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SYNTHESIS OF 2-OXY-1-NAPHTHALDEHYDE SCHIFF BASES AND THEIR SPECTROSCOPIC ANALYSIS

Abstract

In this article, new Schiff bases of 2-oxy-1-naphthaldehyde with amines of different nature (norsulfazol-Na, sulfapyridazine, thiosemicarbazide, 2-aminopyrimidine, 4-amino-2-chloro-6,7-dimethoxyquinazoline) were synthesized. Some physico-chemical parameters of the synthesized Schiff bases were studied and their chemical structures were characterized based on optical spectroscopy (UV-, IR-) methods.

Key words: 2-oxy-1-naphthaldehyde, primary amines, Schiff's base, thin layer chromatography, UV-, IR-spectroscopy.

2-ОКСИ-1-НАФТАЛЬДЕГИДНИНГ ШИФФ АСОСЛАРИ СИНТЕЗИ ВА УЛАРНИНГ СПЕКТРОСКОПИК ТАҲЛИЛЛАРИ

Аннотация

Ушбу мақолада 2-окси-1-нафтальдегиднинг турли хил табиатли аминлар (норсульфазол-Na, сульфапиридазин, тиосемикарбазид, 2-аминопиримидин, 4-амино-2-хлор-6,7-диметоксихиназолин) билан янги Шифф асослари синтез қилинган. Синтез қилинган Шифф асосларининг айрим физик-кимёвий катталиклари ўрганилган ҳамда кимёвий тузилишлари оптик спектроскопия (УБ-, ИҚ-) усуллари асосида тавсифланган.

Калит сўзлар: 2-окси-1-нафтальдегид, бирламчи аминлар, Шифф асоси, юпқа қатламли хроматография, УБ-, ИҚ-спектроскопия.

СИНТЕЗ 2-ОКСИ-1-НАФТАЛЬДЕГИДНЫХ ОСНОВАНИЙ ШИФФА И ИХ СПЕКТРОСКОПИЧЕСКИЙ АНАЛИЗ

Аннотация

В данной статье впервые синтезированы новые основания Шиффа 2-окси-1-нафтальдегида с аминами различной природы (норсульфазол-Na, сульфапиридазин, тиосемикарбазид, 2-аминопиримидин, 4-амино-2-хлор-6,7-диметоксихиназолин). Методами оптической спектроскопии (УФ-, ИК-) изучены некоторые физико-химические параметры синтезированных оснований Шиффа и охарактеризовано их химическое строение.

Ключевые слова: 2-окси-1-нафтальдегид, первичные амины, основание Шиффа, тонкослойная хроматография, УФ-, ИК-спектроскопия.

Introduction. Currently, one of the promising directions of chemical research is the synthesis and study of properties of biologically active substances aimed at wide application in medical practice. Therefore, it is necessary to identify and study the aspects that connect the structure of molecules with the properties that ensure the ability of the substance to produce biological activity. In this case, first of all, there are difficulties associated with the need to synthesize organic molecules of a certain structure. On the other hand, experimental confirmation of these properties is a very difficult task. Approaches related to the determination of "structure-activity" relationships can greatly help in solving these problems.

In connection with the above, it is desirable to synthesize and study new 2-oxy-1-naphthaldehyde Schiff bases. Only the research of experimental methods allows to determine the relationship between the structure of the substance and its properties.

Literature reviyew. Schiff bases are condensation products of primary amines with carbonyl compounds and were studied by [1]. A common structural feature of these compounds is an azomethine group of the general formula RHC=N-R_1, where R and R_1 are alkyl, aryl, cycloalkyl, or heterocyclic groups that may be variously substituted. These compounds are also known as anils, imines, or azomethines. In a number of studies [2,3] it has been shown that the presence of a lone pair of electrons in the sp2 hybridized orbital of the nitrogen atom in azomethine groups has important chemical and biological significance.

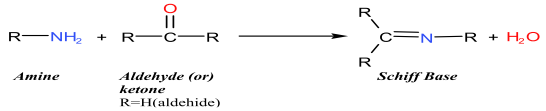
Due to the relative ease of synthesizing azomethines, their synthetic flexibility, and the unique nature of the C=N group, Schiff bases are generally excellent chelating agents. Especially in the presence of a functional group such as -OH or -SH, the azomethine group has been shown to form a five- or six-membered ring with the metal ion [4-7].

