



Liquid Crystalline Behaviors and X-Ray Diffraction Studies of 6-Ethoxy-2-(4-alkoxybenzylideneamino)benzothiazole

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A new homologous series of benzothiazole liquid crystals comprising a terminal ethoxyl substituent and imine linkage was studied. All members can be differed from the number of carbons at the alkoxy chain ($C_nH_{2n+1}O-$, where $n = 2-10, 12, 14, 16, 18$). Mesomorphic behaviours of the present compounds was characterised and studied by differential scanning calorimetry and polarizing optical microscopy. All the present molecules with 2-(benzylideneamino)benzothiazole as core system exhibited mesomorphism. Early members ($n = 2-7$) are pure nematogenic liquid crystals. Medium members ($n = 8-10, 12, 14, 16$) are polymorphic liquid crystals wherein these compounds exhibited nematic and smectic phases. However, the properties of the medium members still differ in terms of transition temperatures, phase stability (monotropic or enantiotropic) and types of smectic phase (smectic A or C). The last member with the longest alkoxy chain is pure smectogenic A liquid crystal. In addition, X-ray diffraction technique was used and it confirmed monolayer arrangement of SmA phase in *n*-tetradecanoyloxy derivative.

Keywords: X-ray diffraction analysis, Schiff bases, Benzothiazole, Smectic, Nematic.

INTRODUCTION

Liquid crystals are fluid phases of matter where the constituent molecules are sufficiently disordered to be classified as a liquid and generate flow properties, yet maintain varying degrees of ordering depending on the actual type of mesophase¹. It is generally agreed that the type of molecular ordering in mesophases depends greatly on the core system. This includes geometry, polarizability, molecular conformation, the length-to-breadth ratio as well as the number and position of permanent dipole moments in the core system. The heterocyclic compounds possess lower symmetry and different polarizability than the corresponding phenyl analogues. Additional permanent dipole moment present in the heterocyclic compounds can affect the magnitude and direction of total molecular dipole moment without increasing molecular breadth².

Terminal groups played an important role in the molecular structure of liquid crystals because of their polarity. Basically, terminally substituent compounds exhibit more stable mesophases compared to unsubstituted mesomorphic compounds³. In order to explore the effect of terminal substituent compound, we had designed a new type of mesogenic compounds which

is benzothiazole substituted with an ethoxyl terminal group as a mesogenic core. The compounds studied are 6-ethoxy-2-(4-alkoxybenzylideneamino)benzothiazole (nOEtBTH) (Fig. 1). Here, in this article, we report the mesomorphic and X-ray diffraction studies for a complete series of nOEtBTH with 13 homologues ranging from $n = 2-10, 12, 14, 16$ and 18.

EXPERIMENTAL

Thermal analysis: Phase transition temperatures and enthalpy changes were obtained using either Differential Scanning Calorimeter Mettler Toledo DSC823e or SII Nanotechnologies Co. DSC6100.

Microscopy technique: Carl Zeiss polarizing optical microscope attached with Linkam hotstage was used for liquid crystal texture studies. Video camera (Video Master coomo-20P) attached to the polarizing microscope was coupled with video capture card, allowing real-time video recording and image saving. Textures exhibited by the samples were observed using polarized light with crossed polarizers. Thin film technique with samples sandwiched between glass slides and cover slip were used for the studies. Liquid crystal texture conformation

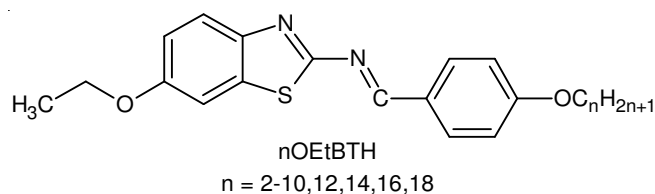


Fig. 1. Molecular structure of 6-ethoxy-2-(4-alkoxybenzylideneamino)-benzothiazole

was made by comparing the experimental with the literature textures⁴.

X-Ray diffraction analysis: Synchrotron powder X-ray diffraction (XRD) measurement was performed at beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The preparation and measurement methods were performed according to a previously reported method⁴.

All chemicals were purchased and used as obtained without further purification. The title compounds were prepared according to the methods that described in our previous work⁵.

RESULTS AND DISCUSSION

Mesomorphic properties: The optical photomicrographs of 8OEtBTH are illustrated in Fig. 2. On cooling from isotropic liquid phase, nematic droplets (Fig. 2a) emerged and coalesced to form nematic phase with marble-like texture (Fig. 2b). By further cooling, nematic mesophase transformed to SmC phase. Fig. 2c shows the photomicrograph captured during the transition of nematic to SmC phase.

