

NOTE

Synthesis of 5-Chloro-2-(4-tetradecanoyloxybenzylidenamino)benzoxazole

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A new compound, 5-chloro-2-(4-tetradecanoyloxybenzylidenamino)benzoxazole was synthesized and characterized by IR, NMR and MS analysis.

Key Words: 5-Chloro-2-(4-tetradecanoyloxybenzylidenamino)benzoxazole, Liquid crystal, Smectic A.

Liquid crystalline materials have many practical applications in scientific and technological areas, particularly as display devices, organic light emitting diodes, anisotropic networks, photoconductors and semiconductor materials¹⁻³. Strong demand of new liquid crystals (LCs) for applications has led to the search for numerous mesogens in particular, thermotropic liquid crystals^{4,5}. A great deal of thermotropic liquid crystals containing heterocyclic units have been synthesized and interest in such structures is constantly growing^{6,7}. These heterocyclic structures basically incorporated unsaturated atoms, such as O, N, S and/or others and the presence of such electronegative atoms often resulted in a reduced symmetry for the overall molecules; and a stronger polar induction⁶. However, there are relatively rare examples of benzoxazole-based liquid crystals reported in the literature⁸ and some of them are polymer liquid crystals⁹⁻¹².

In order to further explore benzoxazole as a mesogenic core in liquid crystals, here, we report the synthesis of new benzoxazole liquid crystals. The synthetic route for 5-chloro-2-(4-tetradecanoyloxybenzylidenamino)benzoxazole is illustrated in **Scheme-I**. The structure of title compound was on the basis of ¹H NMR (Fig. 1), ¹³C NMR, IR and MS spectral data. The new compound is smectic A type liquid crystal.

Preparation of 5-chloro-2-(4-tetradecanoyloxybenzylidenamino)benzoxazole (CL14BZX): Firstly, a mixture of 2-amino-5-chlorobenzoxazole (6.72 g, 40 mmol) and 4-hydroxybenzaldehyde (4.88 g, 40 mmol) in 60 mL dichloromethane, with added two drops of acetic acid as catalyst, was refluxed for 3 h with stirring. The mixture was then filtered and the filtrate was left evaporated to dryness.

The Schiff base [5-chloro-2-(4-hydroxybenzyliden-amino)-benzoxazole] formed was recrystallized with ethanol. Then, 5-chloro-2-(4-hydroxybenzylidenamino)benzoxazole (1.36 g, 5 mmol), tetradecanoic acid (1.28 g, 5 mmol) and 4-dimethylaminopyridine (DMAP, 1 mmol, 0.12 g) were dissolved in 40 mL mixture of dichloromethane and dimethyl formamide and stirred at 0 °C. *N,N'*-dicyclohexylcarbodiimide (DCC, 5 mmol, 1.03 g) dissolved in 10 mL of dichloromethane was added dropwise into the mixture and continuously stirred for 1 h at 0 °C. The mixture was then filtered and the filtrate was left to evaporate. The obtained yellow solid was recrystallized using hexane and ethanol to give 0.72 g (30 %). EI-MS *m/z* (rel. int. %): 483 (9) [*M*⁺], 272 (100), IR (KBr, $\nu_{\max}$, cm⁻¹): 2917, 2850 (C-H aliphatic); 1751 (C=O ester); 1602 (C=N oxazole); 1449 (C=C aromatic); ¹H NMR (400 MHz, CDCl₃): δ 0.8 (t, 3H, CH₃-), 1.2-1.4 (m, 24H, CH₃- (CH₂)₁₂-), 1.8 (m, 2H, -CH₂-CH₂-COO-), 2.6 (t, 2H, -CH₂-COO-), 6.8 (s, 1H, Ar-H), 7.3 (d, 1H, Ar-H), 7.4 (d, 1H, Ar-H), 7.7 (d, 1H, Ar-H), 8.1 (d, 1H, Ar-H), 9.8 (s, 1H, -N=CH-), ¹³C NMR (100 MHz, CDCl₃): δ 14.12 (CH₃), 22.69, 24.84, 29.08, 29.24, 29.36, 29.44, 29.59, 29.65, 29.68, 31.92 for methylene carbons (CH₃(CH₂)₁₂-), 29.63 (-CH₂CH₂COO-), 34.43 (-CH₂COO-), 104.24, 110.56, 111.27, 119.85, 122.524, 125.34, 131.99, 135.85, 145.73, 155.37, 157.72, 163.03, 165.15 for aromatic carbons, 168.87 (CH=N), 171.64 (COO).