Schiff bases are characterized by the -N=CH-(*imine*) group, which is involved in explaining the mechanism of transamination and racemization reactions in the biological system [8, 9].

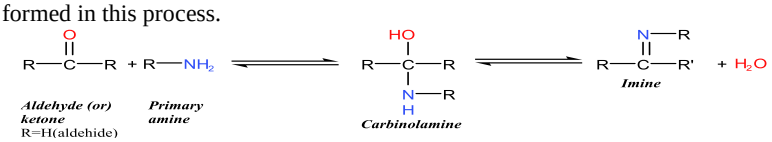
Aromatic aldehydes form stable Schiff bases with a particularly efficient conjugation system because these aliphatic aldehydes are unstable and easily polymerized [10]. Schiff base ligands are formed more easily with aldehydes than with ketones (carbonyl carbon). Schiff bases are very flexible and have different structures. A wide range of Schiff base compounds and their properties have been studied [11]. Their physico-chemical properties, for example, in the synthesis of aldehyde or ketones, in identification, in the identification of carbonyl and amino compounds, and in the use of these compounds in complex or sensitive reactions, have been studied by scientists in various fields [12,13].

Since the hydrolysis of the Schiff base is involved in a number of enzyme-mediated processes, the detailed mechanism of hydrolytic cleavage of C and N double bonds has been carefully studied both *in vivo* and *in vitro* [14]. Therefore, the versatility of Schiff's base derivatives and their biological, analytical and industrial applications are one of the urgent problems. In this regard, the goal of our research work is to synthesize new 2-oxy-1-naphthaldehyde Schiff derivatives, to determine their chemical structures based on modern physico-chemical methods, and then to study their biological activity.

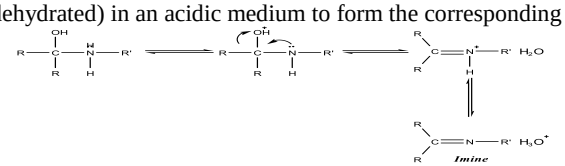
Research Methodology. It is known that Schiff base studies are carried out according to the following reaction scheme.



Reaction mechanism: Schiff base formation from aldehydes or ketones usually occurs as a reversible reaction with acid or base catalysts or heating. Most Schiff bases can be hydrolyzed in acidic or basic media. The corresponding aldehydes or ketones and amines are formed in this process.

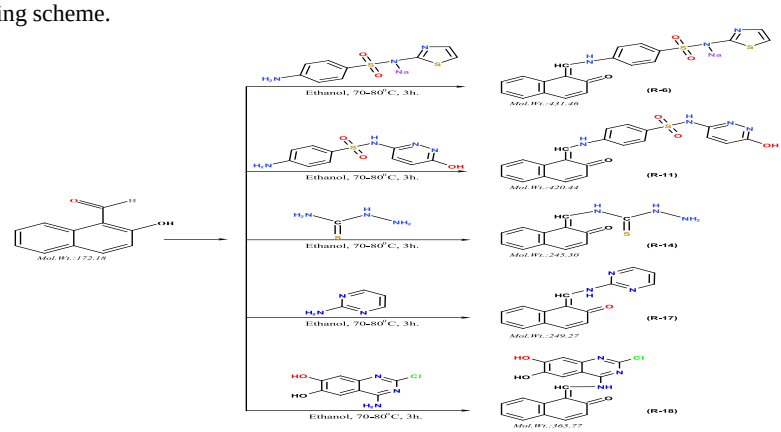


In the formation of Schiff bases, initially aldehydes or ketones combine with amines to form carbinolamines. This intermediate is then decomposed (dehydrated) in an acidic medium to form the corresponding Schiff base.



But the acid concentration cannot be too high, because amines are basic compounds. In a strongly acidic environment, amino compounds are protonated, and due to the loss of nucleophilic properties, the equilibrium shifts to the left in this reaction, resulting in a decrease in the probability of carbinolamine formation. Therefore, it is desirable to use mildly acidic pH medium in the synthesis of Schiff bases.

Analysis and results. New Schiff bases of 2-oxy-1-naphthaldehyde with some primary amines were synthesized according to the following scheme.



