ISSN 1070-3632, Russian Journal of General Chemistry, 2018, Vol. 88, No. 9, pp. 2000–2012. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © E.A. Danilova, T.V. Kudayarova, M.K. Islyaikin, O.I. Koifman, 2016, published in Rossiiskii Khimicheskii Zhurnal, 2016, Vol. 60, No. 2, pp. 59–74.

Synthon-Based Approach to the Design of Macroheterocyclic Compounds Using Diaminothiadiazoles and Diamonotriazoles

E. A. Danilova[a]*, T. V. Kudayarova[a], M. K. Islyaikin[a], and O. I. Koifman[a]

[a] *Ivanovo State University of Chemistry and Technology, pr. Sheremetevskii 7, Ivanovo, 15300 Russia*
**e-mail: danilova@isuct.ru*

Received March 15, 2016

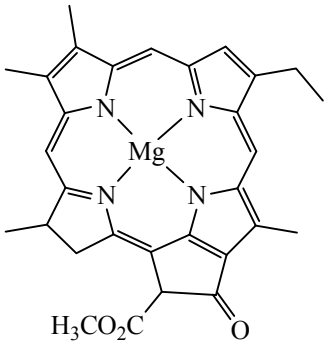
Abstract—Synthesis and properties of 2,5-diamino-1,3,4-thiadiazole, 3,5-diamino-1,2,4-thiadiazole, 3,5-diamino-1*H*-1,2,4-triazole, 3*N*-alkyl-5-amino-3-imino-1,3,4-thiadiazolines, 2*N*-alkyl-5-amino-3-imino-1,2,4-thiadiazolines, and 1-alkyl-3,5-diamino-1,2,4-triazoles as building blocks of macroheterocycles compounds are reviewed.

Keywords: 2,5-diamino-1,3,4-thiadiazole, 3,5-diamino-1,2,4-thiadiazole, 3,5-diamino-1*H*-1,2,4-triazole, synthesis, properties
DOI: 10.1134/S1070363218090438

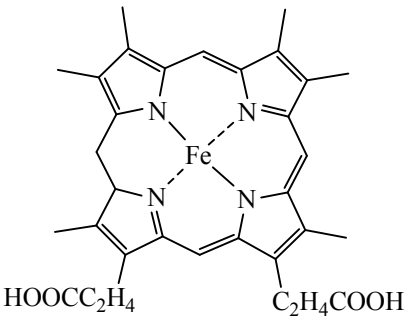
INTRODUCTION

Five-membered heteroaromatic compounds having no less than two heteroatoms in the ring, at least one of which is nitrogen, as well as bi- and polycyclic compounds containing such heteroring are commonly named *azoles* [1]. Amines, amides, azoles and other nitrogen-containing compounds plays the central role in organic and bioorganic synthesis. As known, the fist organic compound synthesized by Wöhler in 1827 from two inorganic ones is a precursor of a number of nitrogen-containing compounds including azoles. Evidence for this postulate is provided by the fact that the nature chose pyrrole and other nitrogen-containing derivatives (amino acids and nucleotides) are considered to be the building blocks for the molecules of life: hemoglobin and chlorophyll [5–7]. The similarity of the structures of azole-containing compounds and biomolecules gave impetus to the development of pharmaceutical and agrochemical industries.

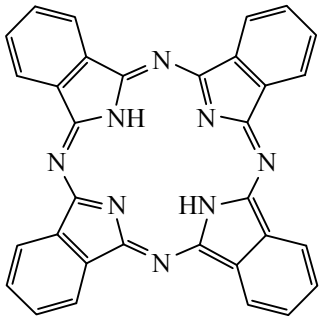
Thus, the targeted synthesis and study of thiadiazoles led to the synthesis of a wide range of medicines with diverse biological activity [8–10]. For example, Diacarb, Ethazol, and Tizanidine contain a 1,3,4-thiadiazole fragment; the 1,2,4-triazole fragment is the basic structural motif of known antiviral (Ribavirin), antifungal (Fluconazole), and sedative (Triazolam) drugs [11].



Chlorophyll



Hemoglobin



Phthalocyanine

Furthermore, nitrogen-containing five-membered heterocycles have found application in the production of dyes, detergents, surfactants, fabric softeners, stabilizers, epoxide hardeners, and vulcanizing agents and additives in petroleum industry [12–15].

The green plant pigment chlorophyll has long been used for curing skin wounds and sores. Over the past years new curative qualities of chlorophyll as a remedy against infectious and cancer diseases have been discovered [16].

At the beginning of XX century researchers found evidence showing that blood hemoglobin is structurally similar to chlorophyll. The only difference is that the first, protein structure forms around iron and the second, peptide structure forms around magnesium. Chlorophyll was given the name "*the green blood of plants*" [17].

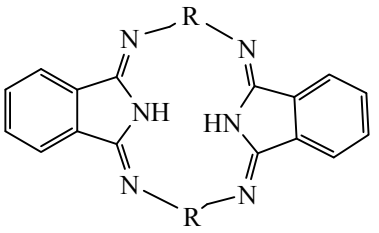
Such natural compounds predetermine the very possibility of the existence and development of life on the Earth, because they are involved in photosynthesis and breathing. Photosynthesis attracts attention of biologists, biochemists, chemists, and physicists; studying such processes on model compounds opens prospects for a deeper understanding and explaining processes that occur in a living body.

The phthalocyanine molecule can be considered as an aza analog of hemoglobin and chlorophyll. The conjugated aromatic system of phthalocyanine consists of four isoindole fragments linked to each other by aza bridges, which form a "rigid" cavity capable to coordinate the metal ions [18].

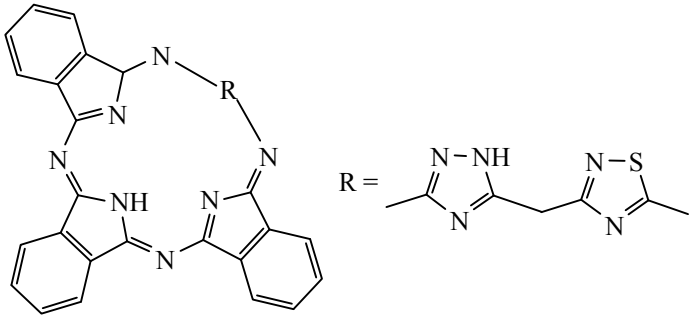
Design of a new complex compound synthesis is not infrequently based on the retrospective analysis, when the target molecule is disconnected into simple and readily accessible synthons. Such synthon approach allows to design macroheterocyclic systems differing in the composition and number of small cycles, which, unlike phthalocyanine, are isoindole fragments and residues of aromatic carbo- and heterocyclic diamines.

As a result, macroheterocyclic compounds (Mc) differing in the composition and size of the coordination cavity were synthesized [19–30].

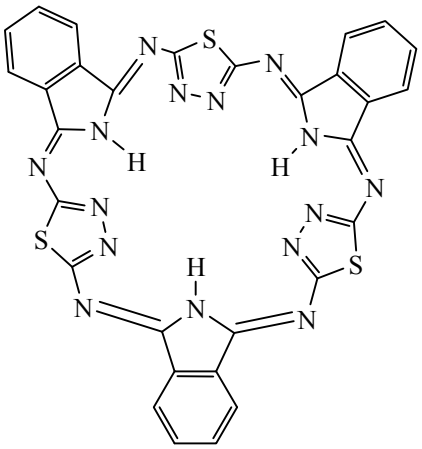
Macroheterocyclic compounds are cyclic sequences of 4 (^{4}Mc) or 6 (^{6}Mc) small cycles: carbo- and heterocyclic diamine residues (**A**) and pyrrole or isoindole fragments (**B**), linked to each other via aza bridges. The number of **A** and **B** fragments can be different and is used as the basis of classification of macroheterocycles: **ABAB**, **ABBB**, **AABAAB**, **ABBABB**, and **ABABAB**.



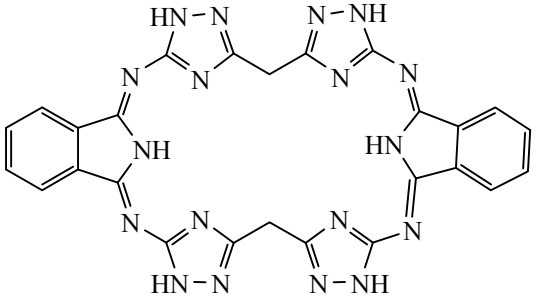
ABAB



ABBB



ABABAB



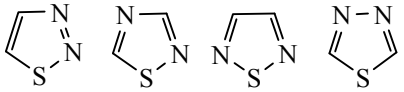
AABAAB

Five-member diaminoazoles are widely used as precursors of macroheterocyclic compounds [31–39].

