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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.

Keywords: Schiff bases; Benzoxazoles; Mesomorphic; Smectic A; Structure–property relationship

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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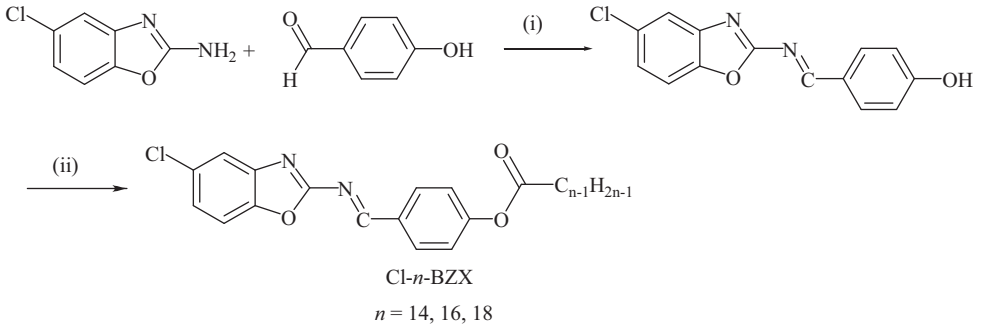

Cl-*n*-BZX

$n = 14, 16, 18$

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

Table 1
Phase transition and transition enthalpy changes for Cl-*n*-BZX upon heating and cooling.

Compound	Phase transition, °C (corresponding enthalpy changes, kJ mol^{-1})
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.

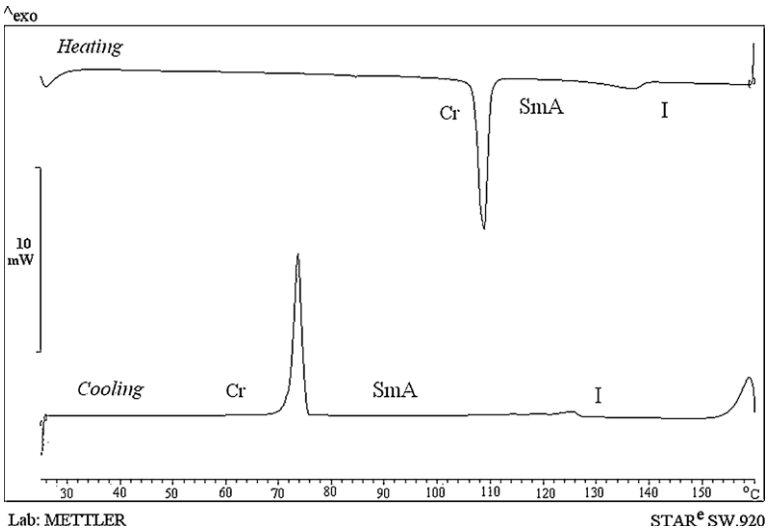

Fig. 1. DSC thermogram of Cl-16-BZX during heating and cooling cycles.