

Short Note

Synthesis of a New Liquid Crystal, 3-Hydroxy-4-[[6-methoxy-1,3-benzothiazol-2-yl)imino]methyl}phenyl Palmitate

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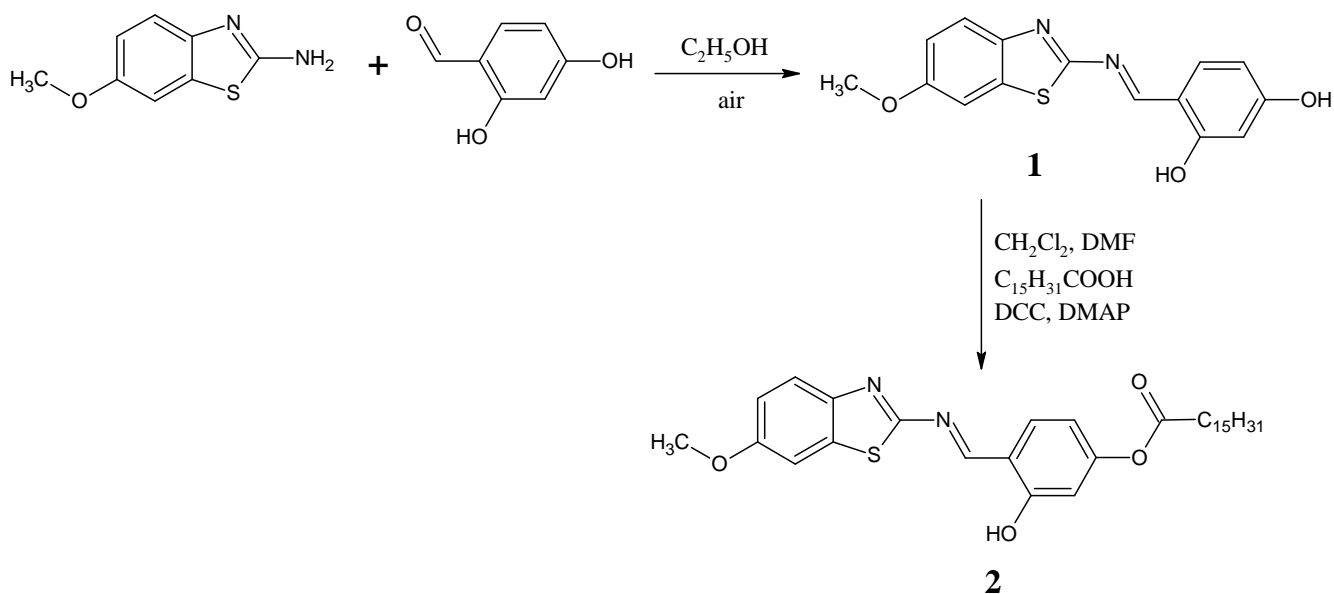
Abstract: A new Schiff base ester comprising of heterocyclic moiety, 3-hydroxy-4-[[6-methoxy-1,3-benzothiazol-2-yl)imino]methyl}phenyl palmitate was synthesized and its IR, ¹H NMR, ¹³C NMR, elemental analysis and MS spectroscopic data are presented.

Keywords: Schiff base; liquid crystal; ester chain; 3-hydroxy-4-[[6-methoxy-1,3-benzothiazol-2-yl)imino]methyl}phenyl palmitate

Schiff bases have received overwhelming attention ever since the discovery of first room temperature liquid crystal, 4-methoxybenzylidene-4'-butylaniline (MBBA) [1]. Many kinds of heterocyclic structures, such as 1,3,4-thiadiazole [2], thiopene [3], 2,1,3-benzoxadiazole [4] and benzothiazole [5] have been introduced as core centre in liquid crystalline compounds. In this paper, we report here the synthesis of new Schiff base ester comprising benzothiazole unit, 6-methoxy-2-(2-hydroxy-4-hexadecanoyloxybenzylidenamino)benzothiazole. This new compound exhibited enantio-tropic nematic phase.

