

## NOTE

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

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

**Key Words:** 5-Chloro-2-(4-tetradecanoyloxybenzylideneamino)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 materials<sup>1-3</sup>. Strong demand of new liquid crystals (LCs) for applications has led to the search for numerous mesogens in particular, thermotropic liquid crystals<sup>4,5</sup>. A great deal of thermotropic liquid crystals containing heterocyclic units have been synthesized and interest in such structures is constantly growing<sup>6,7</sup>. 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 induction<sup>6</sup>. However, there are relatively rare examples of benzoxazole-based liquid crystals reported in the literature<sup>8</sup> and some of them are polymer liquid crystals<sup>9-12</sup>.

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 <sup>1</sup>H NMR (Fig. 1), <sup>13</sup>C 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*<sup>+</sup>], 272 (100), IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 2917, 2850 (C-H aliphatic); 1751 (C=O ester); 1602 (C=N oxazole); 1449 (C=C aromatic); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.8 (t, 3H, CH<sub>3</sub>-), 1.2-1.4 (m, 24H, CH<sub>3</sub>- (CH<sub>2</sub>)<sub>12</sub>-), 1.8 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-COO-), 2.6 (t, 2H, -CH<sub>2</sub>-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-), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  14.12 (CH<sub>3</sub>), 22.69, 24.84, 29.08, 29.24, 29.36, 29.44, 29.59, 29.65, 29.68, 31.92 for methylene carbons (CH<sub>3</sub>(CH<sub>2</sub>)<sub>12</sub>-), 29.63 (-CH<sub>2</sub>CH<sub>2</sub>COO-), 34.43 (-CH<sub>2</sub>COO-), 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 <sup>1</sup>H NMR spectrum of CL14BZX, a singlet corresponding to the azomethine proton (-N=CH-) appeared at  $\delta$  = 9.8 ppm. This further supported the fact that condensation reaction between 2-amino-5-chlorobenzoxazole and 4-hydroxybenzaldehyde has taken place. The

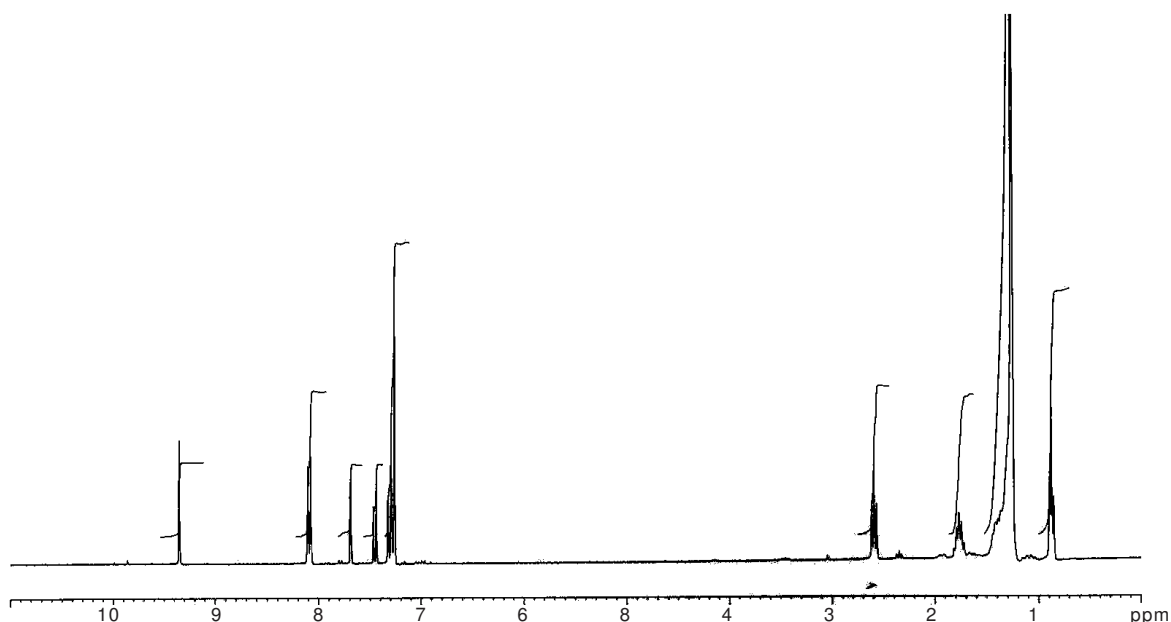
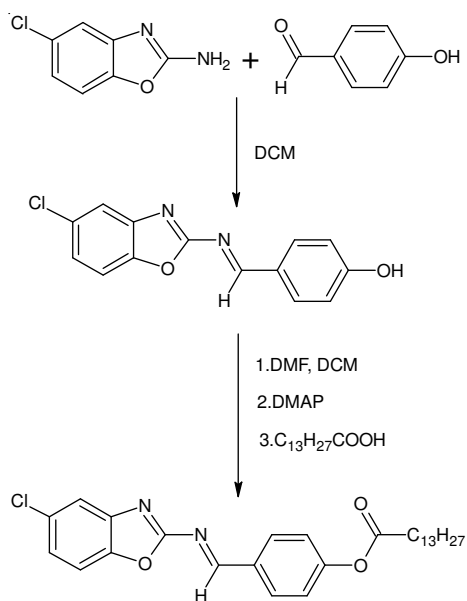