Spectral interpretations: In ¹H NMR spectrum of CL14BZX, a singlet corresponding to the azomethine proton (-N=CH-) appeared at δ = 9.8 ppm. This further supported the fact that condensation reaction between 2-amino-5-chlorobenzoxazole and 4-hydroxybenzaldehyde has taken place. The

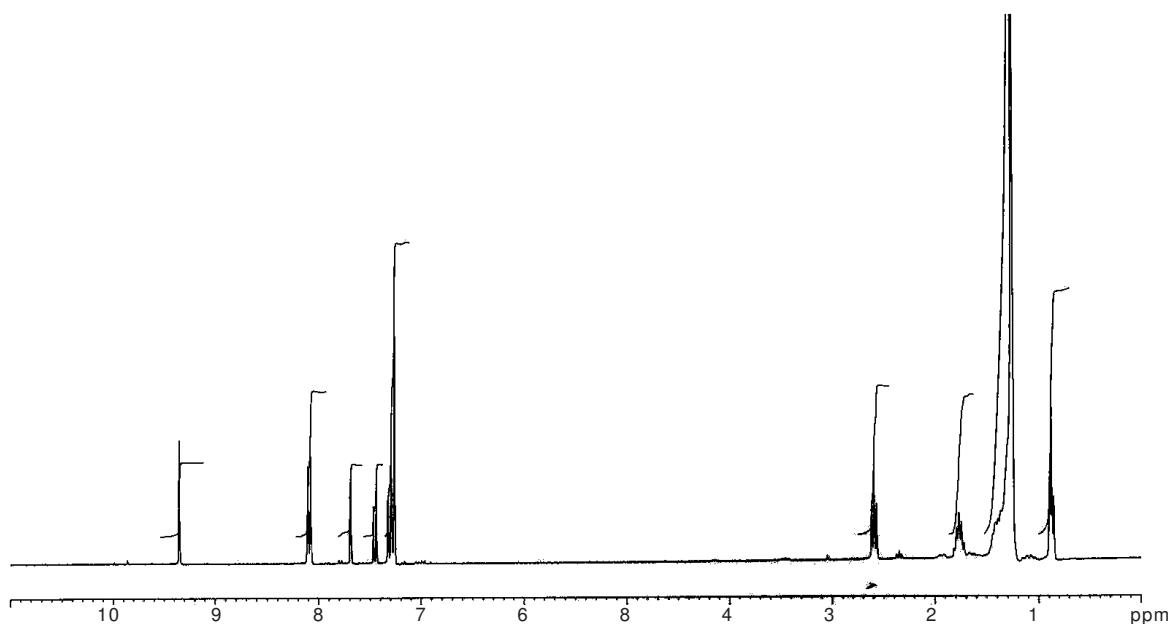
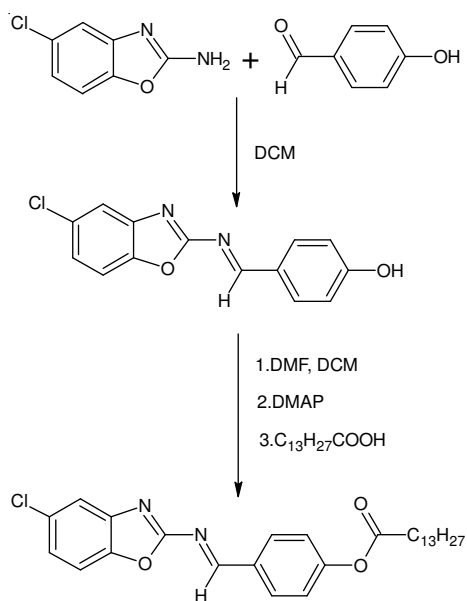


Fig. 1. ^1H NMR spectrum of 5-chloro-2-(4-tetradecanoyloxybenzylidenamino)benzoxazole

characteristic resonance peak for other aromatic protons were observed in relatively downfield region at $\delta = 6.8\text{--}8.1$ ppm. As for the aliphatic protons, it appeared at the upfield region at $\delta = 0.8\text{--}2.6$ ppm.



Scheme-I: Synthetic route towards the formation of 5-chloro-2-(4-tetradecanoyloxybenzylidenamino)benzoxazole

The structure of the compound was further substantiated by the ^{13}C NMR data. Carbonyl carbon exhibited its signal at the highest chemical shift ($\delta = 171.64$ ppm). This confirmed that Steglich reaction has been successfully carried out. In addition, formation of the Schiff base linkage can be evident from the appearance of the signal at $\delta = 168.87$ ppm. Aromatic carbons exhibited ^{13}C signals at the chemical shift range of $\delta = 104.24\text{--}165.15$ ppm. As for the aliphatic carbons, the characteristic resonance peaks appeared at $\delta = 14.12\text{--}31.92$ ppm.

The prominent molecular ion peak at $483\text{ }m/z$ in the mass spectrum of CL14BZX established its molecular formula as $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_3\text{Cl}$, supporting the proposed structure.

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