Scheme 1. General reaction scheme for the synthesis of Schiff bases of 2-oxy-1-naphthaldehyde

Some physico-chemical parameters of the newly synthesized Schiff bases were determined (Table 1).

Table 1.

Some physico-chemical quantities and spectral data of Schiff bases of 2-oxy-1-naphthaldehyde

Number of compounds	mp, ^{0}C	*R_f	UV-spectrum, nm, λ_{max} (*log*ε), *methanol*	IR spectrum, cm^{-1}	Empirical formula	Yield, %
R-6	384±2	0.78	220(4.03), 260(3.91), 290(4.13), 335(3.76), 350(4.11)	ν(NH)=3352, ν(C=O)=1593 (ketone), ν(C=C, C=N)=1525, δ(CH)=1481, 1445, 1375, 1328, 1230, ν(SO_2)=1129, δ(=CH)=934, δ(Ar)=824, 764, 684, δ(C-S-C)= 555	$C_{20}H_{14}O_3N_3S_2Na$	78.3
R-11	392±2	0.63	232(3.75), 265(3.88), 320(4.06), 440(3.89), 470(4.00)	ν(OH)=3250, ν(NH)=3100, ν(C=O)=1651 (ketone), ν(C=C, C=N)=1592, δ(CH)=1461, 1413, 1392, 1333, ν(SO_2)=1190, δ(=CH)=912, δ(Ar)= 817, 779, 737	$C_{21}H_{16}O_4N_4S$	72.1
R-14	381±2	0.81	210(3.97), 240(4.13), 260(3.93), 330(3.78), 365(4.04)	ν(NH)=3449, 3247, 3162, ν(C=O)=1626, 1606 (ketone), ν(C=C, C=N)=1570, 1529, δ(CH)=1470, 1393, 1330, 1275, ν(C=S)=1238, δ(=CH)=952, δ(Ar)= 815, 778, 746	$C_{12}H_{11}ON_3S$	78.9
R-17	373±2	0.74	220(4.05),	ν(NH)=3075, ν(CH)=2886, ν(C=O)=1669 (ketone),	$C_{15}H_{11}ON_3$	82.7

			240(3.73), 325(3.96), 365(3.83), 445(4.09)	ν(C=C, C=N)=1621, 1567, δ(CH)=1435, 1313, 1242, 1160, δ(Ar)=863, 794, 750, δ(C=N)=529		
R-18	366±2	0.85	215(4.02), 245(3.99), 280(4.01), 332(3.94), 335(4.07)	ν(OH)=3485, 3111, ν(NH)=3111, ν(C=O)=1645 (carboxyl), ν(C=O)=1581 (ketone), ν(C=C, C=N)=1559, δ(CH)=1486, 1458, 1278, 1247, δ(OH)=1247, δ(Ar)= 839, 829, 773, ν(C-Cl)=748, δ(C-Cl)= 455	$C_{19}H_{12}O_3N_3Cl$	64.8

**System: $CHCl_3$:methanol (3:7)*

The UV spectra of the synthesized Schiff bases and the starting compounds were studied by comparison (Figure 1).

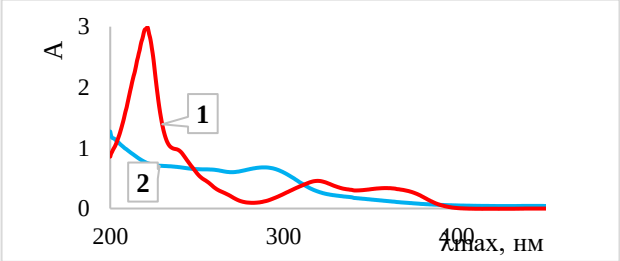


Figure 1. UV spectra of the new Schiff base.

1)-2-oxy-1-naphthaldehyde, 2)-R-6 Schiff's base

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

In the UV spectrum of the R-6 Schiff base, changes in absorption maxima related to n→σ*, n→π* and π→π* electronic transitions did not differ from the absorption maxima in the UV spectrum of 2-oxy-1-naphthaldehyde. However, at 260, 290 nm, absorption maxima, which were characteristic of π→π* electronic transitions, appeared that were not observed in the initial compound. These absorption maxima were observed in the weak energy region compared to the absorption maxima of π→π* electronic transitions in the original substances.

