Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 2016. V. 59. N 10

DOI: 10.6060/tcct.20165910.5438

Для цитирования:
Бутина Ю.В., Кудаярова Т.В., Данилова Е.А., Семенишин Н.Н. Синтез и свойства макрогетероциклического соединения ABBB-типа с фрагментом 5-амино-2-додецил-3-имино-1,2,4-тиадиазолина. *Изв. вузов. Химия и хим. технология*. 2016. Т. 59. Вып. 10. С. 36–40.

For citation:
Butina Yu.V., Kudayarova T.V., Danilova E.A., Semenishin N.N. Synthesis and properties of macroheterocyclic compound of ABBB-type with fragment of 5-amino-2-dodecyl-3-imino-1,2,4-thiadiazoline. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*. 2016. V. 59. N 10. P. 36–40.

УДК: 54.057:547.794.3

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СИНТЕЗ И СВОЙСТВА МАКРОГЕТЕРОЦИКЛИЧЕСКОГО СОЕДИНЕНИЯ ABBB-ТИПА С ФРАГМЕНТОМ 5-АМИНО-2-ДОДЕЦИЛ-3-ИМИНО-1,2,4-ТИАДИАЗОЛИНА

Данная работа посвящена описанию синтеза, методов очистки и физико-химических характеристик макрогетероциклического соединения ABBB-типа, которое содержит фрагмент 5-амино-2-додецил-3-имино-1,2,4-тиадиазолина. Это соединение обладает тетраазабактериохлорино-подобной структурой и может быть использовано как потенциальный сенсибилизатор в фотодинамической терапии онкологических заболеваний. Кроме того, 3,5-диамино-1,2,4-тиадиазол – это эталонный антигипоксант, и целевой продукт может приобрести его биологические свойства. Исходное соединение, 5-амино-2-додецил-3-имино-1,2,4-тиадиазолин, синтезировали прямым алкилированием 3,5-диамино-1,2,4-тиадиазола 1-бромдодеканом. Макрогетероциклическое соединение ABBB-типа получали конденсацией 1,3-дииминоизоиндолина (фрагмент B) и 5-амино-2-додецил-3-имино-1,2,4-тиадиазолина (фрагмент A) в феноле. Очистку полученного соединения осуществляли методом колоночной хроматографии на силикагеле, используя в качестве элюирующей смеси CH2Cl2:MeOH:C6H14. Оба соединения охарактеризованы данными масс-спектрального анализа, 1H ЯМР, ИК и электронной спектроскопии. Показано, что в электронных спектрах макрогетероциклического соединения в кислой среде наблюдается батохромный сдвиг максимума поглощения от 480 до 555 нм и появляются новые инфлексии при 692 и 721 нм, что подтверждает протонирование полученного соединения. Кислотно-основные свойства этого соединения будут описаны в следующей работе.

Ключевые слова: макрогетероциклическое соединения, строение тетраазабактериохлорина, алкилирование, 5-амино-2-додецил-3-имино-1,2,4-тиадиазол

UDC 54.057:547.794.3

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SYNTHESIS AND PROPERTIES OF MACROHETEROCYCLIC COMPOUND OF ABBB-TYPE WITH FRAGMENT OF 5-AMINO-2-DODECYL-3-IMINO-1,2,4-THIADIAZOLINE

This work describes synthesis, methods of purification and physical-chemical characteristics of ABBB-type macroheterocyclic compound, which contains fragment of 5-amino-2-dodecyl-3-imino-1,2,4-thiadiazoline. This compound has similar to tetraazabacteriochlorin structure and it can be used as potentially sensitizer for photodynamic therapy of cancer. Moreover, 3,5-diamino-1,2,4-thiadiazole is standard antihypoxant and its biological properties can occur in desired macroheterocyclic product. Parent compound, namely 5-amino-2-dodecyl-3-imino-1,2,4-thiadiazoline, was synthesized by alkylation of 3,5-diamino-1,2,4-thiadiazole by 1-bromododecane. Macroheterocyclic compound of ABBB-type has been prepared by condensation 1,3-diiminoizoindoline (fragment B) and 5-amino-2-dodecyl-3-imino-1,2,4-thiadiazoline (fragment A) in phenol. Purification of obtained compound was carry out by method of column chromatography on silica gel using eluting mixture CH_2Cl_2:MeOH:C_6H_{14}. Both compounds were characterized by mass-spectrometry, ^{1}H NMR, UV-vis, IR spectroscopy. It was shown, that bathochromic shift of absorbtion maximum from 480 to 555 nm and emergence of new inflection at 692 and 721 nm are observed in UV-vis spectra of macroheterocyclic compound in acid medium, that confirms protonation of obtained compound. Acid-based behavior of this compound will be described in the next work.

