SYNTHESIS OF 2-OXY-1-NAPHTHALDEHYDE SCHIFF BASES: ANALYSIS OF PHYSICO-CHEMICAL PROPERTIES AND SPECTROSCOPIC RESULTS

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Abstract. In the article, new Schiff bases of 2-oxy-1-naphthaldehyde were synthesized as a result of the condensation reaction with some primary amines of different structures. Physico-chemical properties of new Schiff bases were studied. The purity of 2-oxy-1-naphthaldehyde Schiff bases was determined by thin-layer chromatography and high-performance liquid chromatography. In determining the chemical structures of substances, it was analyzed by means of comparative comparison using modern spectroscopy methods. In the ultraviolet spectrum, 446 nm and 468 nm are characteristic of π→π* electron transitions, and absorption maxima, which were not observed in the starting substances, were observed. In the infrared spectrum, the deformation vibrations of C-H bonds in the aromatic ring were shown at 793 cm^{-1}, 742 cm^{-1}. In addition, at 653 cm^{-1} vibrational frequencies corresponding to C=N bonds of the Schiff basis were observed.

Keywords: 2-oxy-1-naphthaldehyde, primary amines, Schiff base, structure, ultraviolet (electron) and infrared spectroscopy, thin layer chromatography, high performance liquid chromatography

Introduction

It is known from the literature that Schiff's bases are compounds containing the -C=N- group and are formed by the reaction of aldehyde or ketone with primary amines [1]. Schiff bases are the most widely used organic compounds in organic chemistry. Schiff bases have been reported to be used as pigments, dyes, catalysts, intermediates in organic synthesis, and polymer stabilizers [2].

Azomethines of 2-oxy-1-naphthaldehyde and arylamides were studied in detail by [3]. Azomethines of 3,5-dibromosalicylaldehyde were synthesized in scientific works [4]. Some complexes of azomethines have been synthesized with heterocyclic, aromatic amines and salicylaldehyde [5]. The mesomorphic properties of some azomethine compounds derived from phenyl and thienyl-1,3,4,-thiadiazole have been studied [6] and some other azomethines have been synthesized from p-dimethylaminocinnamaldehyde [7].

2-oxy-1-naphthaldehyde - plays a very important role in the chemistry of naphthalene. They also serve as important starting reagents in the preparation of complex organic compounds, including biologically active and natural substances.

One of the analogues functionally similar to 2-oxy-1-naphthaldehyde is gossypol, which is a natural compound with a polyphenolic nature. Gossypol and its derivatives of Schiff's bases are the main source in the creation of drugs against various viral diseases, colds, gastrointestinal ulcers and swellings, along with the uniqueness of their chemical structure and biological activity [8, 10]. Currently, most of the Schiff bases synthesized on the basis of gossypol have shown interferon inducers, immunomodulators, immunosuppressive and other properties [8-10]. According to the results of research carried out in recent years, derivatives of gossypol obtained with primary amines with different structures have been found to have higher physiological activity compared to gossypol [8-14]. Searching, synthesizing and studying the properties of medicinal compounds with such a wide range of biological activity and high pharmacological potential motivates many organic chemists to develop effective directions.

In this context, the main goal of our research work is to synthesize new Schiff bases of 2-oxy-1-naphthaldehyde with some primary amines of different structures, to study their physico-chemical properties, structure and future biological activity.

Based on the above information, new Schiff bases of 2-oxy-1-naphthaldehyde were synthesized with some primary amines. Modern spectroscopic methods were used to study their physico-chemical quantities and structures.

