

Synthesis and mesomorphic evaluation of new calamitic liquid crystals containing benzothiazole core

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Abstract

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

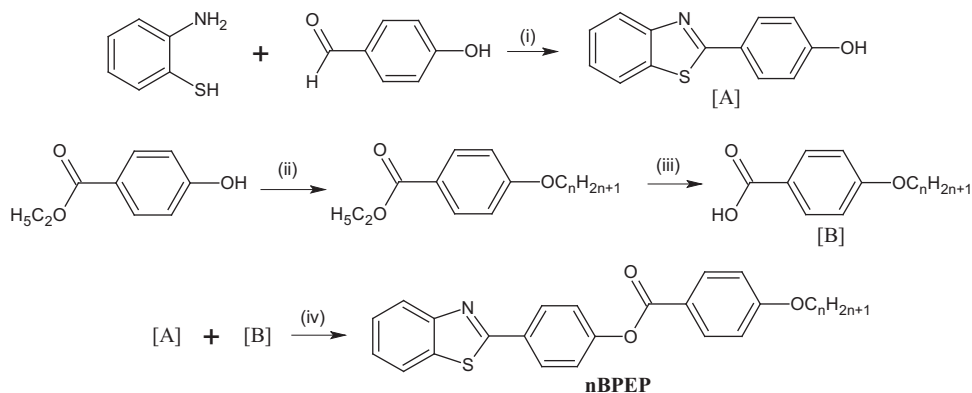
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Liquid crystals (LCs) have gained additional attention as new type of organic semiconductor exhibiting self-organization, liquid crystal display and separation membrane materials [1]. In the 1970s, much attention has been focused on the electrical properties of LCs, as a result, the electrical properties of different calamitic LCs have been examined [2,3]. Research focus shifted from calamitic to discotic LCs since the discovery of discotic LCs in 1977 [4]. High hole mobility found in the hexagonal columnar phase of hexapenthyloxy-triphenylene becomes an important milestone in the electronic studies of LCs [1]. 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 2-phenylbenzothiazole

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Scheme 1. Synthetic route for the target compounds. (i) EtOH, reflux 6 h, (ii) $C_nH_{2n+1}Br$, K_2CO_3 , CH_3COCH_3 , reflux 5 h, (iii) $H_2O:EtOH$ (1:1) reflux 5 h, KOH, conc. HCl, (iv) DCC, DMAP, DCM, DMF, reflux 5 h. Yield of 8BPEP (48%), 10BPEP (51%), 12BPEP (56%), 14BPEP (66%), and 16BPEP (74%).

derivatives [5,6]. In fact, smectic phases exhibit stronger intermolecular interaction than that of the nematic phase, resulting in a higher order in terms of the molecular alignment and in a higher viscosity [5]. Furthermore, the layer structure present in all smectic LCs induces π - π stacking interactions which facilitate hopping of charge carrier mobility.

In our previous studies on LCs [7–10], 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 Scheme 1. 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 turn strengthen the mesomorphic properties.

The synthetic route toward the title compounds, 2-[4-(4-alkoxybenzoyloxy)phenyl]benzothiazoles (nBPEP, where $n = 8, 10, 12, 14, 16$) is illustrated in Scheme 1. 2-Aminothiophenol was condensed with 4-hydroxybenzaldehyde upon refluxing in ethanol for 5 h and yield intermediate A [7]. Ethyl-4-hydroxybenzoate undergone Williamson ether synthesis in acetone with appropriate 1-bromoalkane and followed by acidification by concentrated hydrochloric acid to produce intermediate B [11]. Intermediate 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 procedure [12]. All the crude products were purified upon repeated recrystallization using ethanol until constant melting points were obtained. Structural elucidation of the title compound was carried out *via* elemental analysis, FT-IR, NMR and EI-MS spectroscopic techniques [13].

The liquid crystalline textures of the title compounds were observed under polarizing optical microscope (POM) and phase identification was made by comparing the observed textures with those reported in the literature [14,15]. Transition temperatures and corresponding enthalpy changes were determined using a differential scanning calorimeter (DSC) and the data was tabulated in Table 1.

From Table 1, it can be noted that all synthesized compounds are mesogenic. Nematic phase was observed in all the compounds, however, only 8BPEP is pure nematogenic compound. SmA phase emerged as monotropic phase (metastable) in 10BPEP. From C12 derivative onwards, SmA phase exists as enantiotropic phase (stable) and persists to C16 derivative.

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

Table 1
Phase transition and transition enthalpy changes for nBPEP upon heating and cooling.

Compound	Phase transition, °C (corresponding enthalpy changes, kJ mol ⁻¹)	Heating
		Cooling
8BPEP	Cr 137.3 (30.6) N 187.9 (0.6) I Cr 109.2 (33.6) N 184.4 (1.2) I	
10BPEP	Cr 134.3 (29.0) N 186.2 (0.9) I Cr 100.0 (23.8) SmA 132.3 (0.8) N 183.8 (1.0) I	
12BPEP	Cr 127.7 (33.3) SmA 142.5 (1.0) N 176.1 (0.9) I Cr 92.3 (27.7) SmA 140.4 (1.2) N 173.7 (1.0) I	
14BPEP	Cr ₁ 103.6 (16.8) Cr ₂ 121.4 (31.2) SmA 156.0 (1.3) N 174.5 (1.2) I Cr ₁ 87.0 (29.9) Cr ₂ 95.6 (4.23) SmA 154.5 (1.4) N 172.8 (1.5) I	
16BPEP	Cr 110.3 (49.5.6) SmA 158.8 (1.4) N 168.8 (1.5) I Cr ₁ 81.7 (37.6) Cr ₂ 95.5 (6.4) SmA 157.4 (1.6) N 167.4 (1.6) I	

Cr = crystal; N = nematic; SmA = smectic A; I = isotropic.