Key words: macroheterocyclic compound, tetraazabacteriochlorin structure, alkylation, 5-amino-2-dodecyl-3-imino-1,2,4-thiadiazoline

INTRODUCTION

Thiadiazoles and their derivatives reveal a wide range of biological activities [1-3]. For instance, 3,5-diamino-1,2,4-thiadiazole (**1**) is well known medicinal product Amtizol [4]. Some of its derivatives were used as antimicrobial, antifungal and anti-inflammatory agents, dyes, lubricants and analytical reagents [5]. Diaminoderivatives of thiadiazoles, particularly, 2,5-diamino-1,3,4-thiadiazole and 3,5-diamino-1,2,4-thiadiazole, were successfully used as starting materials to synthesize macroheterocyclic compounds of ABABAB [6-11], ABAB [7, 12] and ABBB types [7, 13], correspondingly.

In recent times, scientists' attention is dedicated to development of synthetic hydrated porphyrin derivatives such as chlorins and bacterioclorins, which absorb light in long wavelength range of spectrum [14] and are used as therapeutic agents for photodynamic therapy of cancer [15, 16].

Macroheterocyclic structures similar to tetraazachlorin- and tetraazabacteriochlorin can be obtained only using 2N-substituted 3,5-diamino-1,2,4-thiadiazoles. Moreover, it is expected, that maximum of absorption of these compounds will shift in high IR region of spectrum that significantly will increase therapeutic effect of sensitizer. These compounds weren't described in the literature earlier.

5-Amino-2-imino-3-pentyl-1,3,4-thiadiazoline obtained by direct alkylation of 2,5-diamino-1,3,4-thiadiazole [17, 18] was used for synthesis of

three-units product [19, 20] and macroheterocyclic compound [7].

It seems to be very attractive to use alkylated 3,5-diamino-1,2,4-thiadiazoles for this purpose. But to our knowledge, synthesis of these products was not founded in literature. Hence the first step of this work was to find a method to synthesize 5-amino-2-dodecyl-3-imino-1,2,4-thiadiazoline.

X-Ray study of protonated forms of **1** showed that the nitrogen atom located into the position 2 of 1,2,4-thiadiazole ring is to be the most pronounced nucleophilic center of 3,5-diamino-1,2,4-thiadiazole [21]. Therefore, it is the most probable that direct alkylation of the last can be directed toward this atom.

EXPERIMENTAL PART

UV-vis spectra were measured with HITACHI U-2001 spectrophotometer. IR spectra were recorded with an AVATAR 360 FT-IR spectrometer. ESI-MS mass-spectra were measured with a Bruker Reflex III instrument, MALDI-TOF mass-spectra were registrated out with a AXIMA Confidence (SHIMADZU). ^{1}H NMR spectra were measured with a Bruker spectrometer in $CDCl_3$ at 500 MHz. Column chromatography was performed on silica gel Merck-60 (230-400 mesh, 60 Å). TLC was performed on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck).

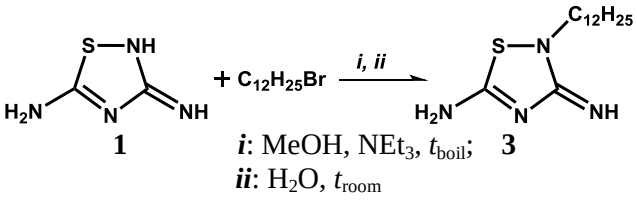
3,5-Diamino-1,2,4-thiadiazole (1) and *1,3-diiminoisoindoline (2).* The synthesis of compound 1 and 2 was carried out as described in studies [22, 23].

*5-Amino-2-dodecyl-3-imino-1,2,4-thiadiazoline (**3**).* Solution of 1-bromododecane (14.5 mL, 60.4 mmol) in CH_2Cl_2, **1** (2 g, 17.2 mmol) and MeOH (80 mL) was stirred with refluxing for 20 h. After triethylamine (4.2 mL, 30.2 mmol) was added to the reaction, the mixture was refluxed during 4 h. The solvent was evaporated and the resultant product was washed with water. The desired product was extracted by $CHCl_3$. The solvent was evaporated and a yellow oily was produced, which is soluble in low-polar organic solvents, and not soluble in water and hexane. Yield: 2.4 g (49%). Calc. EM 284.20. ESI-MS, *m/z:* 285 $[M+H]^+$. IR: ν (red glass)/cm^{-1}: 3309, 3142 (N-H, v), 2920, 2851 (C-H, alk), 1613 (N-H, d), 1541 (C=N, v), 1463, 1377, 1165, 720, 648, 565. UV-vis: λ_{max}/nm (CH_2Cl_2, C = $2.74\cdot10^{-4}$ mol·L^{-1}) (lgε): 252 (2.97). ^{1}H NMR: δ_H ($CDCl_3$, 500 MHz), ppm: 7.36 (s, 1H, -NH), 5.43 (s, 2H, -NH_2); 3.41 (tr, 2H, N-CH_2-.); 1.85 (m, 2H, N-CH_2-CH_2-); 1.57-1.28 (m, 18H, -CH_2); 0.88 (tr, 3H, -CH_3).

