

The liquid crystalline textures of the title compounds were observed by polarizing optical microscope and phase identification was made by comparing the observed textures with those reported in the literature [18,19].

Transition temperatures and corresponding enthalpy changes were determined using a differential scanning calorimeter and the data tabulated in Table 1.

Referring to Table 1, all synthesized compounds exhibited both liquid crystal phase and nematic phase. A higher ordered SmC phase emerged from dodecyloxy derivatives, which contain a relatively longer flexible chain. Due to the thermally unstable

Table 1
Phase transition and transition enthalpy changes for C_2H_5O -nBSPEP upon heating.

Compound	Phase transition, °C (corresponding enthalpy changes, kJ/mol)
C_2H_5O -7BSPEP	Cr ₁ 68.0 (9.1) Cr ₂ 126.9 (40.9) N 256.2 (2.1) I
C_2H_5O -8BSPEP	Cr 137.8 (38.8) N 248.5 (2.3) I
C_2H_5O -9BSPEP	Cr 124.8 (42.3) N 250.6 (1.5) I
C_2H_5O -10BSPEP	Cr 138.3 (44.4) N 250.2 (1.9) I
C_2H_5O -12BSPEP	Cr 91.0 (51.2) SmC 158.5 (0.5) N 223.2 (1.7) I
C_2H_5O -14BSPEP	Cr ₁ 69.9 (24.1) Cr ₂ 96.9 (26.3) SmC 172.1 (0.4) N 223.6 (1.6)

Cr₁, crystal 1; Cr₂, crystal 2; N, nematic; SmC, smectic C; I, isotropic.

properties of these compounds, all the transition temperatures can be only obtained from the heating cycle in DSC analysis. This is due to the partial decomposition of the compounds during heating, a phenomenon also reported in the work of Wei *et al.* [20].

Representative optical photomicrographs of C_2H_5O -12BSPEP are shown in Fig. 1. The presence of the nematic phases in C_2H_5O -12BSPEP is evidenced by a typical marble-like texture upon cooling the compound from the isotropic liquid phase. Upon further cooling the nematic phase to a lower temperature, a higher ordered SmC phase formed and exhibited the transition bar textures which in turn confirmed the conversion from the nematic to the SmC phase (Fig. 1b) [21].

A plot of transition temperatures against the number of carbons in the alkoxy chain during the heating cycle is shown in Fig. 2. Firstly, it is evident that both melting (Cr-SmC/N) and clearing (N-I) points were greatly influenced by the length of alkoxy chain in the compounds. The fluctuation of melting and clearing points observed in C7 to C10 compounds was due to the odd–even

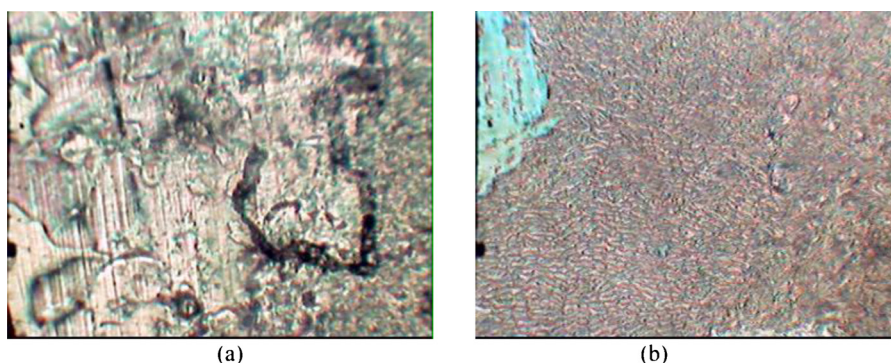


Fig. 1. Optical photomicrographs (100×) of (a) nematic phase showing marble-like texture and (b) SmC phase exhibiting typical transition bar texture in C_2H_5O -12BSPEP.

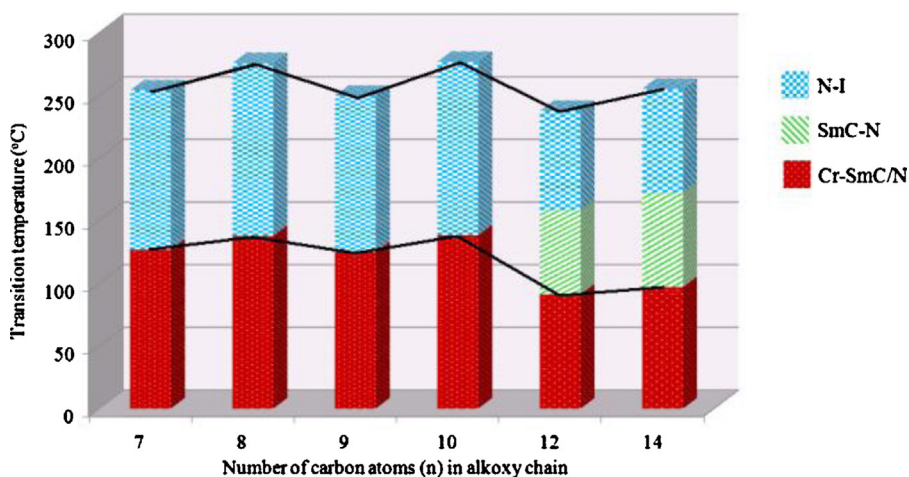


Fig. 2. Phase behaviour of C_2H_5O -nBSPEP.

effect. The odd–even effect can be explained by the fact that the extra carbon causes the chain to deviate from the linear structure, and this deviation from the linearity of the structure causes a reduced melting or clearing point. This fluctuation was commonly investigated for short chain derivatives in a homologous series [22–25]. Secondly, a higher ordered SmC phase was observed only in the homologues with relatively longer chain members, C12 and C14 in this case. It can be understood that a longer terminal alkoxy chain may favour the lamellar arrangement in the smectic layer structure due to higher Van der Waals interactions and the possibilities of intertwining between alkoxy chains. Lastly, the nematic phase range (Δ_N) was reduced and the SmC phase range (Δ_{SmA}) was increased as the chain length increased. The increasing Van der Waals attractive forces provide stronger lateral attractive interactions, which in turn, resulted in formation of layer packing.

4. Conclusion

Conclusively, all the synthesized compounds exhibited liquid crystal behaviour in which nematic and SmC phases were observed. The length of the terminal alkoxy chain greatly affects properties, such as melting and clearing temperatures, and liquid crystal phase ranges. In our future work, molecular modifications on this homologous series will be planned in order to yield liquid crystal compounds with high thermal stability.

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