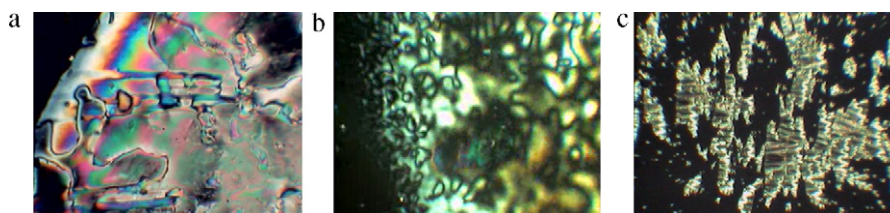


Fig. 1. Polarizing optical photomicrographs (100×) of (a) nematic phase in 8BPEP, (b) nematic phase in 16BPEP and (c) SmA phase in 16BPEP.

A plot of transition temperatures against the number of carbons in the alkoxy chain during the heating cycle is shown in Fig. 2. Based on the plot, both melting (Cr-SmA/N) and clearing (N-I) points showed a descending trend 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 temperatures of compounds nBPEP [17]. 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 only as the chain length increased. Furthermore, the nematic phase range (Δ_N) is reduced and the SmA phase range (Δ_{SmA}) is increased as the alkyl chain length ascended. 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.

In 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 becomes potential interest in electrical studies for device application.

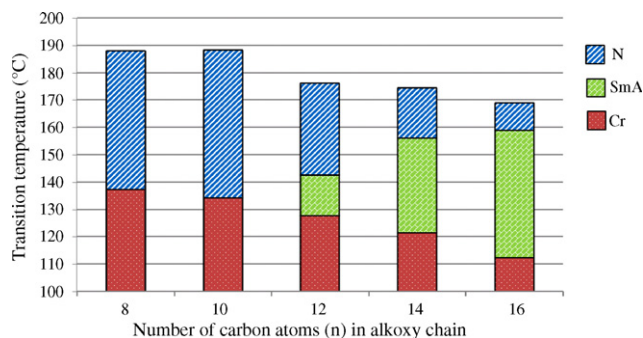


Fig. 2. Liquid crystal phase behaviour of nBPEP.

Acknowledgments

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- [13] Analytical and spectroscopic data for the representative compound 12BPEP: Yield 56%; EI-MS *m/z* (rel. int.%): 515 (4) [M+], 289 (100); IR (KBr, cm^{-1}): 3053 (C–H aromatic), 2921, 2850 (C–H aliphatic), 1733 (C=O ester), 1608 (C=N thiazole), 1260 (C–O, aromatic ether); ^1H NMR (400 MHz, CDCl_3): δ 0.9 (t, 3H, $J = 6.6$ Hz, CH_3 –), 1.3 (m, 16H, CH_3 – $(\text{CH}_2)_8$ – $(\text{CH}_2)_3$ –O–), 1.5 (p, 2H, $J = 7.1$ Hz, $-\text{CH}_2$ – CH_2 – CH_2 –O–), 1.8 (p, 2H, $J = 6.8$ Hz, $-\text{CH}_2$ – CH_2 –O–), 4.0 (t, 2H, $J = 6.4$ Hz, $-\text{CH}_2$ –O–), 7.0 (d, 2H, $J = 8.8$ Hz, Ar–H), 7.3 (d, 2H, $J = 6.8$ Hz, Ar–H), 7.4 (t, 1H, $J = 8.1$ Hz, Ar–H), 7.5 (t, 1H, $J = 7.3$ Hz, Ar–H), 7.9 (d, 1H, $J = 7.8$ Hz, Ar–H), 8.1 (d, 1H, $J = 8.3$ Hz, Ar–H), 8.2 (d, 2H, $J = 7.1$ Hz, Ar–H), 8.2 (d, 2H, $J = 7.1$ Hz, Ar–H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.10 (CH_3 –), 22.67, 25.96, 29.07, 29.32, 29.34, 29.54, 29.56, 29.61, 29.64, 31.90 for methylene carbons (CH_3 – $(\text{CH}_2)_{10}$ –), 68.35 ($-\text{CH}_2\text{O}-$), 114.36, 121.11, 121.60, 122.47, 123.21, 125.20, 126.35, 128.73, 131.13, 132.35, 135.11, 153.22, 154.14, 163.72, 164.64 for aromatic carbons, 167.05 ($-\text{COO}-$); Anal. calcd. for $\text{C}_{32}\text{H}_{37}\text{NO}_3\text{S}$: C, 74.53%, H, 7.23%, N, 2.72%; Found: C, 74.60%, H, 7.18%, N, 2.67%.
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