2-Dodecyl-3,12,19,24-tetraimino-5,10,17,26-tetranitrylo-1-thio-28H,30H-tribenzo[f,k,p](1,6,10,15)-tetraazacyclooctadecene (**4**). The solution of **2** (130 mg, 0.9 mmol) and **3** (85 mg, 0.3 mmol) in phenol was stirred for 60 h at temperature 100-110 °C. The reaction mixture was washed from phenol by hot water. The desired product was purified by column chromatography (silica gel, CH_2Cl_2:MeOH:C_6H_{14} = 10:1:3). A maroon zone was collected and the solvent was evaporated. Formed after washing in acetonitrile and removing solvent a powder was dried under vacuum. Yield: 7 mg (3.7 %). Calc. EM 653.30. MALDI-TOF (DHB), *m/z:* 690.6 $[M+K-2H]^+$. ν (KBr)/cm^{-1}: 3237, 2964, 2925, 2853 (C-H_{alk}), 1739, 1647, 1556 (C=N ν), 1461 (C-C ν), 1378, 1264, 1091, 875, 713. UV-vis: λ_{max}/nm (CH_2Cl_2, c = $1.49\cdot10^{-4}$ mol·L^{-1}) (lgε): 263 (4.41), 480 (3.60); λ_{max}/nm (acetone, c = $1.49\cdot10^{-3}$ mol·L^{-1}) (lgε): 457 (2.85); λ_{max}/nm (2,2,2-CF_3COOH, c = $1.49\cdot10^{-4}$ mol·L^{-1}) (lgε): 555 (3.82), 692 (3.39), 721 (3.37). ^{1}H NMR: δ_H ($CDCl_3$, 500 MHz): 11,18 (s, 2H, N-H_{cycl}), 8.10-7.69 (m, 12H_{arom}), 1.86-0.88 (25H_{alkyl}).

RESULTS AND DISCUSSION

Compound **3** was prepared by alkylation of **1** by 1-bromdodecane in boiling MeOH (Scheme 1).

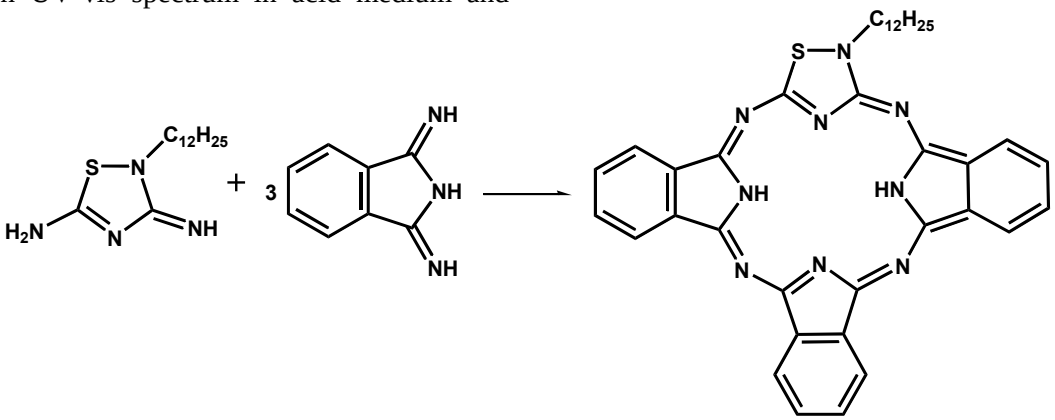


Scheme 1. The synthesis of 5-amino-2-dodecyl-3-imino-1,2,4-thiadiazoline
Схема 1. Синтез 5-амино-2-додецил-3-имино-1,2,4- тиадиазола

The mass spectrum of compound **3** is characterized by the present of a peak corresponding to the molecular ion with *m/z* = 285 in form $[M+H]^+$. In the IR spectrum of **3**, a series of bands at 3309, 3142 and 1613 cm^{-1} can be assigned to asymmetrical, symmetrical stretching, and deformation vibrations of the amino groups. A series of bands at 2920, 2851 cm^{-1} can be characterized as stretching valence C-H vibrations of the alkyl group. ^{1}H NMR spectrum of compound **3** reveals the signals at 0.88, 1.28-1.57, 1.85 and 3.41 ppm, which can be assigned to the protons of dodecyl group. Two singlets at 5.43 and 7.36 ppm characterize the resonance of the protons of amino and imino groups. Integral intensities of the signals confirm these assignments. These results are consistent with published for 3-alkyl-5-amino-2-imino-1,3, 4-thiadiazolines [17, 18] and pentylsubstituted 1,2,4-thiadiazoline [24].