Taking the aforesaid into account, the development or improvement of known methods of synthesis of heterocyclic compounds and their alkyl derivatives to be used as precursors of drugs [11], dyes [40], or macroheterocyclic compounds can be considered as actual task in terms of the synthesis of practically important organic compounds [41].

In the present review we consider the methods of synthesis of 2,5-diamino-1,3,4-thiadiazole, 3,5-diamino-1,2,4-thiadiazole, and 3,5-diamino-1*H*-1,2,4-triazole as the most important precursors of Mc.

2,5-Diamino-1,3,4-thiadiazole. Depending on the positions of the nitrogen and sulfur atoms in the five-membered ring, four thiadiazole structures are differentiated: 1,2,3-thiadiazole (**1**), 1,2,4-thiadiazole (**2**), 1,2,5-thiadiazole (**3**), and 1,3,4-thiadiazole (**4**):



1 **2** **3** **4**

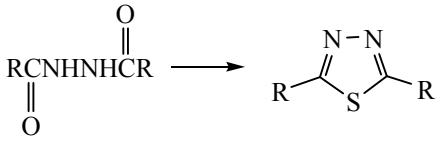
Thiadiazoles have a 6 π-electron aromatic system. The physical and chemical properties of thiadiazoles are similar to those of five-membered diazoles, where the sulfur atom is replaced by a methylene group [42].

3,5-Diamino-1,2,4- (**2**) and 2,5-diamino-1,3,4-thiadiazoles (**4**) are used as precursors of Mc [19–23, 25, 27–29, 36, 41–46]. At present, 2,5-diamino-1,3,4-thiadiazole is the most studied among the isomeric thiadiazoles [47].

1,3,4-Thiadiazoles were prepared by the cyclization of the corresponding carbamoylthiosemicarbazides under the action of acylating agents followed by the dehydration of the resulting products with phosphoric or sulfuric acid, or their anhydrides [48] (Scheme 1).

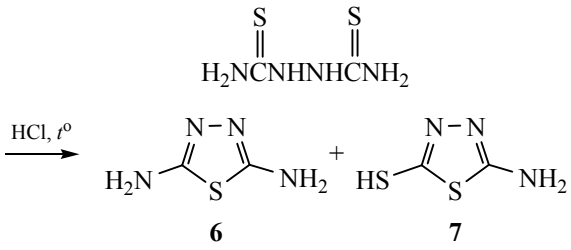
Treatment of dithiourea (**5**) or its derivatives with HCl or phosgene, too, gave thiadiazoles which were

Scheme 1.



R = NH_2, Alk, Ar.

Scheme 2.



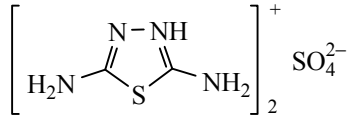
6 **7**

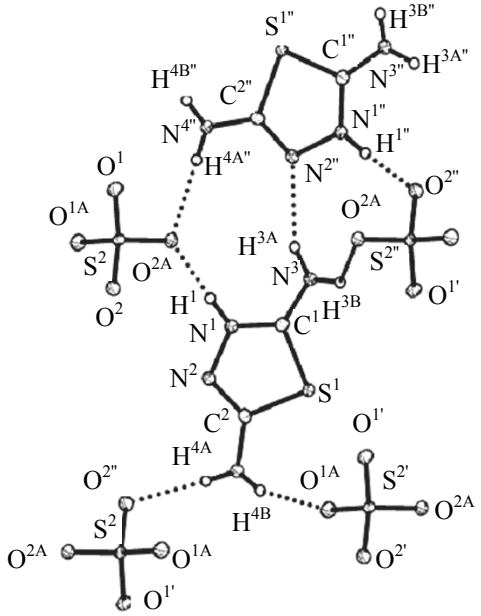
initially misidentified as triazoles [49]. Later the products were identified as substituted 1,3,4-thiadiazoles **6** and **7** [50] (Scheme 2).

The above-described methods did not find practical application, because carbamoylthiosemicarbazides are hardly accessible and the yield of the target product is low in both cases.

Analysis of published data showed that compound **6** is easier synthesized by oxidative condensation of dithiourea [51] (Scheme 3).

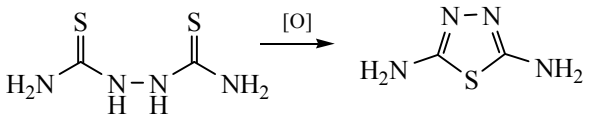
2,5-Diamino-1,3,4-thiadiazole was prepared in a yield of 40–43% [43]; the structure of compound **8** after this synthesis was established by X-ray analisys analysis [36, 52].





8

Scheme 3.



5 **6**

The use of 26% H_2O_2 together with the analytical control of oxidative condensation allowed the yield of compound **6** to be increased to 79–98% [53].

In 2011–2014, Adediji et al. published a series of works [54–56], where compound **6** was synthesized in a yield of 96% by treatment of dithiourea with H_2O_2 for 1 h at 50–60°C. However, we failed to reproduce this synthesis.

3-Alkyl-5-amino-2-imino-1,3,4-thiadiazolines. The question of the reactivity of 2,5-diamino-1,3,4-thiadiazole in electrophilic substitution reactions is still under discussion.

In 1929 Stolle and Fehrebach [57] suggested that 2,5-diamino-1,3,4-thiadiazole (**6**) can exist in three tautomeric forms: 2,5-diamino-1,3,4-thiadiazole (**6**), 2-imino-5-amino-1,3,4-thiadiazoline (**6a**), 2,5-diimino-1,3,4-thiadiazolidine (**6b**) (Scheme 4).

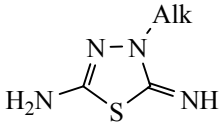
Initially it was considered that the acylation of compound **6** involves the ring imino nitrogens in the 3 and 4 positions (**6b**) [58]. However, Fromm [51] obtained opposite results and provided evidence that acylation involves the primary amino groups (**6**).

Diazotization of 2,5-diamino-1,3,4-thiadiazole in conc. HCl resulted in exclusive formation of a monoazonium salt whose coupling with phenol gave an azocompound [57]. As shown in [59–61], the reaction of compound **6** with benzaldehyde also involves one aminogroup. Al-Shammary in 2012 [62] reported the synthesis of a bisazomethine derivative by the reaction of compound **6** with benzaldehyde in a 1 : 1 molar ratio; however, the product was characterized only by elemental analysis.

In 1977 [37], 2-amino-1,3,4-thiadiazole was alkylated with methyl iodide to form 3*N*-methyl-2-imino-1,3,4-thiadiazoline.

First publications on the direct 3N-alkylation of 2,5-diamino-1,3,4-thiadiazole date back to 2004 [63]. Compound **6** was alkylated with butyl bromide in boiling MeOH. 5-Amino-3-butyl-2-imino-1,3,4-thiadiazoline (**10**) was isolated after treatment of the reaction mixture with aqueous ammonia solution(Scheme 4).

Later we synthesized *N*-alkyl-1,3,4-thiadiazolines **11**–**15** [37, 64]. The structures of compounds **10**–**15** were established by elemental analysis, mass spectrometry, and IR and ^{1}H NMR spectroscopy.

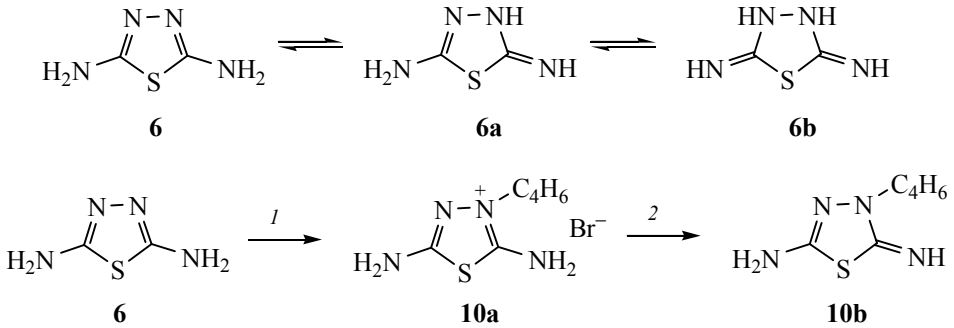


11–15

Alk = C_5H_{11} (**11**), $C_{10}H_{21}$ (**12**), $C_{12}H_{25}$ (**13**), $C_{15}H_{31}$ (**14**), $C_{16}H_{33}$ (**15**).