For compound 12OEtBTH, nematic mesophase with Schlieren texture was observed during cooling cycle from isotropic liquid. Upon cooling, SmA phase with homeotropic (dark area) textures were observed. On further cooling, SmC phase with gray texture was formed before crystallization (Fig. 3a). Interestingly, 12OEtBTH is the only compound that exhibited three types of mesophase (N, SmA and SmC). Therefore, it can be proposed that the present molecule needs to have exactly twelve carbons ($n = 12$) at the alkoxy chain in order to generate polymorphism of N, SmA and SmC in benzothiazole LCs. As for 18OEtBTH, SmA phase with focal-conic texture (Fig. 3b) was observed during heating and cooling cycles.

The results from microscope observation were confirmed with the differential scanning calorimeter data. Phase transition temperatures and enthalpy changes upon heating and cooling



(a)



(b)

Fig. 3. Liquid crystal texture of 12OEtBTH and 18OEtBTH. (a) SmC phase with gray texture of 12OEtBTH (b) SmA phase with focal conic fan-shaped texture of 18OEtBTH

scans obtained from differential scanning calorimeter measurements are summarized in Table-1. Representative of differential scanning calorimeter thermogram of 8OEtBTH is depicted in Fig. 4. There is an additional exothermic peaks occurred from isotropic liquid during cooling scan indicating that the compound exhibited monotropic smectic C phase. On cooling cycle, the first peak from the right of thermogram represents the isotropic liquid-to-nematic transition, the second peak

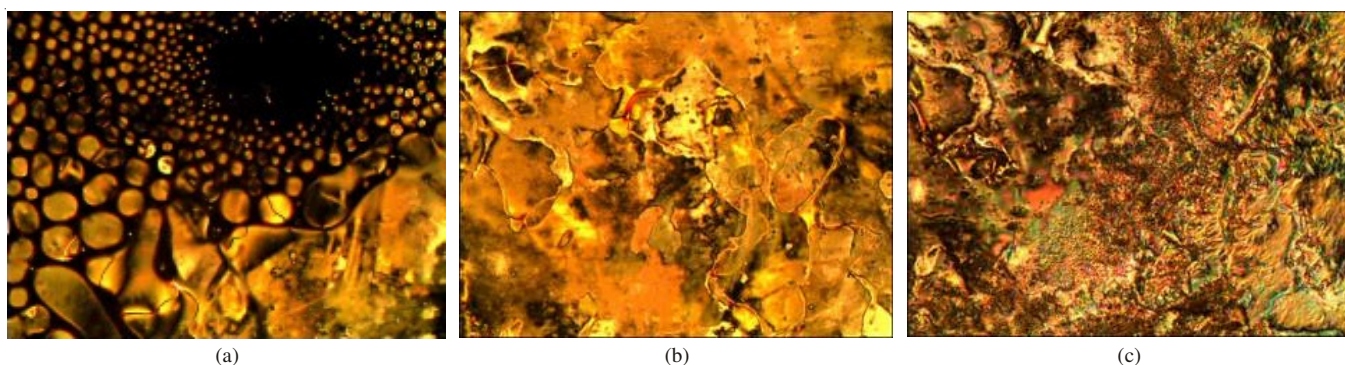


Fig. 2. Liquid crystal textures of 8OEtBTH upon cooling. The nematic droplets (a) appeared and coalesced to form nematic phase with marble-like texture (b). Further cooling, transition of nematic (left) to SmC (right) phase was observed (c)