Compound **4** was synthesized following the scheme 2.

The signal at 690.6 *m/z* in the mass-spectrum of **4** corresponds to $[M+K-2H]^+$ molecular ion. ^1H NMR spectrum in $CDCl_3$ shows the pyrrolic NH protons at 11.18 ppm. Strong absorbance at 263 nm dominates in UV-vis spectrum that demonstrates presence of thidiazole cycle while the band of lower intensity is located at 480 nm. It is similar to that of macroheterocyclic compound of ABBB-type with N-alkilsubstituted 1,3,4-thiadiazole moieties referred in [13]. Bathochromic shift from 480 to 555 nm was observed in UV-vis spectrum in acid medium and absorbance at 692 and 721 nm was appeared indicating protonation of compound **4** (Fig. 1) [25]. Beer-Lambert-Bouguer law is observed at concentration from $5.77\cdot10^{-4}$ to $14.9\cdot10^{-4}$ mol/L that confirms linear dependence of intensive of absorption on the concentration of solution **4** (Fig. 2). In the IR spectrum of **4**, the bands at 2964, 2925 and 2853 cm^{-1} correspond to C-H stretching vibrations of alkyl groups. The band at 3237 cm^{-1} can be assigned to stretching vibrations of isoindole N-H bond. The ^1H NMR spectrum of **4** reveals a signal at 11.18 ppm, which can be assigned to absorption of proton of the isoindole N-atom [10, 26, 27].



3 2 4

i: PhOH, τ = 60 h, t = 100-110 °C

Scheme 2. The synthesis of ABBB-type macroheterocyclic compound
Схема 2. Синтез макрогетероциклического соединения ABBB типа

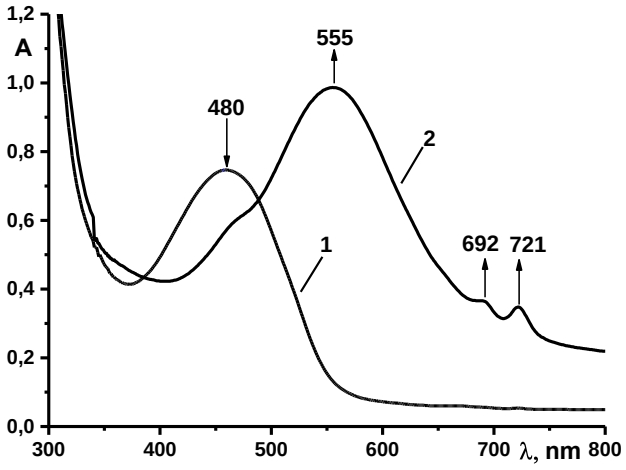


Fig. 1. UV-spectra of 4: 1 – CH_2Cl_2 ($c = 1.49\cdot10^{-4}$ mol·L^{-1}); 2 – CF_3COOH ($c = 1.49\cdot10^{-4}$ mol·L^{-1})
Рис. 1. УФ спектры 4: 1 – CH_2Cl_2 ($c = 1.49\cdot10^{-4}$ моль·л$^{-1}$); 2 – CF_3COOH ($c = 1.49\cdot10^{-4}$ моль·л$^{-1}$)

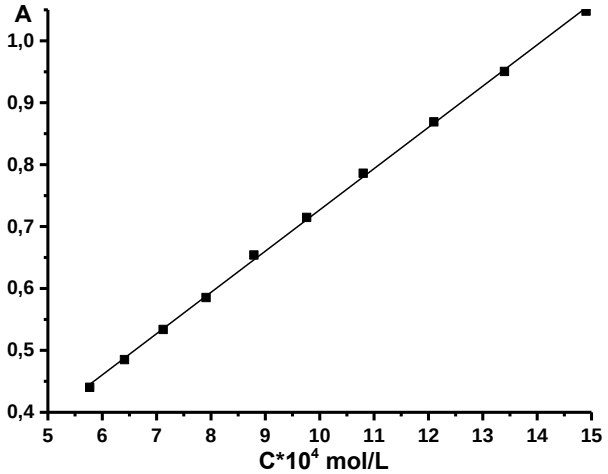


Fig. 2. Dependence of absorption intensity on the concentration of 4 (acetone, λ_{max} = 457 nm)
Рис. 2. Зависимость интенсивности поглощения от концентрации 4 (ацетон, λ_{max} = 457 нм)

CONCLUSIONS

The first representative of macroheterocyclic compound containing three isoindoline and one 2- alkyl-1,2,4-thiadiazoline fragments was synthesized.

ACKNOWLEDGMENT

This work was carried out by financial support from Russian Science Foundation 14-23-00204.

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Поступила в редакцию 23.05.2016
Принята к опубликованию 27.06.2016

Received 23.05.2016
Accepted 27.06.2016