Evidence for the 3N-alkylation of compound **6** was obtained from the X-ray analysis of the trimer obtained from 5-amino-2-imino-3-pentyl-1,3,4-thiadiazoline (**11**) [65]. Further evidence for the alkylation site can be found in the work of Sano et al. [66] who isolated the intermediate product of the reaction of 5-substituted 2-amino-1,3,4-thiadiazole with α-haloketone and performed its X-ray analysis to establish that the substituent entered the 3 position.

Scheme 4.

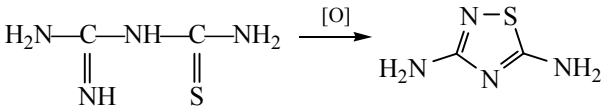


6 **6a** **6b**

6 **10a** **10b**

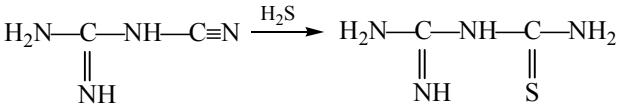
(*1*) *n*-C_4H_9Br, MeOH, 24 h, reflux; (*2*) aqueous NH_3.

Scheme 5.



17 **16**

Scheme 6.



17

Substituted thiadiazolines **10–15** are better soluble in organic solvents: alcohols, benzene, chloroform, and dichloromethane but insoluble in water. As known, most 1,3,4-thiadiazole derivatives exhibit pronounced biological activity: herbicidal, antiviral, antiparasitic, and antitubercular [67]. 2,5-Diamino-1,3,4-thiadiazole (**6**) and alkylated thiadiazolines **11–15** were tested for antimicrobial activity on standard *Escherichia Coli, Staphylococcus aur., Staphylococcus alb.* and *Bacillus sp*. strains [68].

Antimicrobial activity against *Staphylococcus alb.*, as measured by the diameter of the growth inhibition zone (lysis zone dimeter *d*), was revealed in thiadiazole **6** (d = 1.55 mm) and thiadiazolines **12** and **13** containing respectively decyl (d = 1.96 mm) and dodecyl substituents (d = 1.69 mm). The aliphatic chain length in the alkyl substituent is one of the important activity and toxicity factors. Usually, the effect enhances as the number of carbon atoms in the aliphatic chain increases to six. In our case, the effect enhances in going to compound **12** having 10 carbon atoms in the alkyl substituent. Further elongation of the aliphatic chain length in going to compound **13** attenuates the effect, and compounds **14** and **15** show no activity.

3,5-Diamino-1,2,4-thiadiazole. The synthesis of 3,5-diamino-1,2,4-thiadiazole **16** is based on the oxidative condensation of 2-imino-4-thiobiuret **17** [69] (Scheme 5).

2-Imino-4-thiobiuret **17** (reference antihypoxic agent Gutimin) and its derivatives are widely used in medical practice [70–72]. *S*-Allyl derivatives of 2-imino-4-thiobiuret were proposed as antitumor therapeutics [73, 74].

The present interest in compound **17** is also associated with its importance for template self-assembly processes [75, 76]. In this case this compound acts as an organic ligand which can take part in proton transfer, as well as an anion in coordination reactions [77].

Compound **17** is most commonly synthesized by the reaction of dicyandiamide with gaseous hydrogen sulfide [69, 78–80] (Scheme 6).

Compound **17** can also be prepared by prolong passing H_2S through a hot aqueous solution of dicyandiamide and oxalic acid at pH 0.7–3.0 [81]. The yield of the target product by the above-described procedures was low (32–42%).

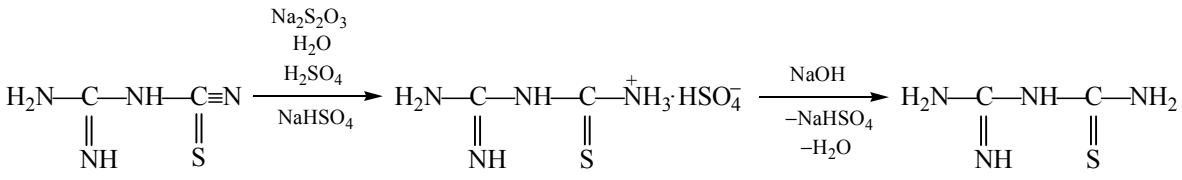
In 1997 Tomchin et al. patented a method which excluded the use of hydrogen sulfide [82]. The yield of the target product was unstable and varied from 25 to 44%. In 2008, a new method of synthesis of compound **17** was patented [83–85], which involved the reaction of dicyandiamide with sodium thiosulfate pentahydrate in dilute H_2SO_4 (Scheme 7).

2-Imino-4-thiobiuret precipitated as colorless transparent prismatic-shaped crystals readily soluble in water at room temperature and in methanol under heating. The product was identified by elemental analysis, IR spectroscopy, mass spectrometry, and X-ray analysis [83–85].

The last-described method of synthesis of compound **17** with an average yield of 84% and excluding the use of gaseous H_2S seems technologically acceptable [84, 88].

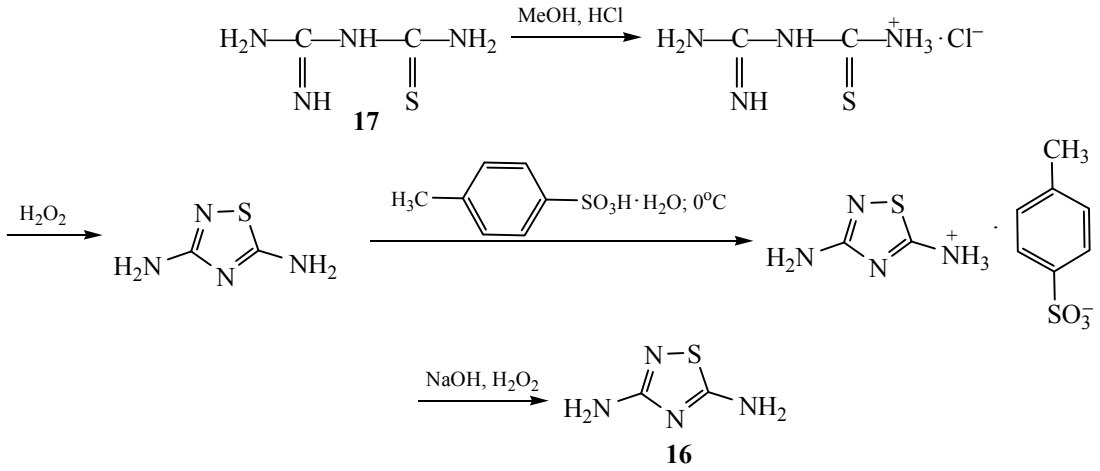
3,5-Diamino-1,2,4-thiadiazole **16** was earlier prepared by the procedure described in [69] (Scheme 8).

Scheme 7.

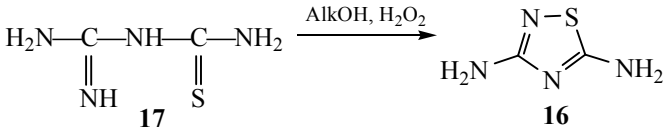


18 **17**

Scheme 8.



Scheme 9.



The total time of the synthesis, isolation, and purification of compound **16** was more than 55 h and its yield was 32–50%.

We proposed a technologically convenient synthesis of compound **16** [86]. The synthesis involves only one stage, owing to which the synthesis time could be decreased to 2 h and the yield of the target product could be increased from 50 to 86% (Scheme 9).

3,5-Diamino-1,2,4-thiadiazole (**16**), like 2,5-diamino-1,3,4-thiadiazole (**6**), can exist in different tautomeric forms [39], as confirmed by quantum-chemical calculations [87], and has several nucleophilic centers available for alkylation.