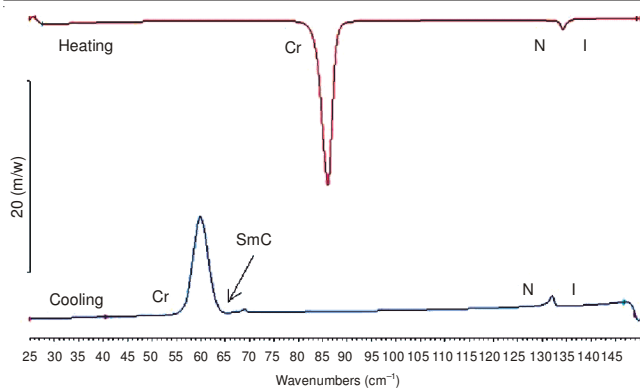


Fig. 4. Differential scanning calorimeter thermogram of 80EtBTH

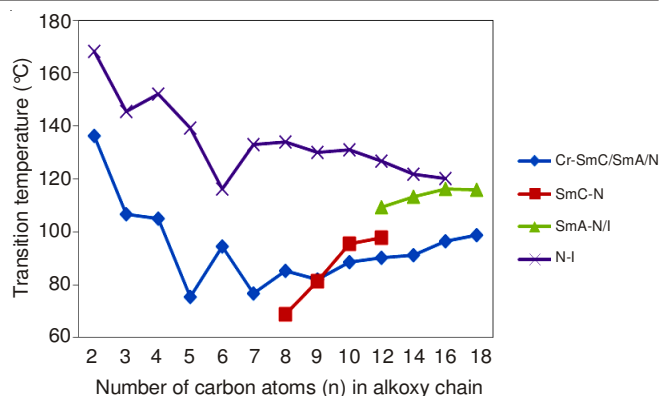
Fig. 5. Plot of transition temperature *versus* the carbon atoms (n) in the alkoxy chain of homologous series nOEtBTH

TABLE-1
PERCENTAGE YIELD OF SYNTHESIS, PHASE TRANSITION TEMPERATURES AND ENTHALPY CHANGES OF nOEtBTH UPON HEATING AND COOLING SCANS

Compound	Yield (%)	Transition temperature (°C)	
		(ΔH , kJ mol ⁻¹)	
2OEtBTH	32	Heating: Cr 136.2 (35.44) N 168.1 (1.16) I	
		Cooling: Cr 107.6 (25.20) N 164.5 (0.94) I	
3OEtBTH	31	Heating: Cr 106.8 (25.47) N 145.7 (0.87) I	
		Cooling: Cr 66.8 (18.57) N 142.8(0.94) I	
4OEtBTH	36	Heating: Cr 105.0 (26.77) N 151.9 (1.24) I	
		Cooling: Cr 68.6 (21.33) N 147.5 (1.29) I	
5OEtBTH	38	Heating: Cr 75.5 (31.25) N 139.3 (0.93) I	
		Cooling: Cr 60.1 (26.61) N 138.1 (1.02) I	
6OEtBTH	44	Heating: Cr 94.57 (38.34) N 116.33 (1.04) I	
		Cooling: Cr 35.35 (15.08) N 112.79 (0.84) I	
7OEtBTH	53	Heating: Cr 76.8 (32.36) N 133.0 (1.07) I	
		Cooling: Cr 56.8 (31.88) N 133.1 (1.15) I	
8OEtBTH	58	Heating: Cr 85.4 (34.75) N 134.1 (1.24) I	
		Cooling: Cr 60.2 (27.96) SmC 68.9 (0.30) N 132.1 (1.11) I	
9OEtBTH	57	Heating: Cr 82.0 (35.66) N 130.2 (1.07) I	
		Cooling: Cr 35.8 (13.07) SmC 81.3 (0.26) N 127.7 (1.36) I	
10OEtBTH	63	Heating: Cr 88.7 (45.52) SmC 95.6 (0.25) N 131.2 (1.58) I	
		Cooling: Cr 57.0 (19.34) SmC 93.9 (0.21) N 129.5 (1.76) I	
12OEtBTH	67	Heating: Cr 90.3 (50.11) SmC 97.7 (2.07) SmA 109.1(1.26) N 126.9 (1.87) I	
		Cooling: Cr 65.9 (45.38) *SmC 92.0 SmA 107.7 (1.02) N 125.4 (2.22) I	
14OEtBTH	69	Heating: Cr 91.3 (51.43) SmA 113.2 (1.65) N 121.8 (1.67) I	
		Cooling: Cr 69.4 (46.98) SmA 111.6 (1.39) N 120.3 (1.86) I	
16OEtBTH	73	Heating: Cr 96.5 (62.28) SmA 116.1 (1.46) N 120.1 (1.40) I	
		Cooling: Cr 67.2 (53.60) SmA 114.5 (1.31) N 118.5 (1.63) I	
18OEtBTH	76	Heating: Cr 98.8 (83.73) SmA 116.0 (7.55) I	
		Cooling: Cr 81.1 (75.46) SmA 117.7 (7.99) I	

*Polarizing optical microscopy data. The phase is undetectable using DSC technique

reflects the transition from nematic-to-smectic C transition and the last peak indicates the smectic C-to-crystal transition.

