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Synthesis, Characterization and Investigation of Mesomorphic Properties of Thermotropic Liquid Crystalline 2,5-Dimethoxy Derivative Schiff Base

Hülya ELMALI GÜLBAŞ[*1]

[*1]*Chemical Technology Department, Banaz Vocational School, Usak University, Uşak*

[*]*(hulya.elmali@usak.edu.tr)*

Abstract **–** Liquid crystal compounds have a wide range of applications in the field of industrial and technological materials due to their unique optical, electroptic and physical properties. In this study, 2,5-(dimethoxy)-2-[[4-(tetradecyloxy)phenyl)imino]methyl]benzene (**TLC1**) mesogenic Schiff base, which has thermotropic liquid crystal properties and has the potential to be used in technological applications, was synthesized. The structure of the synthesized Schiff base (**TLC1**) compound was characterized by classical spectroscopic methods (FT-IR, ^{1}H-NMR and ^{13}C-NMR). The mesogenic properties of the synthesized Shiff's base (**TLC1**) were determined by Optical Polarization Microscope (PM). 2,5-Dimethoxy derivative Shiff's base TLC1 has been determined that mesogenic properties and has been exhibited thermotropic enantiotropic Simectic X mesophases.

Keywords – Schiff Base Liquid Crystals, 2,5-Dimethoxy Liquid Crystal, Thermotropic Liquid Crystals, Imin Liquid Crystal, nSchiff Base

I. INTRODUCTION

In recent years, liquid crystals (LC) have been established in a wide range of technological products such as displays, light-emitting diodes sensing materials and optoelectronic display materials [1-4] . Liquid crystal properties occur with different effects such as temperature and solvent. Liquid crystal compounds that show mesogenic properties with the effect of heat are called thermotropic liquid crystals [5]. Schiff bases, also known as azomethine or imine, are formed as a result of the condensation reaction of primary amines with aldehydes or ketones [6]. Schiff bases represent an important class of organic compounds containing imine (-C=N-) bonds with many interesting applications in various fields, including photochromism [7], medicine [8], catalysis [9], corrosion chemistry [10]. Schiff bases or imines are widely studied as liquid crystalline materials. After the discovery that the Schiff base 4-methoxybenzylidene-4'-butylaniline exhibits a nematic mesophase at room temperature, many studies have been focused on Schiff bases [11-12]. Schiff bases have been extensively studied because the polarity of the imine bond creates a linear geometry between hard core structures and increases mesophase formation while maintaining thermal stability [13-14]. Schiff base has been investigated their liquid crystal properties from the point of view of their rich polymorphism. [15].

The purpose of this study is the synthesis and characterization of the noval 2,5-dimethoxy derivate Schiff base. For this aim, 2,5-(dimethoxy)-2-[[4-(tetradecyloxy)phenyl)imino]methyl]benzene (**TLC1**) mesogenic Schiff base has been synthesized, characterized and its mesogenic behaviours was examined. Characterization of the Schiff base was investigated by using classical spectroscopic methods (UV-VIS, FTIR, ^{1}H-NMR, ^{13}C-NMR).

The thermal and mesogenic behaviours of 2,5-dimethoxy derivate Schiff base **TLC1** was detected by optical polarizing microscopy (PM).

II. MATERIALS AND METHOD

A. *Materials*

The reagents p-nitrophenol, 2-butanone, 1-bromtetradecane, toluene, acetone, methanol, ethanol, p-toluene sulfonic acid are commercially available from Merck, 2,5-dimethoxybenzaldehyde from Alfa Easer and Pd/C catalyst from Aldrich chemical company was obtained and used without purification.

Fourier Transform Infrared (FT-IR) spectra of the synthesized TLC1 were recorded on the "Thermo Scientific Nicolet 380" brand spectrophotometer using an ATR head, NMR (^{1}H-NMR and ^{13}C-NMR) spectra were recorded with chloroform-D (in $CDCl_3$) tetramethylsilane (TMS) standard. Measured using Varian Unity 400 spectrometer.

Mesomorphic properties and mesophase textures of the synthesized **TLC1** were examined with a Leitz Laborlux 12 Polarization Microscope and a Linkam TMS93 temperature-controlled, Linkam TMS 600 heated table.

B. *Synthesis of 2,5-(dimethoxy)-2-[[4-(tetradecyloxy)phenyl)imino]methyl]benzene (**TLC1**)*

Tetradecyloxyaniline which will be used for the synthesis of Shiff's base, was synthesized as the reaction of tetradecyloxybromide with p-nitrophenol, using the method in the literature [], and the coumpound was reduced in the presence of H_2 gas under Pd/C catalysis and tetradecyloxyaniline compound was synthesized, respectively.