Along with compounds with *N*-alkyl-substituted end amino groups, which were synthesized from alkylated thioureas [88, 89], the structures of 3,5-diamino-2*H*-1,2,4-thiadiazoles **19** and **20** established by X-ray analysis were also reported [90] (Scheme 10).

It can be suggested that the N^4 atom of compound **16** is the most basic one, like that takes place in the case of compound **6**, can act as a nucleophilic center in electrophilic substitution reactions leading to N-substituted thiadiazolines. Evidence for this suggestion is provided by the synthesis of previously unknown N^2-alkyl-5-amino-3-imino-1,2,4-thiadiazolines **21** and **22** (Scheme 11).

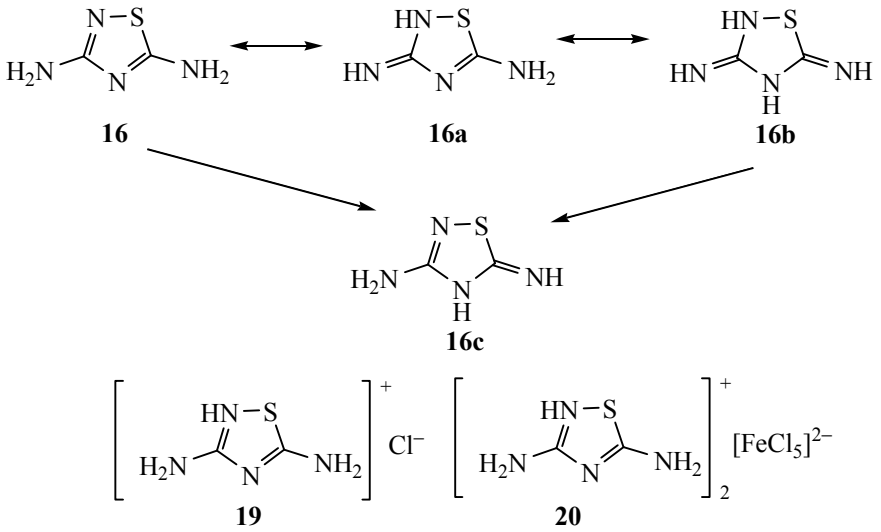
Alkylation was performed with pentyl and dodecyl bromides in methanol. The structures of the products were established by mass spectrometry, electronic absorption (EA) and IR spectroscopy, and elemental analysis [91].

The mass spectrum of compound **21** contains a molecular ion peak (*m/z* 186); the observed isotopic distribution of the molecular ion is completely coincident with theoretical one.

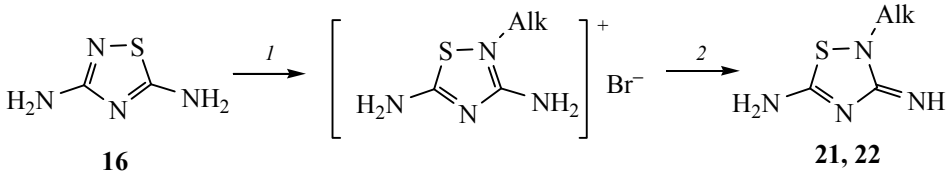
The EA spectra of solutions of compounds **21** and **22** in methylene chloride contain strong absorption bands with maxima at 261 and 263 nm, respectively. As the alkyl chain length increases, the absorption maximum slightly shifts to higher wavelengths site.

The IR spectra of the synthesized alkyl-1,2,4-thiadiazolines are similar to each other. Thus, the bands at 3428 and 3270 cm^{-1} correspond to asymmetric and symmetric stretching vibrations of the N–H band son the primary amino group. The band at 3057 cm^{-1} relates to stretching vibrations of the imino N–H bond. The bands at 2992 and 2854 cm^{-1} are assignable to asymmetric and symmetric stretching

Scheme 10.



Scheme 11.



Alk = C_5H_{11} (**21**), $C_{12}H_{25}$ (**22**); (*1*) *n*-AlkBr, MeOH, 24 h, reflux; (*2*) aq. NH_3.

vibrations of alkyl C–H bonds, and the bands at 1616 and 1586 cm^{-1}, to skeletal deformation vibrations and stretching vibrations of the C=N bonds.

The ^{13}C NMR spectra show signals of alkyl carbons atoms 47.51, 29.15, 27.89, 22.61, and 14.26 ppm, as well as signals of thiadiazole ring carbons atoms 162.77 and 147.49 ppm.

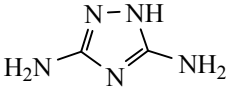
The yield of the target products was not higher than 7–10%. The low yield of compounds **21** and **22** is explained by the fact that the heteroring proved to be unstable in alkaline medium and decomposed to the starting dicyandiamide. Using metallic potassium or lithium instead of sodium and ethanol or butanol as solvent, as well as raising the reaction temperature, too, did not lead to success. The starting thiadiazole either did not react (in the case of potassium) or completely decomposed to give thiourea (in the case of lithium) [92].

To increase the yield of alkylthiadiazolines, we resorted to microwave activation. The reaction of compound **16** with dodecyl bromide in methanol in the presence of potash and tetrabutylammonium bromide was performed on a Discover LabMate microwave system at a power of 5 W, synthesis time 10–60 min. After that, the white suspension was poured onto ice, the precipitate that formed was filtered off, the filtrate was extracted with chloroform, and the solvent was removed. The product was purified and characterized by IR spectroscopy. When the synthesis was prolonged to 60 min, the yield of compound **22** increased from 8 to 80%.

Thus, microwave assisted direct alkylation of diaminothiadiazole with alkyl bromides allowed to synthesize of previously unknown N^2-alkyl-3,5-diamino-1,2,4-thiadiasolines.

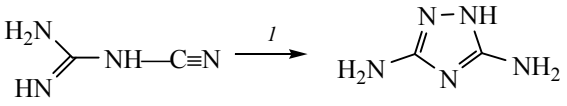
3,5-Diamino-1,2,4-triazoles. The high stability of the 1,2,4-triazole core is explained by its aromatic character. The aromatic sextet is formed by four π electrons of from double-bonded atoms and the lone electron pair of the secondary nitrogen atom.

3,5-Diamino-1,2,4-triazole (guanazole) (**23**) has a number of useful properties.



23

Scheme 12.



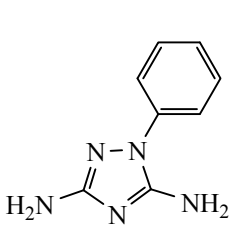
23

The 1,2,4-triazole fragment is frequently considered as principal motif in the design of new biologically active compounds, because it has a small size its precence and favors higher water solubility of the resulting structures. 1,2,4-Triazole and its derivatives have found application as precursors in the synthesis of macroheterocycles [93–95], herbicides, fogging inhibitors, drugs [47], and photoemulsion stabilizers [96]. Cationic dyes on the basis of aminotriazoles are light, heat, and wet fast [40].

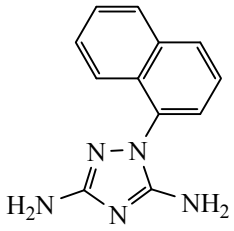
Compound **23** was first synthesized by Pellizzari [97] by heating dicyandiamide and hydrazine salt in the presence of alcohol in a sealed ampule at 100°C. Later Stolle and Krauch synthesized compound **23** by reacting dicyandiamide with hydrazine hydrate at 60–70°C (Scheme 12) [98].

3,5-Diamino-1*H*-1,2,4-triazole can exist in five tautomeric forms: amine–imine (**23c**, **23d**), diimine (**23e**), and diamine (**23a, 23b**). Evidence for the existence of these tautomers was obtained by UV and IR spectroscopy [47]. Quantum-chemical calculations [99] and X-ray analysis [100] established that a solid compound **23** exists as the asymmetric tautomer **23b**. The triazole ring is planar, and the amino groups deviate from the ring plane by 29.5° and 21.5°. The hydrogen atom on N^1, too, deviates from the ring plane (Scheme 13).

N^1-Substituted 3,5-diamino-1*H*-1,2,4-triazoles: 3,5-diamino-1-phenyl-1,2,4-triazole or *phenylguanazole* (**24**) and 3,5-diamino-1-(1-naphthyl)-1,2,4-triazole or *1-naphthylguanazole* (**25**) were synthesized by fusing dicyandiamide with the corresponding hydrazine hydrochloride [97, 101].