Methods and materials

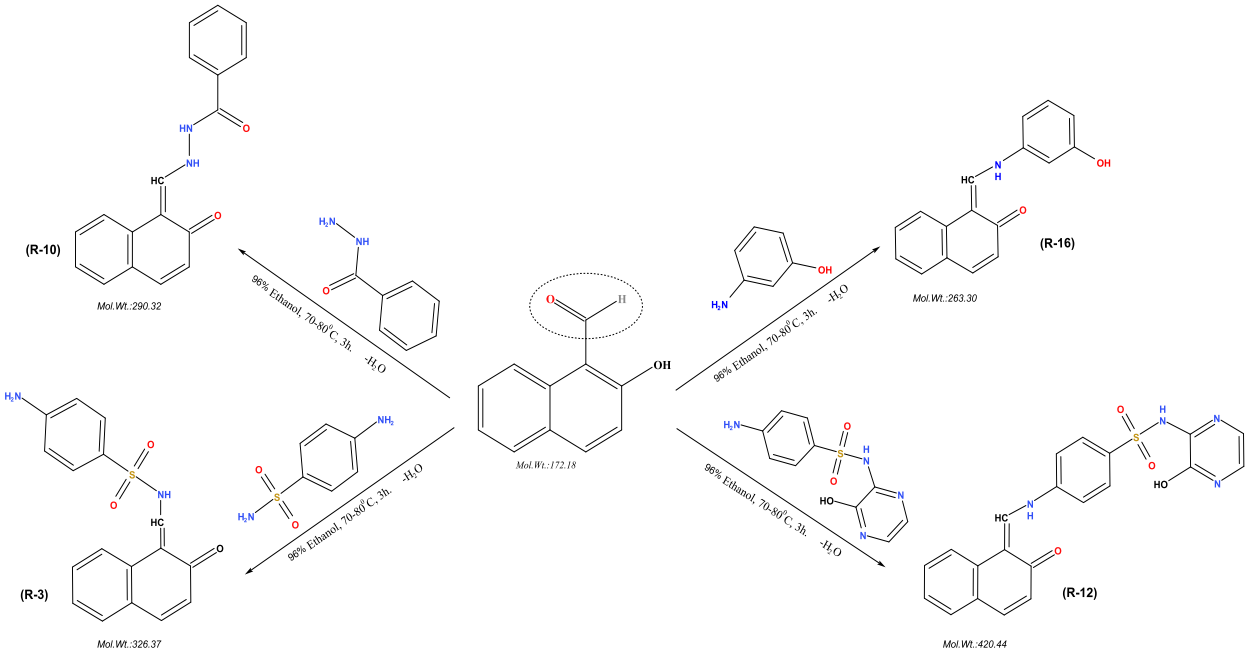
The UV spectra of the synthesized Schiff bases were measured on a Shimadzu 12.80 spectrophotometer (cuvette 1×1), and the IR spectrum on a Perkin Elmer-10.6.1 (USA) device. Thin layer chromatography (TLC) method was used to determine the purity of substances (plate Silufol UV-254, Czech Republic).

The fluidization temperature of compounds was determined on the PTP TU 25-11-1144 device. Purity of substances was determined by high-performance liquid chromatography (HPLC, Agilent Technologies 1200, USA).

Chromatographic analysis conditions: column - Poroshell 120 EC-C18, 2.7 μm, 4.6×100 mm, detector - diode matrix detector (UV detector can also be used), eluent -acetonitrile: 0.1% trifluoroacetic acid (70:30, isocratic method), flow rate - 0.75 ml/min, detection - 254, 234, 272, 378 nm, amount introduced into the column - 2μl, thermostat temperature - 25^{0}C, analysis time - 15 min. Technologies 1200, USA) method was determined.

Results and discussion

Schiff bases of 2-oxy-1-naphthaldehyde were synthesized with some primary amines (Scheme 1).



Scheme 1. General reaction scheme for the synthesis of new Schiff bases of 2-oxy-1-naphthaldehyde with some primary amines

The physicochemical properties of the newly synthesized Schiff bases were determined (Table 1).

Table 1.

Physicochemical properties of new Schiff bases of 2-oxy-1-naphthaldehyde

Number of compounds	*R_f	mp, ^{0}C	UV-spectrum, nm, λ_{max} *(log ε)*, ***CHCl*$_3$*, ****метанол*	Empirical formula	Yield, %
R-3	0.73	355±2	**221 (3.84), **270 (3.72), **321 (4.24) **364 (4.37) **450 (4.08)	$C_{17}H_{14}O_3N_2S$	50.7
R-10	0.68	391±2	***236 (3.78), ***261 (3.65), ***327 (4.21) ***366 (3.91) ***378 (3.90)	$C_{18}H_{14}O_2N_2$	65.3
R-12	0.79	376±2	**227 (3.56), **272 (3.61), **305 (4.25) **446 (4.19) **470 (4.02)	$C_{21}H_{16}O_4N_4S$	58.4
R-16	0.71	395±2	***215 (3.27), ***270 (3.45), ***322 (4.04),	$C_{17}H_{13}O_2N$	62.8

			***447 (4.29) ***468 (4.18)		

**System: chloroform:methanol (3:7)*

The UV spectra of the synthesized new Schiff base derivatives of 2-oxy-1-naphthaldehyde were obtained (Figure 1). Solvents of chloroform and methanol were used to obtain the UV spectrum of substances. As can be seen in Table 1, the intense and characteristic absorption maxima of the compounds in the UV region were found to be from 215 nm to 470 nm.

