New Heterocyclic Liquid Crystals with Benzothiazole Core

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Abstract
The design and synthesis of new calamitic benzothiazole-based liquid crystals, 2-[4-(4-alkyloxybenzoyloxy)phenyl]benzothiazoles, are presented. The target compound was characterized using spectroscopic techniques, such as IR, NMR (^{1}H & ^{13}C), microanalysis and EI-MS. The liquid crystalline behaviours of these compounds were thoroughly examined by differential scanning calorimetry and optical polarizing microscope techniques. These materials exhibited enantiotropic nematic phase with high thermal stability (> 168 ^{o}C). Smectic A phase starts to emerge as monotropic (metastable) phase from the C10 member and changes into enantiotropic (stable) phase from the C12 and persists up to C16 members.

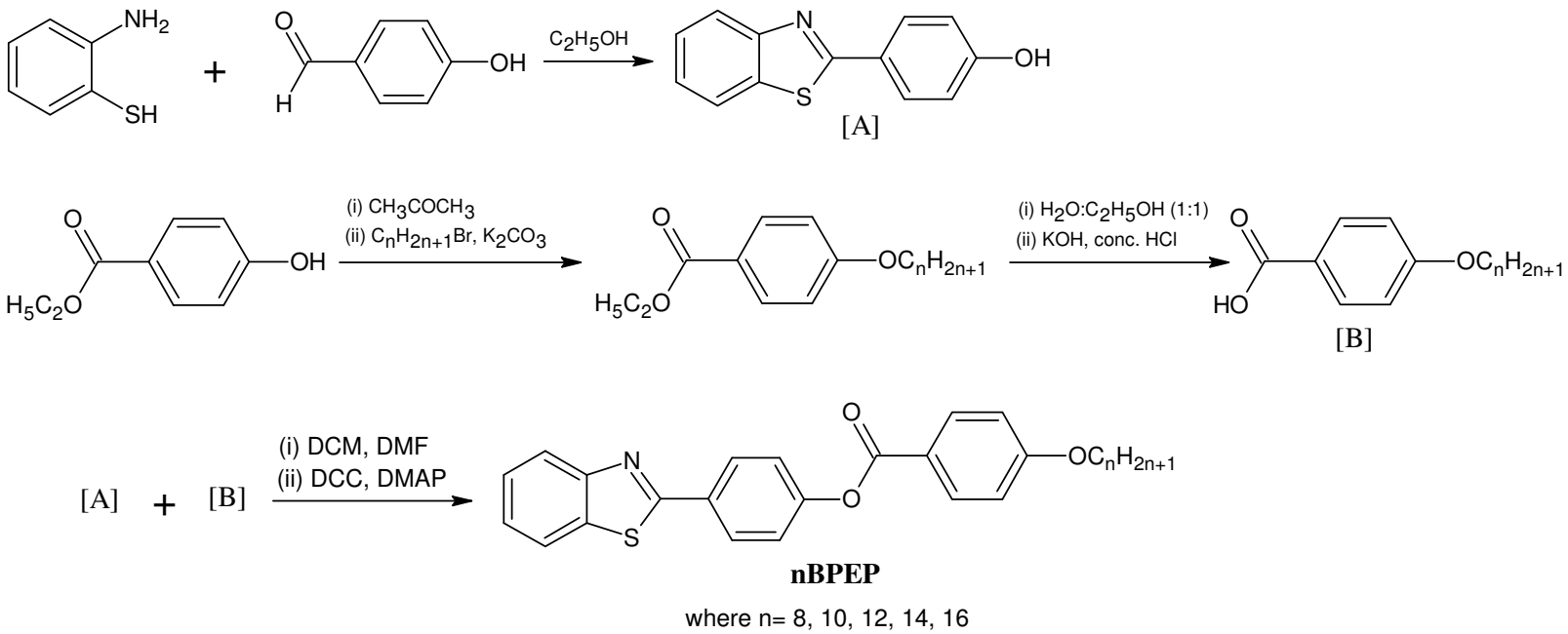
Keywords: benzothiazole, nematic, smectic, enantiotropic

Introduction
Liquid crystals (LCs) have gained additional attention as a new type of organic semiconductor exhibiting self-organization [1]. In the 1970's, the electrical properties of LCs was one of the major interests in the studies, as a result, the electrical properties of different calamitic LCs have been examined [2,3]. An important interest, however, still remains to be explored in calamitic mesophase due to their different degrees of molecular order and arrangement. As for calamitic LCs, the electronic conduction was first established in the SmA phase of a 2-phenylbenzothiazole derivatives [4,5].

