

New mesogenic Schiff base esters comprising benzothiazole moiety: Synthesis and mesomorphic properties

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Abstract

A homologous series of Schiff base esters, 6-methoxy-2-(2-hydroxy-4-alkanoyloxybenzylidenamino)benzothiazoles, comprising a benzothiazole moiety as the core was synthesized. All the members of this series exhibited an enantiotropic nematic phase. The azomethine linkage along with the lateral hydroxyl and terminal methoxyl groups were found to exert an effect on the mesomorphic properties.

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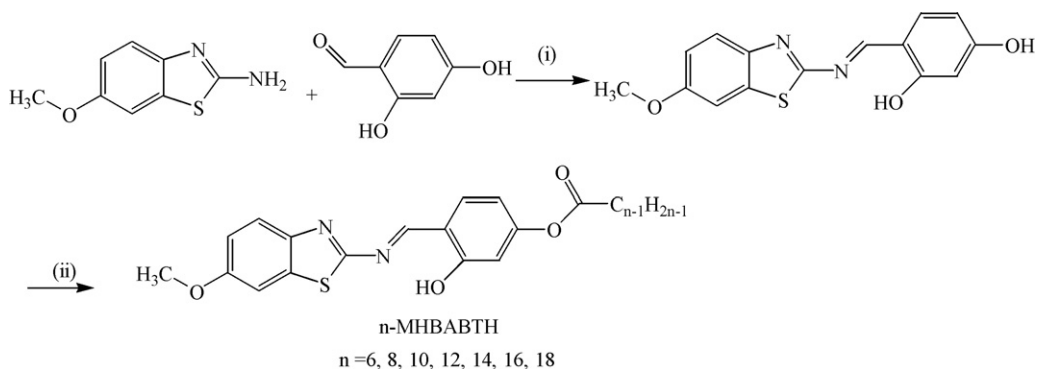
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Liquid crystalline behaviour of an organic compound is essentially dependent on its molecular architecture, in which a slight change in its molecular geometry brings about considerable changes in its mesomorphic properties. Detailed studies by liquid crystal researchers have led to empirical rules, one of which includes the effect of the chemical constitution in the formation of nematogenic and smectogenic mesophases [1]. Most of these studies focus mainly on Schiff's bases since the discovery of 4-methoxybenzylidene-4'-butylaniline which exhibited a nematic phase at room temperature [2].

The mesomorphic properties of aromatic Schiff base esters arising from substituents varying in their polarities have been reported in our previous studies [3–7]. In order to further explore the factors which govern the thermal stability of liquid crystals with a Schiff base core, and the relationship with its molecular structures, we have introduced thiazole, a heterocyclic unit, into the aniline fragment of benzylideneaniline. The novel compounds reported here are 6-methoxy-2-(2-hydroxy-4-alkanoyloxybenzylidenamino)benzothiazoles and their synthetic route is illustrated in Scheme 1. 2-Amino-6-methoxybenzothiazole and 2,4-dihydroxybenzaldehyde were coupled by reflux in ethanol for 3 h, following which the Schiff base intermediate was subjected to Steglich esterification with the appropriate fatty acids in the presence of DCC and DMAP [8–10]. The crude products were purified upon

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Scheme 1. Synthetic route for the target compounds. (i) C_2H_5OH and (ii) $C_{n-1}H_{2n-1}COOH$, DCC, DMAP, CH_2Cl_2 , DMF.

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

Compound	Phase transition ($^{\circ}C$) (corresponding enthalpy changes ($kJ\ mol^{-1}$))
6-MHBABTH	
Heating	Cr 131.1 (38.74) N 155.6 (0.63) I
Cooling	Cr 91.8 (32.89) N 141.8 (0.81) I
8-MHBABTH	
Heating	Cr 133.2 (37.66) N 145.8 (0.60) I
Cooling	Cr 100.7 (33.72) N 132.5 (0.84) I
10-MHBABTH	
Heating	Cr 127.5 (90.04) N 139.8 (1.81) I
Cooling	Cr 98.9 (89.07) N 135.9 (2.55) I
12-MHBABTH	
Heating	Cr 124.9 (43.25) N 136.8 (0.98) I
Cooling	Cr 107.7 (43.28) N 133.8 (0.53) I
14-MHBABTH	
Heating	Cr 123.6 (54.67) N 133.6 (0.84) I
Cooling	Cr 103.7 (53.75) N 130.7 (0.88) I
16-MHBABTH	
Heating	Cr 123.2 (61.86) N 129.7 (1.51) I
Cooling	Cr 95.7 (61.22) N 126.5 (1.51) I
18-MHBABTH	
Heating	Cr 122.3 (61.27) N 125.2 (1.23) I
Cooling	Cr 110.8 (58.31) N 117.0 (0.89) I

Cr = crystal; N = nematic; I = isotropic.

repeated recrystallization using ethanol and their structures were elucidated via elemental analysis, FT-IR, NMR and EI-MS spectroscopic techniques [11].

The liquid crystalline textures of the products were observed under a polarizing optical microscope equipped with a hotstage and temperature regulator. Phase identification was made by comparing the observed textures with those reported in the literature [12,13]. Transition temperatures and associated enthalpy changes were determined using a differential scanning calorimeter. The results are summarized in Table 1.

The target compounds are all nematogens. Upon cooling of the isotropic liquid, small droplets (Fig. 1a) appeared and coalesced to form the classical schlieren or marble texture (Fig. 1b) which is characteristic of a nematic phase. From the DSC results (Table 1), it is clearly noticed that the target compounds showing enantiotropic properties as the mesophase were observed during heating and cooling cycles [14].

The linking group is one of the factors influencing the target compounds in exhibiting the nematic phase instead of a smectic phase. The azomethine ($CH=N$) linking unit confers a stepped structure that disrupts the lamellar packing

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