24



25

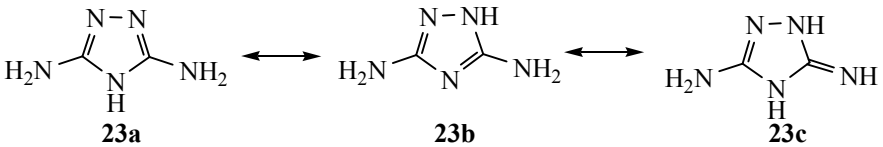
Alkyl derivatives of **23** are used in medicine as histamine and neurokinin receptor antagonists [47], peroxide lipid oxidation inhibitors [102], and anti-diabetic and other drugs [103, 104].

Compound **23** can be alkylated by a traditional procedure involving electrophilic substitution of hydrogen located at the endocyclic nitrogen by an alkyl radical. The most common alkylating agents are alkyl halides [105–110]. The most labor-consuming stage in the synthesis of N^1-alkyl-1,2,4-triazoles that stage of isolation and purification of the target products. Fuentes and Lenoir [105] isolated alkylguanazoles by treatment of the reaction mixtures with picric acid and subsequent conversion of the resulting picrates into free bases by ion-exchange column chromatography. The yields of alkylguanazoles by this procedure were dound to be not higher than 40%.

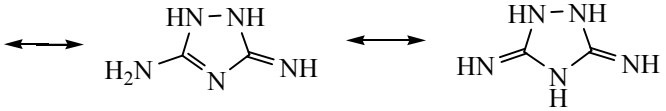
To isolate 1-decyl-3,5-diamino-1,2,4-triazole, Yagodarova et al. [108] first removed the excess of the alkylating agent and then extracted the target product by an organic solvent, which allowed to increase the yield to 73%.

Werber et al. [37] synthesized compounds **26**–**29** by reacting thiazole **23** with the corresponding alkyl bromides in the presence of sodium methanolate in methanol under reflux (Scheme 14).

Scheme 13.

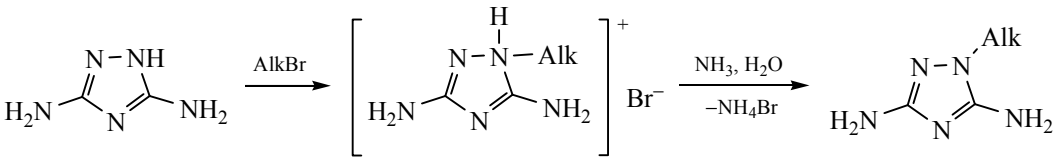


23a **23b** **23c**



23d **23e**

Scheme 14.



23 **23–29**

Alk = C_5H_9 (**26**), $C_{10}H_{21}$ (**27**), $C_{12}H_{25}$ (**28**), $C_{16}H_{31}$ (**29**).

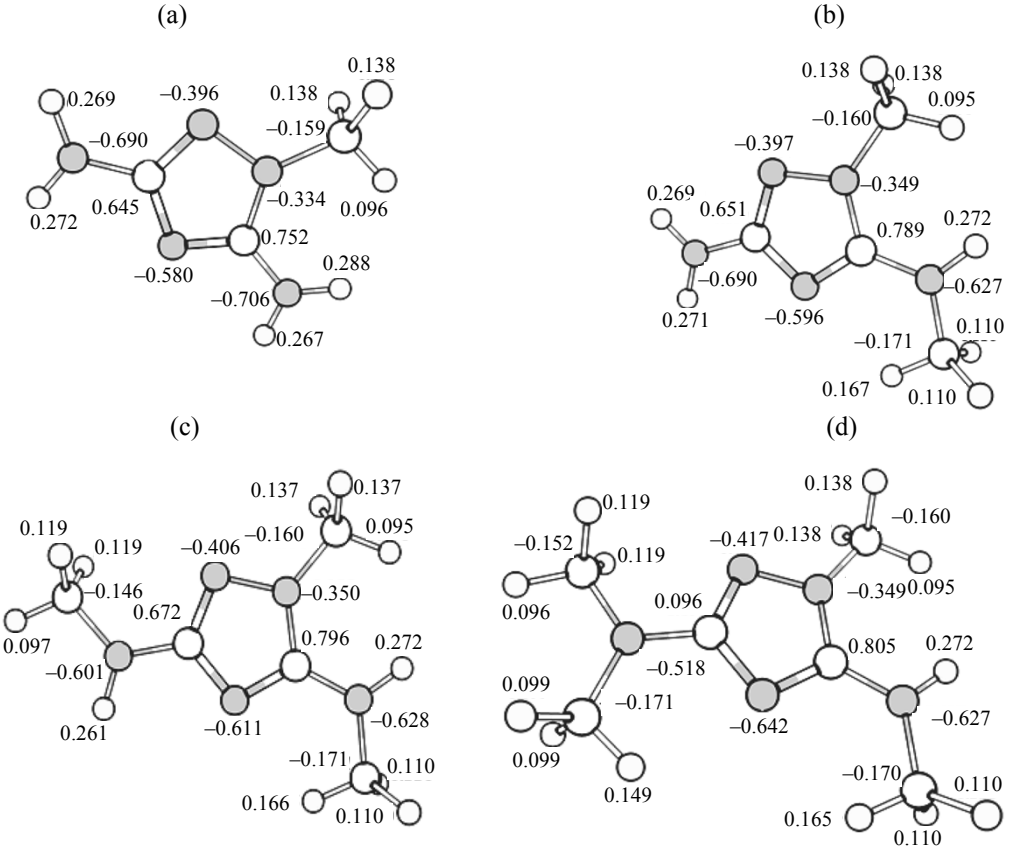
Gas chromatography showed that reaction proceeded nonselectively to give di- and trialkylated guanazoles along the target monoalkylated product [111].

Molecule **23** contains a few nucleophilic centers which can be involved in electrophilic substitution reactions. In this connection it was interesting to determine the order of alkylation of compound **23**. Thus, the probable alkylation products were calculated by DFT method using B3LYP hybrid functional with 6-31G(d,p) basis set using GAMESS V.7 [112, 113].

Selected results of calculations are presented in the figure.

The atomic charges showed that the most preferable alkylation site is the endocyclic N^1 distribution atom (**23a**). Further both nitrogens of amnogroups are consecutively involved in alkylation, first that in the C^5–NH_2 group (**23b**) and then that in the C^3–NH_2 group, to form trialkylated product **23c**. The fourth alkylation step can involve substitution of the remaining hydrogen atom in C^5–NH_2 group (**23d**).

The alkylation of compound **23** with decyl bromide gave mono-, di-, tri-, and tetra-alkylation products [114]. Therefore, the alkylation products should be separated. The best results were obtained by the



Configurations of compounds (a) **23a**, (b) **23b**, (c) **23c**, and (d) **23d**, optimized by the DFT/B3LYP/6-31G(d,p) method.[1]

[1] The calculations were performed by the Master's degree student A.A. Ivolin.

extraction of alkylguanazoles with chloroform from the reaction mixture followed by recrystallization of the residue remaining after removal of the solvent by distillation. By-products were then extracted with hexane, and the solid material was recrystallized from ethanol. Finally, monoalkylated 3,5-diamino-1,2,4-triazoles **26**–**29** were purified by column chromatography on silica (hexane : ethyl acetate 1 : 3) [115]. The yield of the target products was 50–60%.

Some of the synthesized compounds were tested for biological activity [116]. 3,5-Diamino-1,2,4-thiadiazole exhibited antibacterial activity against

Escherichia Coli and *Staphylococcus aur*. and moderate anticancer activity on the L-1210 lymphoid leukemia model, which prompts targeted synthesis and search for more active derivatives among 1,2,4-triazole derivatives.

Thus, advanced methods of synthesis of 2,5-diamino-1,3,4-thiadiazole, 3,5-diamino-1,2,4-thiadiazole, 3,5-diamino-1*H*-1,2,4-triazole, N^3-alkyl-5-amino-2-imino-1,3,4-thiadiazolines, N^2-alkyl-5-amino-3-imino-1,2,4-thiadiazolines, and N^1-alkyl-3,5-diamino-1,2,4- triazoles, described in the present review, allow facile synthesis of diaminoazoles and are technologically feasible, which opens up perspectives for their further use in the synthesis of new drugs and complex macroheterocyclic molecules.

ACKNOWLEDGEMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 14-23-00204).

CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

REFERENCES

1. Knunyants, I.L., *Khimicheskaya entsiklopediya: Ablyatsionnye materialy – Darzana reaktsiya* (Ablation Reactions – Darzen's Reaction), Knunyants, I.L., Ed., Moscow: Sovetskaya Entsiklopediya, 1988, vol. 1.
2. Wöhler, F., *Ann. Phys. Chem*., 1828, vol. 88, no. 2, p. 253. doi 10.1002/ andp.18280880206
3. Kauffman, G.B. and Chooljian, S.H., *J. Chem. Ed*., 1997, vol. 74, no. 12, p. 1493. doi 10.1021/ed074p1493
4. Nicolaou, K.C. and Montagnon, T., *Molecules that Changed the World*, Weinheim: Wiley–VCH, 2008, p. 11. ISBN 978-3-527-30983-2.
5. Waldmann, H., Janning, P., *Chemical Biology. A Practical Course*, Weinheim: Wiley–VCH, 2004, XXIII. ISBN 978-3-527-30778-4
6. Schreiber, S. L., Kapoor, T., and Wess, G., *Chemical Biology: From Small Molecules to Systems Biology and Drug Design*, Weinheim: Wiley–VCH, 2007, vols. 1–3, p. 593.
7. Tyukavkina, N.A. and Bukov, Yu.I., *Bioorganicheskaya khimiya* (Bioorganic Chemistry), Moscow: DROFA, 2004.
8. Kumar, K.A., Kumar, G.V., and Renuka, N., *Int. J. Pharm. Tech. Res*., 2013, vol. 5, no. 1, p. 239. http://www.sphinxsai.com/2013/janmar/pharmpdf/PT=33(239-248)JM13.pdf
9. Marcinkeviciene, J., Rogers, M.J., Kopcho, L., Jiang W., Wang, K., Murphy, D.J., Lippy, J., Link, S., Chung, T.D.Y., Hobbs, F., Haque, T., Trainor, G.L, Slee, A., Stern, A.M., and Copeland, R.A., *J. Biochem. Pharmacol*., 2000, vol. 60, p. 339. doi 10.1016/S0006-2952(00)00348-8
10. Ishikawa, T., Iizawa, Y., Okonogi, K., and Miyake, A., *J. Antibiot*., 2001, vol. 54, p. 257. PMID: 11372783.
11. Mashkovskii, M.D., *Lekarstvennye sredstva* (Drugs), 14th ed., vol. 1, Moscow: Novaya Volna, 2002, p. 540. ISBN 5-7864-0128-67.
12. Chandran, D.V. and Bhatnagar, R.K., *J. Am. Oil Chem. Soc*., 1968, vol. 45, no. 8, p. 581.
13. *Detergency of Specialty Surfactants, Surfactant Science Series: Book 98*, Friedli, F.E., Ed., New York: Marcel Dekker, 2001.
14. Hayes, K.S., *Appl. Catal. A*, 2001, vol. 221, nos. 1–2, p. 187. doi 10.1016/S0926- 860X(01)00813-4
15. Wittcoff, H.A., Reuben, B.G., and Plotkin, J.S., *Industrial Organic Chemicals*, Hoboken, NJ: Wiley–Interscience, 2004.
16. Mironov, A.F., *Itogi Nauki Tekh., Sovr. Probl. Lazer. Fiz*., Moscow: VINITI, 1990, vol. 3.
17. Chernomorsky, S.A. and Segelman, A.B., *New J. Med*., 1988, vol. 85, no. 8, p. 669.
18. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianina* (Coordination Compounds of Porphyrins and Phthalocyanine), Moscow: Nauka, 1978.
19. Bazanov, M.I., Berezin, B.D., Berezin, D.B., Galievskiy, G.A., Golubchikov, O.A., Danilova, E.A., Dzhagarov, B.M., Evstigneeva, R.P., Zhilina, Z.I., Islyaykin, M.K., Ishkov, Yu.V., Kruk, N.N., Kuvshinova, E.M., Kudrik, E.V., Kulinich, V.P., Kurek, S., Lomova, T.N., Mayzlish, V.E., Maua, E.M., Nicolau, M., Ponomarev, G.V., Pukhovskaya, S.G., Reshetnikov, A.V., Siling, S.A., Sokolova, T.N., Torres, T., Turpen, P.I., Usol'tzeva, N.V., Fernandez-Lazare, F., Chirvoniy, V.S., Shaposhnikov, G.P., and Shvetz, V.I.,, *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), Golubchikov, O.A., Ed., St. Petersburg: NII Khimii

S.-Peterb. Gos. Univ., 1999, vol. 2, p. 300.

20. Grin, M.A., Mironov, A.F., Semeikin, A.S., Syrbu, S.A., Koifman, O.I., Klyueva, M.E., Klyuev, M.V., Mamardashvili, N.Zh., Mamardashvili, G.M., Borovkov, V.V., Berezin, B.D., Berezin, D.B., Inoue, Y., Islyaikin, M.K., Danilova, E.A., Romanenko, Yu.V., Khelevina, O.G., Venedictov, E.A., and Perlovich, G.L., *Chemical Processes with Participation of Biological and Related Compounds*, Lomova, T.N. and Zaikov, G.E., Eds., Leiden: Brill, 2008, p. 219. ISBN 978 90 04 16210 5.
21. Islyaikin, M.K. and Danilova, E.A., *Russ. Chem. Bull., Int. Ed*., 2007, vol. 5, no. 4, p. 689. doi 10.1007/s11172-007-0107-z
22. Danilova, E.A., Melenchuk, T.V., Trukhina, O.N., Zakharov, A.V., and Islyaykin, M.K., *Makroheterocycles,* 2010, vol. 3, no. 1, p. 33. doi 10.6060/mhc2010.1.33
23. Islyaykin, M. K., Khelevina, O.G., Danilova, E.A., and Lomova, T.N., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*., 2004, vol. 47, no. 5, p. 35.
24. Zakharov, A.V., Shlykov, S.A., Krasnov, A.V., Girichev, G.V., Bumbina, N.V., Danilova, E.A., and Islyaikin, M.K., *Chem. Commun*., 2008, no. 30, p. 3573. doi 10.1039/b104308f
25. Zakharov, A.V., Shlykov, S.A., Krasnov, A.V., Girichev, G.V., Danilova, E.A., and Islyaikin, M.K., *Phys. Chem. Chem. Phys*., 2009, vol. 11, no. 38, p. 8570. doi 10.1039/B908977B
26. Trukhina, O.N., Rodríguez-Morgade, M.S., Caballero, E., Torres, T., Danilova, E.A., Islyaikin, M.K., Wolfrum, S., Guldi, D.M., Snejko, N., and Gutiérrez-Puebla, E., *J. Am. Chem. Soc*., 2010, vol. 132, no. 37, p. 12991. doi 10.1021/ja104577d
27. Zhabanov, Y.A., Zakharov, A.V., Shlykov, S.A., Trukhina, O.N., Danilova, E.A., Koifman, O.I., and Islyaikin, M.K., *J. Porphyrins Phthalocyanines*, 2013, vol. 17, no. 3, p. 220. doi 10.1142/S1088424613500144
28. Trukhina, O.N., Danilova, E.A., Islyaikin, M.K., Zhabanov, Y.A., and Krasnov, A.V., *J. Porphyrins Phthalocyanines*, 2011, vol. 15, nos. 11–12, p. 1287. doi 10.1142/S108842461100418X
29. Filatov, M.S., Kudayarova, T.V., Danilova, E.A., and Islyaykin, M.K, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*., 2014, vol. 57, no. 7, p. 21.
30. Danilova, E.A., Butina, Yu.V., Kudayarova, T.V., and Islyaykin, M.K., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*., 2014, vol. 57, no. 10, p. 203.
31. Smith, M.B. and March, J., *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*, New York: Wiley, 2001, 5th ed., p. 499.
32. Emerson, W.S., *Organic Reactions*, Adams, E., Ed., New York: Wiley, 1948, vol. 4, p. 175. doi 10.1002/0471264180.or004.03
33. Gribble, G.W., *Chem. Soc. Rev*., 1998, vol. 27, p. 395. doi 10.1039/A827395Z
34. Olsen, C.A., Franzyk, H., and Jaroszewski, J.W., *Synthesis*, 2005, no. 16, p. 2631. ISSN 0039-7881.
35. Melenchuk, T.V., Danilova, E.A., Stryapan, M.G., and Islyaikin, M.K., *Russ. J. Gen. Chem*., 2008, vol. 78, no. 3, p. 480. doi 10.1134/S1070363208030237
36. Danilova, E.A., Melenchuk, T.V., Trukhina, O.N., and Islyaykin, M.K., *Makrogeterotsikly,* 2010, vol. 3, no. 1, p. 68. doi 10.6060/mhc2010.1.68
37. Werber, G., Buccheri, F., and Gentile, M., *J. Heterocycl. Chem*., 1977, vol. 14, no. 7, p. 1263. doi 10.1002/jhet.5570140727
38. Danilova, E.A., Talakueva, A.V., Galiev, R.M., Kudayarova, T.V., and Islyaykin, M.K., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*., 2013, vol. 56, no. 12, p. 107.
39. Moskvin, D.O., Sotsky, V.V., Danilova E.A., Kudayarova, T.V., Smirnova, A.I., and Usol'tseva, N.V., *Acta Phys. Pol. A*, 2015, vol. 127, no. 4, p. 950. doi 10.12693/APhysPolA.127.950
40. *The Chemistry of Synthetic Dyes*, Venkataraman, K., Ed., New York: Academic, 1952, vol. 1. Translated under the title *Khimiya sinteticheskikh krasitelei*, Leningrad: Gos. Nauchno-Tekhnicheskoe izdate'stvo Khimicheskoi Literatury, 1956, vol. 1, p. 803.
41. Danilova, E.A., Islyaykin, M.K., and Shtrygol', S.Yu., *Russ. Chem. Bull. Int. Ed*., 2015, no.7, p. 1610.
42. Joule, J.A. and Mills, K., *Heterocyclic Chemistry*, Chichester: Wiley, 2000, 4th ed. ISBN 0-632-05453-0.
43. Danilova, E.A., Bumbina, N.V., and Islyaykin, M.K., *Macroheterocycles,* 2011, vol. 4, no. 1, p. 47. doi 10.6060/mhc2011.1.10
44. Eckert, A.K., Trukhina, O.N., Rodríguez-Morgade, M.S., Torres, T., Danilova, E.A., and Islyaikin, M.K., *Mendeleev Commun*., 2010, vol. 20, no. 4, p. 192. doi 10.1016/j.mencom.2010.06.002
45. Melenchuk, T.V., Danilova, E.A., Vorontsova, A.A., Islyaykin, M.K., Enakieva, Yu.Yu., and Gorbunova, Yu.G., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*., 2009, vol. 52, no. 8, p. 113.
46. Islyaikin, M.K., Rodríguez-Morgade, M.S., Torres, T., Danilova, E.A., and Yagodarova, L.D., *Org. Lett*., 2001, vol. 3, no. 14, p. 2153. doi 10.1021/ol015924l
47. *Heterocyclic Compounds*, Elderfield, R.C., New York: Wiley, 1951. Translated under the title *Geterotsiklicheskie soedineniya*, Moscow: Mir, 1953, vol. 7, p. 500.
48. Busch, M., *J. Prakt. Chem*., 1930, vol. 124, p. 301.
49. Fromm, E., *Ann*., 1922, vol. 426, no. 3, p. 313. doi 10.1002/jlac.19224260310
50. *Khimiya i biologicheskaya aktivnost' sinteticheskikh i prirodnykh soedinenii. Kislorod- i serusoderzhashchie*