The UV-spectrum of substances was analyzed by comparative comparison based on the obtained results. For example, the UV-spectrum of the new Schiff base R-6 was studied in comparison with the starting compound.

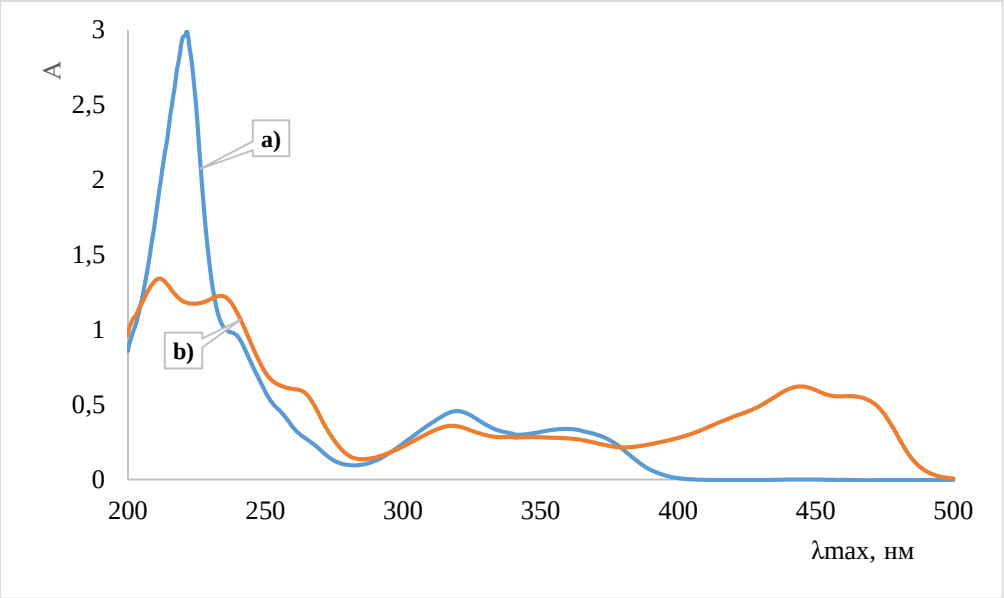


Figure 1. UV spectra of a new Schiff base of 2-oxy-1-naphthaldehyde
a)-2-oxy 1-naphthaldehyde, b)-R-16 new Schiff base

In the UV spectrum of 2-oxy-1-naphthaldehyde, absorption maxima corresponding to n→σ*, n→π* and π→π* electronic transitions were observed at 222 nm, 320 nm and 365 nm.

The changes in the absorption maxima related to n→σ*, n→π* and π→π* electronic transitions in the UV spectrum of the new Schiff base R-16 did not differ from the absorption maxima in the UV spectrum of the starting compound. However, at 446 nm and 468 nm, absorption maxima characteristic of π→π* electron transitions, which were not observed in the initial compound, appeared. These absorption maxima were observed in the weak energy region compared to the absorption maxima of π→π* electronic transitions in the starting compound.

In order to determine the purity level of the newly synthesized Schiff bases and the quality index of the resulting substances, they were checked using high-performance liquid chromatography (Fig. 2).