In the IR spectrum of the Schiff base formed by 2-oxy-1-naphthaldehyde with norsulfazol-sodium, the main vibrational frequencies were shown (Fig. 2).

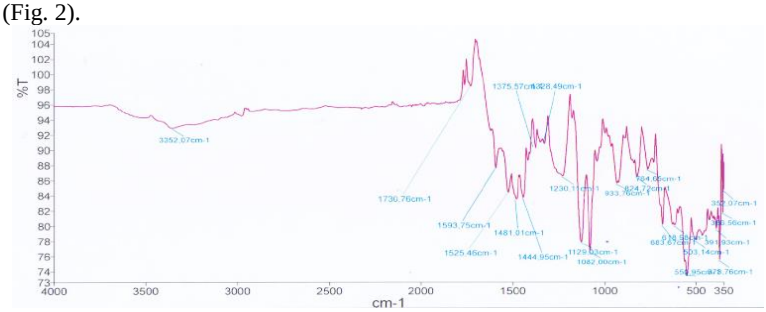


Figure 2. Schiff base IR spectrum of 2-oxy-1-naphthaldehydewith norsulfazole-sodium

The valence vibration frequencies of the NH group in the molecule were observed at 3352 cm^{-1}. At 1593 cm^{-1} we can see the valence vibration of the carbonyl group, and at 1525 cm^{-1} we can see the valence vibrations related to C=C, C=N bonds. Deformation vibrations of CH groups were observed at 1481, 1445, 1375, 1328, 1230 cm^{-1} and vibrations related to the aromatic ring at 824, 764, 684 cm^{-1}.

Valence vibrations of -SO_2- groups at 1129 cm^{-1} and deformational vibrations of C-S-C groups belonging to the thiazole ring appeared at 555 cm^{-1}. In addition, deformation vibration frequencies related to Schiff-based C=N bonds were observed at 647 cm^{-1}, which indicates the formation of a new azomethine bond.

Experience part. 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. The fluidization temperature of compounds was determined on the PTP TU 25-11-1144 device. The thin-layer chromatography (TLC) method was used to determine the purity of substances (plate Silufol UV-254, Czech Republic).

R-6 Schiff base synthesis. 1 mmol (0.172 g) of 2-oxy-1-naphthaldehyde was dissolved in 20 mL of 96% C_2H_5OH in a 200 mL flat-bottomed flask, and then 1 mmol (0.277 g) of a solution of norsulfasol sodium in ethanol was added. The obtained reaction mixture is heated for 3 hours (70-80^{0}C) with a countercooler connected. The progress of the reaction was monitored by thin-layer chromatography, and after completion of the reaction, it was left at room temperature for 24 hours. The precipitated reaction product was filtered off. The resulting precipitate was washed in ethanol (4×20 mL) and dried in a vacuum drying oven for 3-6 h. R-6 is a dark brown powdery substance. The yield is 78.3% (0.337 g).

According to this method, new Schiff bases of 2-oxy-1-naphthaldehyde, shown in Table 1, were synthesized. Currently, scientific and research work on determining the biological activities of substances is ongoing.

Conclusion. For the first time, new Schiff bases of 2-oxy-1-naphthaldehyde with amines of different nature (norsulfazol-Na, sulfapyridazine, thiosemicarbazide, 2-aminopyrimidine, 4-amino-2-chloro-6,7-dimethoxyquinazoline) were synthesized. The chemical structures of the synthesized Schiff bases were studied using optical spectroscopic methods (UV-, IR-). Absorption maxima corresponding to n→σ*, n→π* and π→π* electronic transitions were observed in the ultraviolet spectrum of compounds. In the infrared spectra, we can see the valence and deformation vibrational frequencies related to the Schiff-based C=N bonds. This indicates the formation of a new azomethine bond.

In the future, the main goal of our scientific research work is to study the biological activities of these obtained Schiff bases and determine the contribution of the azomethine bond or unshared electron pairs in the relationships between the structures and biological activities of the substances. As a result, natural biologically active substances such as gossypol, which is

a functional analog of 2-oxy-1-naphthaldehyde, can serve as the most promising model for explaining the biological activities of Schiff bases.

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