Despite there are two hydroxy groups at the *ortho* and *para* position of benzaldehyde fragment (Schiff base **1**), the esterification has taken place at the *para* position and leaving the *ortho* hydroxy moiety untouched. This is assumed because the unhindered hydroxy group (*para*-OH) is more

favourable in the reaction compared to the hindered hydroxy group (*ortho*-OH) [6,7]. This assumption is confirmed by the observation of an *ortho* hydroxy proton at $\delta = 12.5$ ppm in the ^1H NMR spectrum.



In analogy to a recently published procedure [8-11], a solution of 2-amino-6-methoxybenzothiazole (7.21 g, 40 mmol) and 2,4-dihydroxybenzaldehyde (5.52 g, 40 mmol) in absolute ethanol (60 mL) was heated under reflux for 3 hours. The solvent was removed via slow evaporation and Schiff base **1** obtained was recrystallized from absolute ethanol. Then, Schiff base **1** (6.01 g, 20 mmol) in dimethylformamide (DMF) (10 mL), was added to a solution of palmitic acid (5.13 g, 20 mmol) and 4-dimethylaminopyridine (DMAP) (1.22 g, 10 mmol) in dichloromethane (70 mL). The resulting mixture was stirred in an ice bath. To this solution, N,N'-dicyclohexylcarbodiimide (DCC) (4.13 g, 20 mmol) dissolved in dichloromethane (10 mL) was added dropwise while stirring in the ice bath for an hour. The resulting mixture was subsequently stirred at room temperature for another 3 hours. Then, the reaction mixture was filtered and the excess solvent was removed from the filtrate by evaporation. Recrystallization from absolute ethanol gave the Schiff base **2** as yellow solid (6.79 g, 63%).

Phase transition temperature ($^{\circ}\text{C}$): Crystal 123.2 Nematic 129.7 Isotropic

MS (EI): M^+ (m/z) = 538

IR (KBr, cm^{-1}): 3447 (O-H); 3095, 3069 (C-H aromatic); 2920, 2851 (C-H aliphatic); 1757 (C=O ester); 1611 (C=N thiazole); 1460 (C=C aromatic).

^1H NMR (400 MHz, CDCl_3): δ /ppm 0.8 (t, 3H, $J = 6.6$ Hz, CH_3 -), 1.2-1.4 (m, 24H, CH_3 - $(\text{CH}_2)_{12}$ -), 1.7 (qt, 2H, $J = 7.3$ Hz, $-\text{CH}_2$ - CH_2 - COO -), 2.5 (t, 2H, $J = 7.4$ Hz, $-\text{CH}_2$ - COO -), 3.8 (s, 3H, CH_3 -O-), 6.7 (d, $J = 8.5$ Hz, 1H, Ar-H), 6.8 (s, 1H, Ar-H), 7.0 (d, $J = 9.1$ Hz, 1H, Ar-H), 7.2 (s, 1H, Ar-H), 7.4 (d, $J = 8.5$ Hz, 1H, Ar-H), 7.8 (d, $J = 9.1$ Hz 1H, Ar-H), 9.1 (s, 1H, $\text{CH}=\text{N}$), 12.5 (s, 1H, OH).

^{13}C NMR (100 MHz, CDCl_3): δ /ppm 14.06 (CH_3), 22.64, 29.00, 29.18, 29.31, 29.40, 29.55, 29.60, 29.62, 29.64, 31.87 for methylene carbons ($\text{CH}_3(\underline{\text{C}}\text{H}_2)_{12}$ -), 24.77 ($-\underline{\text{C}}\text{H}_2\text{CH}_2\text{COO}-$), 34.36 ($-\underline{\text{C}}\text{H}_2\text{COO}-$), 55.68 (OCH_3), 104.24, 110.57, 113.68, 115.94, 116.24, 123.60, 134.70, 135.86, 145.74, 155.99, 157.73, 163.03, 165.15 for aromatic carbons, 166.25 ($\text{CH}=\text{N}$), 171.33 (COO).

Elemental analysis: Calculated for $\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_4\text{S}$: C, 69.11%, H, 7.86%, N, 5.20%; Found: C, 69.19%, H, 7.79%, N, 5.22%.

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