geterotsikly (Chemistry and Biological Activity of Synthetic and Natural Compounds. Oxygen- and Sulfur-Containing Heterocycles), Kartsev, V.G., Moscow: IBS PRESS, 2003. ISBN 5-902545-02-1.

51. Fromm, E., *Ann. Chem*., 1923, vol. 433, no. 1, p. 1. doi 10.1002/jlac.19234330102
52. Antonili, L., Cornia, A., Fabretti, A.C., and Malawasi, W., *J. Crystallogr. Spectrosc. Res*., 1993, vol. 23, no. 12, p. 967.
53. Melenchuk, T.V., Danilova, E.A., Islyaykin, M.K., and Kolesnikov, N.A., RF Patent 2313523, *Byull. Izobret*., 2007, no. 36.
54. Adediji, J.F., Ahmed, S.A., and Lawal, A., *Life J. Sci*., 2014, vol. 16, no. 1, p. 11.
55. Adeliji, J.F., Adebayo, M.A., and Obaleye, J.A., *Asian J. Appl. Sci*., 2011, vol. 4, no. 4, p. 392. doi 10.3923/ajaps.2011.392.402
56. Obaleye, J.A., Adeliji, J.F., and Adebayo, M.A., *Molecules,* 2011, vol. 16, no. 7, p. 5861. doi 10.3390/molecules16075861
57. Stolle, R. and Fehrebach, K., *J. Prakt. Chem*., 1929, vol. 122, p. 289. doi 10.1002/prac.19291220111
58. Guha, P.C., *J. Am. Chem. Soc*., 1923, vol. 45, no. 4, p. 1036. doi 10.1021/ja01657a024
59. Busch, M. and Holzmann, H, *Chem. Ber*., 1901, vol. 34, no. 1, p. 320. doi 10.1002/cber.19010340152
60. Busch, M. and Schmidt, R., *J. Prakt. Chem*., 1931, vol. 130, p. 342. doi 10.1002/prac.19311300126
61. *Five-Membered Heterocyclic Compounds with Nitrogen and Sulfur or Nitrogen, Sulfur, and Oxygen (Except Thiazole)*, Bambas, L.L., Ed., New York: Interscience, 1952, vol. 4, p. 124.
62. Al-Shammary, K.M.A., *J. Al-Nahrain Univ*., 2012, vol. 15, no. 3, p. 49.
63. Islyaykin, M.K., *Doctoral (Chem.) Dissertation*, Ivanovo, 2004.
64. Danilova, E.A., Melenchuk, N.V., and Islyaikin, M.K., *Proc. 23rd Int. Symp. on the Organic Chemistry of Sulfur*, June 29 – July 4, 2008, Moscow, p. 81.
65. Danilova, E.A., Melenchuk, T.V., Melekhonova, E.E., Tyutina, M.A., and Islyaykin, M.K., *Macroheterocycles*, 2009, vol. 2, nos. 3–4, p. 246.
66. Sano, S., Matsuura, K., Sumiyoshi, H., Miki, A., Kitaike, S., and Nakao, M., *Heterocycles*, 2014, vol. 89, no. 4, p. 1041. doi 10.3987/COM-14-12938
67. Yang Hu, Cui-Yun Li, Xiao-Ming Wang, Yong-Hua Yang, and Hai-Liang Zhu, *Chem. Rev*., 2014, vol. 114, no. 10, p. 5572. doi 10.1021/cr400131u
68. Kudayarova, T.V., Danilova, E.A., Islyaykin, M.K., and Kuznetsov, O.Yu., Abstracts of Papers, *Mezhdunarodnaya molodezhnaya nauchnaya shkola "Khimiya porfirinov i rodstvennykh soedinenii," Festival' Nauki, Ivanovskii gosudarstvennyi khimiko-tekhnologicheskii universitet* (Int. Youth Scientific School "Chemistry of Porphyrins and Related Compounds", Science Festival, Ivanovo State University of Chemical Technology), Ivanovo, 2012, p. 68
69. Kurzer, F., *J. Chem. Soc*., 1955, p. 1. doi 10.1039/JR9550000001
70. Stratton, K. and Davis, E.M., *Int. J. Radiat. Biol*., 1962, vol. 5, no. 2, p. 105. doi 10.1080/09553006214550621
71. Zarubina, I.V., Mironova, O.P., Krivoruchko, B.I., and Smirnov, A.V., *Vopr. Biol. Med. Farm. Nauki: Kvart. Nauch.-Prakt. Zh*., 2001, no. 1, p. 51.
72. Marysheva, V.V., *Obzory Klin. Farm. Lekarstv. Terapii: Retsenzir. Nauch.-Prakt. Zh*., 2007, vol. 5, no. 1, p. 17.
73. Vertesi, C., *Med. Hypotheses*, 1993, vol. 40, no. 6, p. 335. doi 10.1016/0306-9877(93)90214-B
74. Gergely, P., Lang, I., Gonzalez-Cabello R., and Feher, J., *J. Exp. Clin. Med*., 1986, vol. 11, p. 207.
75. Vilar, R., *Eur. J. Inorg. Chem*., 2008, vol. 2008, no. 3, p. 357. doi 10.1002/ejic.200701017
76. Amendola, V. and Fabbrizzi, L., *Chem. Commun*., 2009, vol. 5, p. 513. doi 10.1039/B808264M
77. Kabir, M.K., Yamada, K, Adachi, K., Kondo, M., and Kawata, S., *Acta Crystallogr., Sect. E*, 2002, vol. 58, p. m580. doi 10.1107/S1600536802017038
78. Castro, A., Castano, T., Encinas, A., and Porcal, W., *Bioorg. Med. Chem*., 2006, vol. 14, no. 5, p. 1644. doi 10.1016/j.bmc.2005.10.012
79. Baumann, E., *Ber. Dtsch. Chem. Ges*., 1873, vol. 6, no. 2, p. 1371. doi 10.1002/cber.187300602149
80. Sheehan, J.C., Buchi, G., and Knutson, D., *Organic Synth*., 1963, coll. vol. 4, p. 502.
81. Kondrashova, M.F. and Yarovenko, E.Ya., *Metody polucheniya khimicheskikh reaktivov i preparatov* (Methods of Synthesis of Chemical Reagents and Preparations), Moscow: Inst. Khimicheski Chistykh Reaktivov, 1970, p. 54.
82. Tomchin, A.B., Marysheva, V.V., Legostaeva, E.K., and Gordetsov, A.S., RF Patent 2088572, 1997.
83. Melenchuk, T.V., Konovalova, E.A., Danilova, E.A., Talanova, V.A., and Islyaykin, M.K., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*., 2008, vol. 51, no. 10, p. 125.
84. Danilova, E.A., Melenchuk, T.V., Konovalova, E.A., and Islyaykin, M.K., RF Patent 2381215, *Byull. Izobret*., 2010, no. 4.
85. Danilova E.A., Talakueva A.V., Galiev R.M., Kudayarova T.V., Islyaykin M.K., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*., 2013, vol. 56, no. 12, p. 107.
86. Danilova, E.A., Melenchuk, T.V., Islyaykin, M.K., and Sud'ina, E.E., RF Patent 2348623, *Byull. Izobret*., 2009, no. 7.