Fig. 1.  $^1\text{H}$  NMR spectrum of 5-chloro-2-(4-tetradecanoyloxybenzylideneamino)benzoxazole

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-tetradecanoyloxybenzylideneamino)benzoxazole

The structure of the compound was further substantiated by the  $^{13}\text{C}$  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  $^{13}\text{C}$  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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#### REFERENCES

1. L. Petti, M. Rippa, A. Fiore, L. Manna and P. Mormile, *Opt. Mater.*, **32**, 1011 (2010).
2. N.A. Shurpo, M.S. Vakshtein and N.V. Kamanina, *Tech. Phys. Lett.*, **36**, 319 (2010).
3. M.H. Hoang, M.J. Cho, K.H. Kim, T.W. Lee, J.I. Jin and D.H. Choi, *Chem. Lett.*, **39**, 396 (2010).
4. F. Yuksel, D. Atilla and V. Ahsen, *Polyhedron*, **26**, 4551 (2007).
5. B.Y. Zhang, F.B. Meng, M. Tian and W.Q. Xiao, *React. Funct. Polym.*, **66**, 551 (2005).
6. A. Seed, *Chem. Soc. Rev.*, **36**, 2046 (2007).
7. A.S. Matharu and D. Chambers-Asman, *Liq. Cryst.*, **34**, 1317 (2007); H. Gallardo, R.F. Magnago and A.J. Bortoluzzi, *Liq. Cryst.*, **28**, 1343 (2001); L.L. Lai, C.H. Wang, W.P. Hsien and H.C. Lin, *Mol. Cryst. Liq. Cryst.*, **287**, 177 (1996); V.F. Petrov, A.I. Pavluchenko and N.I. Smirnova, *Mol. Cryst. Liq. Cryst.*, **265**, 47 (1995); M. Parra, J. Belmar, H. Zunza, C. Zuniga, C. Ziga and G. Fuentes, *Bol. Soc. Chil. Quim.*, **38**, 325 (1993); N.L. Campbell, W.L. Duffy, G.I. Thomas, J.H. Wild, S.M. Kelly, K. Bartle, M. O'Neill, V. Minter and R.P. Tuffin, *J. Mater. Chem.*, **12**, 2706 (2002); S.T. Ha, K.L. Foo, R.T. Subramaniam, M.M. Ito, S.S. Sastry and S.T. Ong, *Chin. Chem. Lett.*, **22**, 1191 (2011).
8. (a) C.S. Wang, I.W. Wang, K.L. Cheng and C.K. Lai, *Tetrahedron*, **62**, 9383 (2006); C.K. Lai, H.C. Liu, F.J. Li, K.-L.g Cheng and H.-S. Sheu, *Liq. Cryst.*, **32**, 85 (2005); C.C. Liao, C.S. Wang, H.S. Sheu and C.K. Lai, *Tetrahedron*, **64**, 7977 (2008); H.C. Wang, Y.J. Wang, H.M. Hu, G.-H. Lee and C.K. Lai, *Tetrahedron*, **64**, 4939 (2008); S. Kim and S.Y. Park, *Mol. Cryst. Liq. Cryst.*, **337**, 405 (1999).
9. X.G. Li and M.R. Huang, *Petrochem. Technol.* (English Abstract), **28**, 55 (1999).
10. S. Kim, J. Sohn and S.Y. Park, *Bull. Korean. Chem. Soc.*, **20**, 473 (1999).
11. K.H. Park, W.S. Jahng, S.J. Lim and N. Kim, *Mol. Cryst. Liq. Cryst.*, **280**, 27 (1996).
12. R. Centore, R. Fresca, A. Roviello and A. Sirigu, *Polymer*, **34**, 4536 (1996).