Shiff Base **TLC**1 was synthesized by the condensation reaction of 2,5-dimethoxybenzaldehyde compound (40 mg) in 50 ml toluene (5 mmol) under the catalysis of p-toluene sulfonic acid and (6 mmol) tetradecyloxyaniline in an inert argon atmosphere. The synthesized compound was purified by crystallization in acetone/ethanol mixture. The synthesis of the **TLC1** compound is shown in **Figure 1**.

Yield: 1.72 g, % 72 (beige crystals);

IR: γ (cm-1) = 1602 -C=N.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.80 (s; HC=N), 7.40, 7.32, 7.11, 6.92 (m; 7H,ArH), 3.89 (t; 2H, J ≈ 6.5 Hz; OCH_2), 3.55 (t; 6H, J ≈ 7.0 Hz; OCH_3), 1.90–1.70 (m; OCH_2–CH_2), 1.40–1.20 (m; 22H, 11 CH_2), 0.80 (t; J ≈ 7.4 Hz; CH_3).

^{13}C-NMR (400 MHz, $CDCl_3$): δ (ppm) = 160.1, 158.8, 143.6, 123.5 (3 s; 5C, ArC), 159.9 (d, 1C, HC=N), 123.5, 115.8, 115.0, 107.5 (4d, 7C, ArCH), 68.6, (t, 1C, OCH_2), 59.2 (2 s; 2C,OCH3), 31.2, 29.8, 29.4, 29.4, 29.4, 29.4, 29.4, 29.3, 29.3, 21.7 (11t, 11C, CH_2), 16.1,(q, 1C, CH_3).

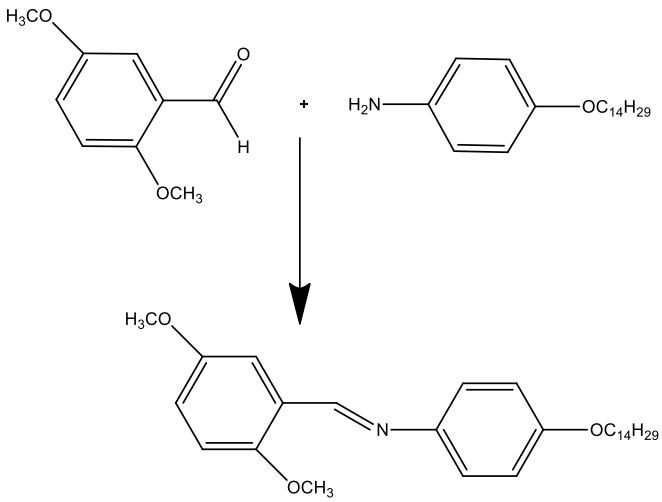


Figure 1. Sythesis of TLC1 compound

III. DISCUSSION

A. *SYNTHESIS AND CHARACTERIZATION OF **TLC1***

The reaction scheme for the synthesis of **TLC1** was given in **Figure 1**.

The of 2,5-dimethoxy derivate Schiff base prepared by the p-toluenesulfonic acid catalized condensation of the 2,5-dimethoxybenzaldehyde with 4-tetradecyloxyaniline.

The chemical structure of the **TLC1** studied by standart methods: UV-VIS, FTIR, ^{1}H-NMR, ^{13}C-NMR. The proposed structure are full agreement with the all spectroscopic data. In the FT-IR spectrum of **TLC1**, a peak of -C=N was observed at 1632 cm^{-1}. ^{1}H-NMR spectra of the **TLC1** was observed at 8.80,3,55 ppm which was assigned to HC=N and –OCH_3, respectivly. ^{13}C-NMR spectra of the **TLC1** was observed at 159.9,59.2 ppm which was assigned to HC=N and –OCH_3, respectivly.

The ^{1}H-NMR and ^{13}C-NMR spectrum of **TLC1** have shown in **Figure 2.** and **Figure 3.**