87. Kuznetsova, A.S., Danilova, E.A., and Islyaykin, M.K., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*., 2014, vol. 57, no. 6, p. 43.
88. Kagami, H., Hanzawa, T., Suzuki, N., Yamaguchi, Sh., Saito, M., and Motoki, Sh., *Bull. Chem. Soc. Jpn*., 1980, vol. 53, no. 12, p. 3658. doi 10.1246/bcsj.53.3658
89. Senda, H. and Maruha, J., *Acta Crystallogr., Sect. C*, 1985, vol. 41, p. 1626. doi 10.1107/S0108270185008812
90. Hołyńska, M., Korabik, M., and Kubiak, M., *Polyhedron*, 2010, vol. 29, no. 1, p. 530. doi 10.1016/j.poly.2009.06.045
91. Danilova, E.A., *Doctoral (Chem.) Dissertation*, Ivanovo, 2011.
92. Maksimova, E.V., Kudayarova, T.V., and Danilova, E.A., *Materialy V Vserossiyskoi konferentsii studentov i molodykh uchenykh "Molodezhnaya nauka v razvitii regionov"* (Proc. V Russian Conf. of Students and Young Scientists "Youth Science in Regional Development"), Perm: Perm. Nats. Issled. Politekh. Univ., 2015, p. 407. ISBN 978-5-398-01412-9.
93. Danilova, E.A., Islyaikin, M.K., and Smirnov, R.P., *Russ. J. Gen. Chem*., 1997, vol. 67, no. 8, p. 1289.
94. Rodríguez-Morgade, M.S., Torres, T., and Islyaikin, M.K., *Eur. J. Org. Chem*., 2002, no. 15, p. 2460. doi 10.1002/1099-0690(200208)2002:15<2460::AID-EJOC2460>3.0.CO;2-H
95. Islyaikin, M.K., Ferro, V.R., and Garcia de la Vega, J.M., *J. Chem. Soc., Perkin Trans. 2*, 2002, no. 12, p. 2104. doi 10.1039/B207034K
96. Polya, J.B., *Comprehensive Heterocyclic Chemistry*, Katritzky, A.R., Rees, C.W., and Potts, K.T., Eds., Oxford: Pergamon, 1984, vol. 5, p. 733.
97. Pellizzari, G., *Gaz. Chem. Ital.,* 1901, vol. 31, no. 1, p. 477.
98. Stolle, R. and Krauch, K., *Chem. Zbc*., 1905, vol. 84, p. 1467.
99. Makarskii, V.V., Zubkov, V.A., Lopyrev, V.A., and Voronkov, N.G., *Khim. Geterotsikl. Soedin*., 1977, no. 4, p. 540.
100. Strogova, G.L. and Frank-Kamenetskaya, O.V., *Khim. Geterotsikl. Soedin*., 1979, no. 10, p. 1422.
101. Pellizzari, G., *Ber. Dtsch. Chem. Ges*., 1891, p. 649.
102. Ivanova, N.V., *Doctoral (Chem.) Dissertation*, Moscow, 2006.
103. Granik, V. G. and Grigor'ev, N.B., *Oksid azota (NO): Novyi put' kpoisku lekarstv* [Nitrogen Monoxide (NO): A New Route in Search for Drugs], Moscow: Vuzovskaya Kniga, 2004.
104. Berecz, G., Reiter, J., Argay, G., and Kalman, A., *J. Heterocycl. Chem*., 2002, vol. 39, no. 2, p. 319. doi 10.1002/jhet.5570390213
105. Fuentes, J.J. and Lenoir, J.A., *Can. J. Chem*., 1976, vol. 54, no. 22, p. 3620. doi 10.1139/v76-520.
106. De la Torre, G. and Torres, T., *J. Org. Chem*., 1996, vol. 61, no. 18, p. 6446. doi 10.1021/jo960704k
107. Fernandez-Lazaro, F., De Mendoza, J., Mó, O., Rodriguez-Morgade, S., Torres, T., Yanez, M., and Elguero, J., *J. Chem. Soc. Perkin Trans. 2*, 1989, p. 797. doi 10.1039/P29890000797
108. Yagodarova, L.D., Danilova, E.A., and Smirnov, R.P., *Russ. J. Gen. Chem*., 2003, vol. 73, no. 2, p. 308.
109. Wang, M. and Wudl, F., *J. Mater. Chem*., 2010, vol. 20, no. 27, p. 5659. doi 10.1039/C0JM00254B
110. Ferrera-Escudero, S., Perozo-Rondón, E., Calvino-Casilda, V., Casal, B., Martín-Aranda, R.M., López-Peinado, A.J., and Durán-Valle, C.J., *Appl. Catal. A*, 2010, vol. 378, no. 1, p. 26. doi 10.1016/j.apcata.2010.01.041
111. Stolyarov, B.V., Savinov, I.M., and Vittenberg, A.G., *Prakticheskaya gazovaya i zhidkostnaya khromatografiya* (Practical Gas and Liquid Chromatography), St. Petersburg: Sankt-Peterb. Gos. Univ., 2002.
112. Granovsky, A.A., *PC GAMESS*, Version 7.1.E (Firefly), Build number 5190. http:classic.chem.msu.su/gran/ gamess/index.html.
113. Zhurko, G.A., http:www.chemcraftprog.com.
114. Danilova, E.A., Ivolin, A.A., Vorontsova, A.A., Islyaykin, M.K., Anan'eva, G.A., Zharnikova, N.V., Bykova, V.V., and Usol'tseva, N.V, *Zhidk. Krist. Praktich. Ispol'z*., 2011, no. 3, p. 5.
115. Dubrovina, T.E., Kudayarova, T.V., and Danilova, E.A., *Zhidk. Krist. Praktich. Ispol'z*., 2015, vol. 15, no. 1, p. 28.
116. Islyaykin, M.K., Danilova, E.A., Kudrik, E.V., Smirnov, R.P., Budunova, A.P., and Kinzirskii, A.S., *Pharm. Chem. J,* 1997, vol.31, no. 8, p. 409..