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## Heterocyclic benzoxazole-based liquid crystals: Synthesis and mesomorphic properties

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## Abstract

New Schiff base liquid crystals containing benzoxazole core and alkanoyloxy chain at the end group of the molecules  $(C_{n-1}H_{2n-1}COO-, n = 14, 16, 18)$  was synthesized. The present compounds are enantiotropic smectic A liquid crystals. It was also found that the end groups of the molecules and polar chloro substituent at the benzoxazole fragment had effect on the mesomorphic properties.

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Interest in the study of mesomorphic heterocycles has dramatically increased in the recent years due to their wider range of structural templates, as well as their optical and photochemical properties [1–3]. These heterocyclic structures generally incorporated unsaturated atoms, such as, O, N, S and/or others, and the presence of such electronegative atoms often resulted in a reduced symmetry for the overall molecules; and a stronger polar induction [1]. In addition, heterocyclic ring fused with benzene ring has also become popular mesogenic core in liquid crystal research. Examples of heterocyclic fused-ring derivatives are benzothiazole [4], benzopyran-4-one [5] and benzothiadiazole [6]. Materials with lower melting temperatures, potential candidates for further applications, are often generated by such compounds.

Benzoxazole, another kind of heterocyclic fused-ring system, have been studied in a variety of research areas, including non-linear optics, organic light-emitting diodes and polymeric materials. However, examples of benzoxazole-based liquid crystals are relatively rare [7] and some of them are polymer liquid crystals [8–12]. Therefore, in the search of new benzoxazole liquid crystals, we describe here mesomorphic properties of 5-chloro-2-(4-alkanoyloxybenzylidenamino)benzoxazoles. The synthetic route is illustrated in Scheme 1. 2-Amino-5-

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Scheme 1. Synthetic route for the target compounds. (i)  $CH_2Cl_2$  (ii)  $C_{n-1}H_{2n-1}COOH$ , DCC, DMAP,  $CH_2Cl_2$ , DMF.

chlorobenzoxazole and 4-hydroxybenzaldehyde were coupled by reflux in dichloromethane for 24 h, following which the Schiff base intermediate was subjected to Steglich esterification with the appropriate fatty acids in the presence of DCC and DMAP [12]. The crude products were purified upon repeated recrystallization using ethanol and their structures were elucidated *via* FT-IR, NMR and EI-MS spectroscopic techniques [13].

The liquid crystalline textures of the products were observed under a polarizing optical microscope equipped with a Linkam hotstage and temperature regulator. Phase identification was made by comparing the observed textures with those reported in the literature [14,15]. Transition temperatures and enthalpy changes were determined using a differential scanning calorimeter. The results are summarized in Table 1.

All synthesized compounds showed two endotherms in the DSC thermograms (Fig. 1) which can be attributed to the isotropic-mesophase and mesophase-crystal transitions. From Table 1, it is clearly noticed that the target

Phase transition and transition enthalpy changes for Cl-n-BZX upon heating and cooling.

Compound	Phase transition, $^{\circ}C$ (corresponding enthalpy changes, kJ mol <sup>-1</sup> )
Cl-14-BZX	Heating: Cr 105.9 (47.4) SmA 143.0 (8.9) I
	Cooling: Cr 67.7 (51.1) SmA 134.9 (7.0) I
Cl-16-BZX	Heating: Cr 108.5 (47.1) SmA 136.7 (7.7) I
	Cooling: Cr 74.0 (46.7) SmA 125.4 (2.8) I
Cl-18-BZX	Heating: Cr 109.1 (44.9) SmA 130.3 (5.7) I
	Cooling: Cr 75.2 (43.4) SmA 118.9 (1.7) I

Cr, crystal; SmA, smectic A; I, isotropic. Value in the bracket is enthalpy change.



Fig. 1. DSC thermogram of Cl-16-BZX during heating and cooling cycles.

Table 1



Fig. 2. Liquid crystal textures of Cl-14-BZX upon cooling. The filament textures (at 132  $^{\circ}$ C) (a) coalesced to form focal-conic fan texture of smectic A phase in (b) (at 97  $^{\circ}$ C).

compounds showing enantiotropic properties as the mesophase were observed during heating and cooling cycles [16]. Upon cooling of the isotropic liquid, compound Cl-14-BZX exhibited filament textures which coalesce to form a focal-conic fan texture on further cooling. Fig. 2a shows the filament growth pattern appearing below the isotropic. During this growth process, the filaments buckle quasi-continuously and eventually coalesce to focal-conic domains of smectic A phase (Fig. 2b). The characteristics of filament texture is similar to that reported for N,N'-bis[(2-hydroxy-4-alkoxyphenyl)methylene]benzene-1,4-diamine and N-[4-(4-n-alkanoyloxybenzoyloxy)benzylidene]-4-cyanoaniline [17].

Linking group is one of the factors influencing the target compounds in exhibiting the smectic phase instead of a nematic phase. The ester linking group favour the lamellar packing due to the dipole–dipole interaction which ultimately generated the smectic phase. Then, a conjugative interaction over the entire molecule is better achieved between the polar (chloro) substituent and benzoxazole, and led to smectic property in Cl-*n*-BZX. This suggests that polar terminal substituent has substantial effect on influencing certain phase.

Smectic-isotropic transition (clearing) temperatures exhibited ascending trend as length of alkanoyloxy chain increased from *n*-tetradecanoyloxy to *n*-octadecanoyloxy. It was attributed to the increasing *van der Waals* forces between the alkyl chains [18]. However, the clearing temperature descended with the increase in the length of the carbon chain due to the dilution of the mesogenic core resulting from the flexibility provided by the terminal alkanoyloxy chain [19]. Decrement of phase range { $\Delta$ SmA: 37 °C (C14)  $\rightarrow$  28 °C (C16)  $\rightarrow$  21 °C (C18)} was noticed as the chain length keeps increasing. Certain extent of flexibility is essential for promoting liquid crystal phase [20,21]. However, further increasing of the carbon chain of compound (from C14 to C16) will cause the molecule to be too flexible, hence, reducing the stability of mesophase (in term of phase range) [22,23].

In conclusion, all the target compounds exhibited enantiotropic smectic A phase. The length of the terminal alkanoyloxy chain (end molecule) affects the melting, clearing temperatures and phase ranges. The ester linking group and the polar (chloro) substituent at the benzothiazole moiety were among the factors influencing the formation of the smectic phase in the target compounds [24].

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