Plot of transition temperature *versus* the carbon atoms in the alkoxy chain of nOEtBTH is shown in Fig. 5. This plot illustrates how alkoxy chain length influences the mesomorphic trend of nOEtBTH. It can be obviously inferred that the terminal chains length can majorly affect the mesomorphic

properties of the compounds. It is important to note that the shortest alkoxy chain length ($n = 2$) capable of exhibiting mesophase. This indicates that the present core structure is a good building block of liquid crystals. Compounds with short carbon chains ($n = 2$ to 7) exhibit wider nematic temperature ranges than compounds with longer alkoxy chains ($n = 8$ to 18)⁶. Smectogenic properties started to emerge as the chain length increased. A metastable smectic phase commenced from C₈ member as monotropic phase and become a stable enantiotropic smectic phase from C₁₀ member and persistent till the end of the series. The odd-even effect on the melting temperature was observed from C₄ to C₁₀ members.

From the plot, the clearing temperature showed smooth descending trends when the carbon chain length increased except for C₃ and C₆ which showed drastic decrease of temperature. The flexible terminal alkoxy chain acts as a diluent to the mesogenic core rings system, hence, depressed the clearing temperature of nOEtBTH. The descending direction was in agreement with the series of 6-methoxy-2-(2-alkanoyloxybenzylidene-amino) benzothiazoles in which the homologous with the longest chain possessed the lowest thermal stability⁴. As can be seen from the plot, the nematic mesophase range (Δ_N) is narrowed and disappeared at C₁₈ while the smectic mesophase range (Δ_{Sm}) did not show consistent trend as the alkoxy chain length increased. Metastable SmC phase commenced from C₈ member as monotropic phase. However, the smectic phase became more stable and exhibited enantiotropic phase from C₁₀ and onwards. The increasing van der Waals forces resulted from the lengthening of alkyl chain that plays an important role in stabilizing the smectic mesophase by facilitating the lamellar packing; on the other hand, it inhibited the nematic mesophase range⁷. In addition, the elongation of the carbon chain which been intertwined and attracted, in turn stimulates the packing ability and reduce the nematic mesophase range⁸.

X-Ray diffraction studies: In order to study the molecular arrangement of the mesophase, temperature-dependent XRD analysis was carried out for 14OEtBTH. The X-ray diffraction pattern of 14OEtBTH at 121 °C on heating consists of one sharp peak at 1.74 Å (Fig. 6, Table-2). In higher-angle region a broad diffuse scattering indicates the liquid-like order of the molecules within the layers⁹. The d -spacing (33.7 Å) is approximate to the calculated molecular length, L (33.89 Å).

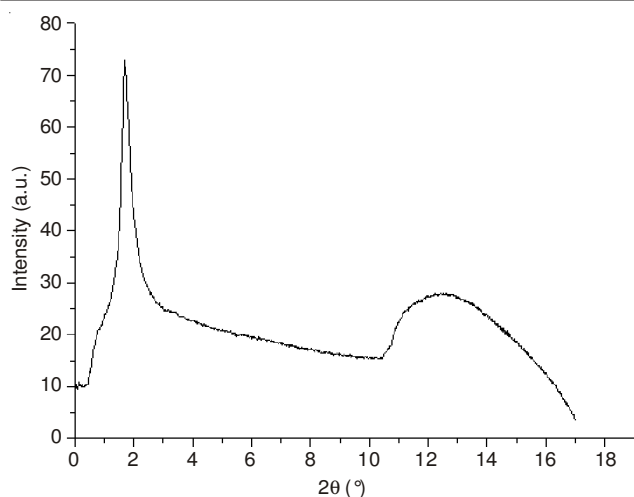


Fig. 6. XRD diffractogram of compound 14OEtBTH

TABLE-2
POWDER XRD DATA OF 14OEtBTH

2θ (°)	1.74
d-spacing	33.7 Å
L	33.89 Å
d/L	0.98
Phase	SmA
Arrangement	Monolayer arrangement

Since the d/L ratio is lower to 1, thus, it was said to correspond to the monolayer arrangement of the smectic A phase in compound 14OEtBTH¹⁰.

Conclusion

The synthesis and mesomorphic behaviour of homologous series of 6-ethoxy-2-(4-alkoxybenzylidenamino)benzothiazole is reported in the current paper. It was found that 2-(benzylidenamino)benzothiazole is a good core system of liquid crystals as the mesophase can be detected even in the member with the shortest alkoxy chain, $n = 2$. All members displayed

nematic phase except for the compound with the longest alkoxy chain, $n = 18$. Early members with $n = 2-7$ showed solely nematic phase. As the number of carbons at the alkoxy chain increased to $n = 8, 9$ and 10 , the additional smectic C (SmC) phase was observed. Member with $n = 12$ is the only compound that exhibited three types of mesophase (N, SmA and SmC). Moving to $n = 14$ and 16 , the SmC phase disappeared. Further lengthen to $n = 18$, the nematic property diminished and this compound became pure SmA liquid crystal.

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