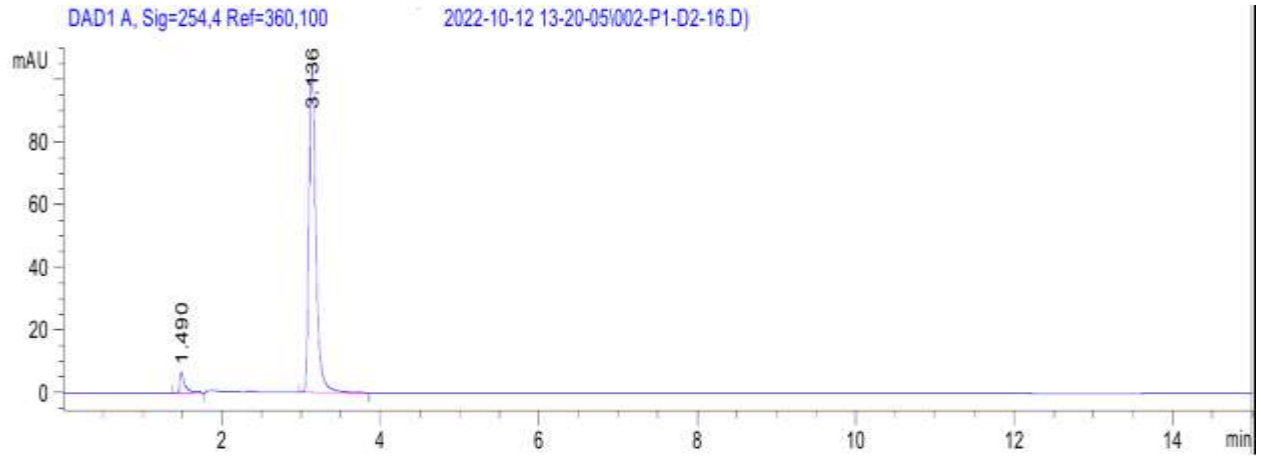


Figure 2. Chromatogram of the new Schiff base R-16 in high performance liquid chromatography

According to the results of the analysis obtained by high-performance liquid chromatography, the purity of the new Schiff's base R-16 was determined to be 93.01%.

The main vibration frequencies in the IR spectrum of 2-oxy-1-naphthaldehyde are as follows: in the 3150 cm^{-1} region, we can see that the valence vibration frequencies of phenol OH groups are formed. The valence vibration frequencies of CH groups in the molecule were observed at 2889 cm-1, the valence vibration of the carbonyl group was at 1620 cm^{-1}, the valence vibrations of C=C bonds were at 1568 cm^{-1}, and the deformation vibrations of phenol hydroxyl groups were observed at 1463 cm^{-1}. Deformation vibrations of C-H bonds in the aromatic ring were observed at 794 cm^{-1}, 744 cm^{-1}, 715 cm^{-1}.

The following fundamental vibrational frequencies were observed in the IR spectrum of the new R-16 Schiff base. We can see that the valence vibration frequencies of phenol hydroxyl groups in the molecule are formed in the region of 3275 cm^{-1}. The valence vibration frequencies of the CH groups in the molecule were observed at 2890 cm^{-1}, 2975 cm^{-1}, the valence vibration of the carbonyl group was at 1601 cm^{-1}, the deformation vibrations of phenol hydroxyl groups were at 1507 cm^{-1}, and the valence vibrations of C=C, C=N bonds were observed at 1544 cm^{-1}. Deformation vibrations of C-H bonds in the aromatic ring were observed at 793 cm^{-1}, 742 cm^{-1}. In addition, we can see that the Schiff base C=N bond vibrational frequencies appear at 653 cm^{-1}. Therefore, according to the results of the IR-spectrum analysis, a new azomethine bond was formed with the primary amino compound of 2-oxy-1-naphthaldehyde, and a new Schiff base R-16 was formed to the aldehyde group of 2-oxy-1-naphthaldehyde.

Experience part

R-16 Schiff base synthesis. The synthesis procedure was carried out as follows. Primary amines with 2-oxy-1-naphthaldehyde in a 1:1 mmol ratio were weighed on an analytical balance. They were then placed in a 300 mL flat-bottomed flask and dissolved in 50 mL of 96% C_2H_5OH, and the reaction mixture was heated (70-80^{0}C) for 3 hours under reflux. The progress of the reaction was monitored by thin layer chromatography. The precipitated reaction product was filtered and dried in a vacuum drying oven for 3-6 hours. R-16 is a powdery substance of bright color. The yield is 62.8% (0.165 g).

UV spectrum, λ_{max}, *nm, (log ε)*, methanol, 215 (3.27), 270 (3.45), 322 (4.04), 447 (4.29), 468 (4.18). Rf=0,71 (system: chloroform:methanol (3:7)).

IR spectrum of 2-oxy-1-naphthaldehyde cm^{-1} (ν, δ). ν(OH)=3150, ν(CH)=2889, ν(C=O)=1620 (aldehyde), ν(C=C)=1568, δ(OH)=1463, δ(COH, CH)=1399, 1311, 794, 744, 715.

R-16 Schiff base IR spectrum cm^{-1} (ν, δ). ν(OH)= 3275, ν(CH)=2890, 2975, ν(C=O)=1601 (ketone), ν(C=C, C=N)=1544, δ(OH)=1507, δ(CH)=793, 742, δ(C=N)=653.

Scientific research experiments are being continued.

Conclusions

1. For the first time, new Schiff bases of 2-oxy-1-naphthaldehydes with some primary amines were synthesized and their physicochemical properties were studied.

2. When the new Schiff bases of the synthesized 2-oxy-1-naphthaldehyde were tested in high performance liquid chromatography, the purity level was found to be 93.01%.

3. Based on the results obtained from modern UV-, IR-spectroscopy methods, the chemical structure formula of the compounds was shown.

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