In our previous studies on LCs [6,7], we found that rod-like molecules incorporated with benzothiazole core ring enabled them to exhibit mesophase easily. Here, we designed and synthesized a homologues series of compounds according to Synthetic Scheme. The heterocyclic benzothiazole ring containing electron-rich sulfur atom was used to induce a smectic phase. Three core unit (one benzothiazole and two phenyl rings) was coupled together in order to enhance the π stacking within the smectic layer structures. An ester linkage that connected two phenyl rings increases the anisotropy polarizability which in turned strengthen the mesomorphic properties.

Results and Discussion
The liquid crystalline textures of the title compounds were observed under optical polarizing microscope and phase identification was made by comparing the observed textures with those reported in the literature [8,9].

Synthetic Scheme

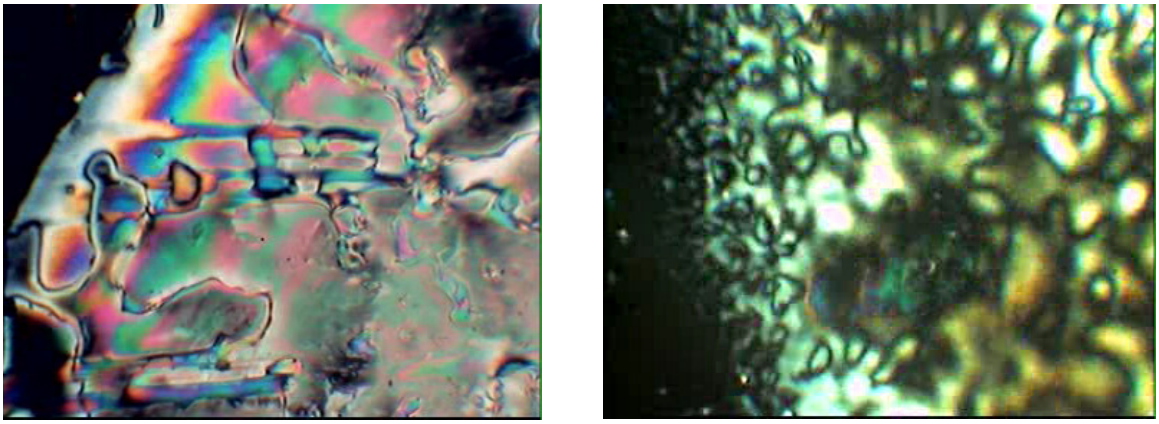


nBPEP

where n= 8, 10, 12, 14, 16

The occurrence of nematic phases in **8BPEP** was evidenced by observation of *Schlieren* texture of nematic phase. As a representative case of nematic phase, the photomicrograph of **8BPEP** is illustrated in Figure 1(a). Upon cooling the isotropic liquid, the appearance of colorful birefringence domains was noted. Representative optical photomicrograph of **16BPEP** is depicted in Figure 1(b) and Figure 2. By cooling the isotropic liquid phase, *Schlieren* texture showing a network of black brushed connecting centers of point and line defects, Figure 1(b), was observed. On further cooling the nematic phase, more ordered SmA phase was observed at lower temperature, Figure 2. The co-existence of the homogeneous (fan-shaped texture) and homeotropic (dark area) textures confirmed the presence of SmA [10].