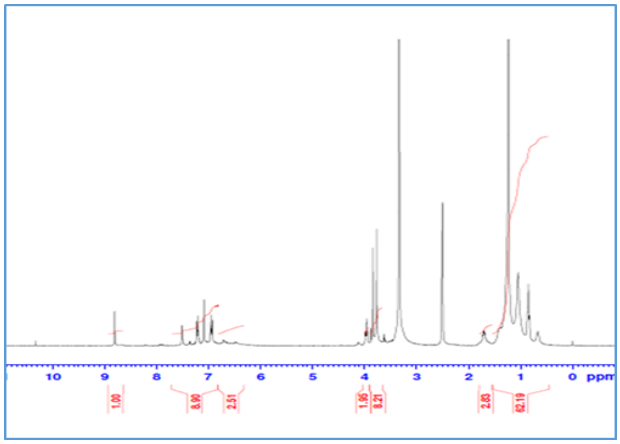


Figure 2. The ^{1}H-NMR spectrum of TLC1

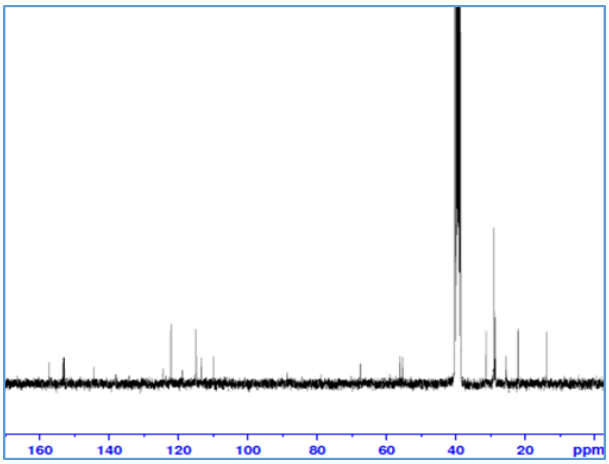


Figure 3. The ^{13}C-NMR spectrum of TLC1

B. Liquid Crystalline Behavior of ***TLC1***

The mesomorphic properties of **TLC1** studied by optical polarizing microscopy (PM).

Optical polarizing microscopic and morphologic investigations of 2,5-dimethoxy derivate Schiff base showed that the **TLC1** exhibit liquid crystalline properities. The 2,5-dimetoxy derivate Schiff base has been showed thermotropic mesophase. **TLC1** has been exhibited enantiotropic Smectic mesophase. This mesophase has been confirmed by textures of SmX. The texture of **TLC1** showed in **Figure 4.** and **Figure 5.**

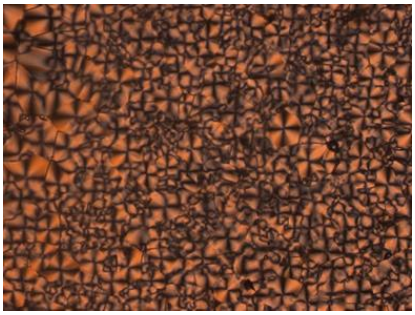


Figure 4. Optical texture (200 x) observed on cooling from the isotropic phase for the TLC1 SmX phase at 55 ^{o}C.

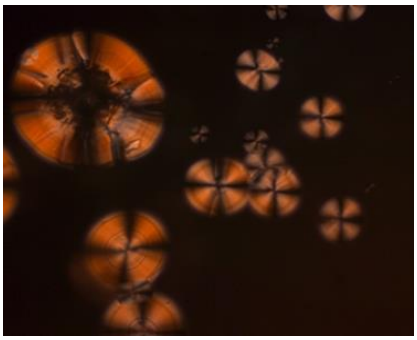
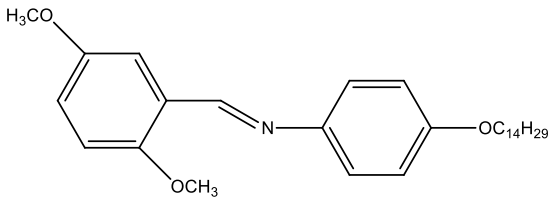


Figure 5. Optical texture (200 x) observed on cooling from the isotropic phase for the TLC1 SmX phase at 55 ^{o}C.

The transition temperatures and mesophase types observed for **TLC1** are given in **Table 1.**

Table 1. Phase transation temperatures T (^{o}C)[a] of **TLC1**
Cr: crystalline, Sm: smectic and Iso: isotropic phase.



TLC1

Compound	R	T °C[a]
TLC1	$C_{14}H_{29}$	K 53.1 SmX 62.5 Iso

[a] *Heating rates are 10.0 °C min-1 for the melting and for the clearing processes.*

IV. CONCLUSION

Thermotropic liquid crystalline Shiff's base 2,5-(dimethoxy)-2-[[4-(tetradecyloxy)phenyl)imino]methyl]benzene (**TLC1**) was synthesized and the chemical structure of **TLC1** was investigated by UV-VIS, FT-IR, ^{1}H-NMR, ^{13}C-NMR. 2,5-Dimethoxy derivative Shiff's base **TLC1** has been found out that thermotropic enantiotropic mesogenic properties. POM

investigation has been specified that the 2,5-dimethoxy derivative Shiff's base **TLC1** has been exhibited liquid crystalline phase of Simectic X textures.

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