A plot of transition temperatures against the number of carbons in the alkoxy chain during the heating cycle is shown in Figure 3. Based on the plot, both melting (Cr-SmA/N) and clearing (N-I) point showed a descending trends as the length of the carbon chain increased. The flexible terminal alkoxy chain acts as a diluent to the mesogenic core ring system, hence, depressed both melting and clearing temperature of compounds **nBPEP** [11]. As can be seen from the graph, the length of alkoxy chain also influenced the types of mesophase formed. All the compounds exhibited enantiotropic nematic phase and smectogenic properties commenced as the chain length increased. Furthermore, the nematic phase range (ΔN) is reduced and the SmA phase range (ΔSmA) is increased as the alkoxy chain lengthen. The increasing van der Waals forces tend to stabilize the SmA phase by favouring the lamellar packing, on the other hand, suppressed the nematic phase range.



(a) (b)

Figure 1: Optical photomicrograph (100x) of (a) nematic phase in **8BPEP** and (b) nematic phase in **16BPEP**.

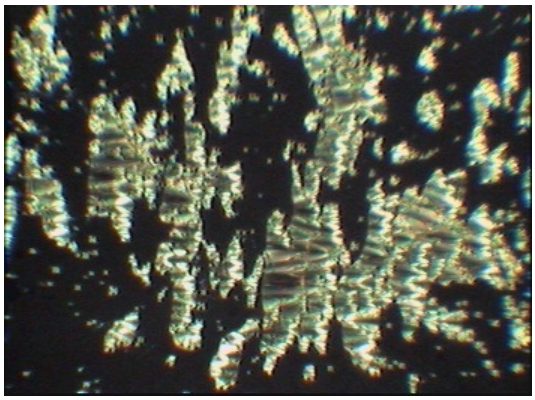


Figure 2: Optical photomicrograph (100x) of SmA phase in **16BPEP**.

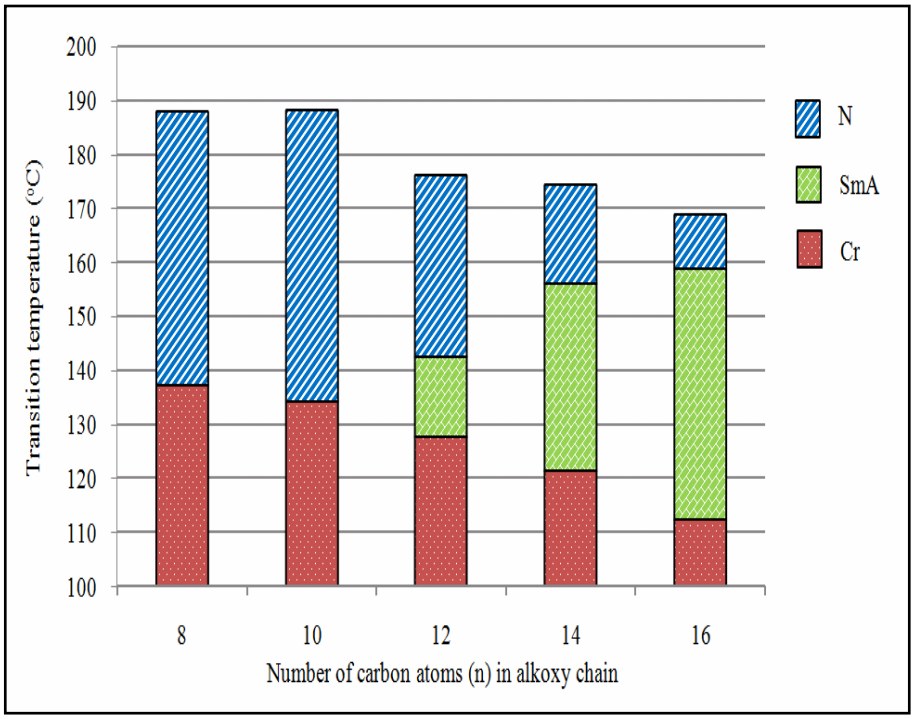


Figure 3: LC phase behavior of **nBPEP**.

Conclusion

All the synthesized compounds exhibited mesomorphic properties whereby nematic phase with high thermal stability exists throughout the whole series and SmA phase emerged from the C10 derivatives onwards. The presence of the ordered smectic structure in the title compounds become potential interest in electrical studies for device application.

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