Russian Journal of Organic Chemistry, Vol. 40, No. 4, 2004, pp. 543–550. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 4, 2004, pp. 572–579.

2-Nitroguanidine Derivatives: V.* Synthesis and Structure of 3,5-Bis(nitroamino)-1,2,4-triazole Salts. Acid–Base Properties of 3,5-Bis(nitroamino)-1,2,4-triazole

E. L. Metelkina

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia

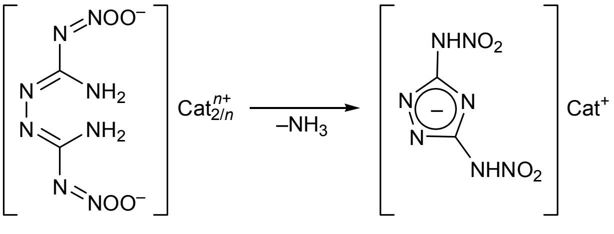
Received March 5, 2003

Abstract—Heterocyclization of hydrazine-1,2-bis(N^2-nitrocarboximidamide) and salts derived therefrom provides a procedure for the synthesis of 3,5-bis(nitroamino)-1,2,4-triazole salts. The presence of two acceptor nitroamino groups conjugated with the triazole ring considerably enhances the acidity of 3,5-bis(nitroamino)-1,2,4-triazole ($pK_a^1 = -2.0$, $pK_a^2 = 4.8$, $pK_a^3 = 10.6$) as compared to mononitroaminotriazole, so that formation of salts with the corresponding dianion becomes possible.

According to published data [2], heating of bis(aminoguanidinium) salt of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**I**) with 10 equiv of ammonium chloride results in formation of 1,6-dinitro(2-aminoguanyl)biguanidine ammonium salt. Analysis of this transformation led us to presume that under the given conditions intramolecular cyclization should be preferred, for acyl derivatives of nitroaminoguanidine are known [3, 4] to undergo base-catalyzed cyclization to give 3(5)-nitroamino-1,2,4-triazoles. Assuming that hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) is a nitroaminoguanidine derivative having an electron-acceptor nitroamidino group (which promotes considerable increase in the acidity [5] and favors formation of salts [6]), it was reasonable to examine cyclization of hydrazine-1,2-bis(N^2-nitrocarboximidamide) salts [6], which should be favored by alkaline medium of their aqueous solutions.

In fact, heating of hydrazine-1,2-bis(N^2-nitrocarboximidamide) salts **I** and **III**–**VIII** in boiling water for 10–15 min was accompanied by evolution of ammonia, and the subsequent acidification of the cooled reaction mixture afforded the corresponding 3,5-bis(nitroamino)-1,2,4-triazole salts **IX**–**XV** in high yield (Scheme 1). Aminoguanidinium salt **IX** thus obtained showed no depression of the melting point on mixing with a sample prepared by the procedure described in [2], which was assigned the structure of 1,6-dinitro(2-aminoguanyl)biguanidine. Compound **XIV** turned out to be identical to 3,5-bis(nitroamino)-1,2,4-triazole monopotassium salt which was obtained by diazotization of 1,6-dinitro(2-aminoguanyl)biguanidine [2].

Scheme 1.



I, **III**–**VIII** **IX**–**XV**

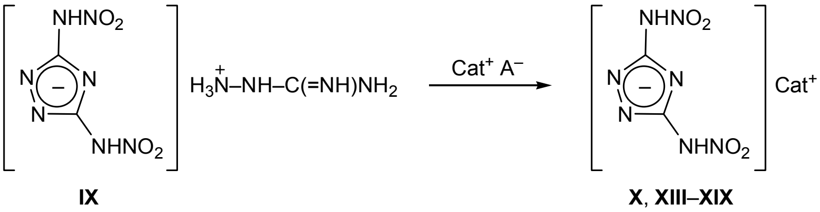
I, **IX**, Cat = $NH_3NHC(=NH)NH_2$; **III**, **X**, Cat = $NH_3C(=NH)NH_2$; **IV**, **XI**, Cat = NH_4; **V**, **XII**, Cat = Li; **VI**, **XIII**, Cat = Na; **VII**, **XIV**, Cat = K; **VIII**, **XV**, Cat = Ba.

An additional proof for the salt-like structure of compound **IX** is the ease of its exchange reactions with inorganic and organic salts. These reactions made it possible to considerably extend the series of 3,5-bis(nitroamino)-1,2,4-triazole salts and obtain salts containing hydrazinium and heavy metal cations (Pb, Ag, Hg) (compounds **XV**–**XIX**; Scheme 2). Furthermore, it was found that heating of an aqueous solution of aminoguanidinium salt **IX** with 6–8 equiv of ammonium chloride or aqueous ammonia leads to formation of mixed 3,5-bis(nitroamino)-1,2,4-triazole ammonium–aminoguanidinium salt **XX** whose physical constants fully coincide with those of the intermediate

---

* For communication IV, see [1].

Scheme 2.



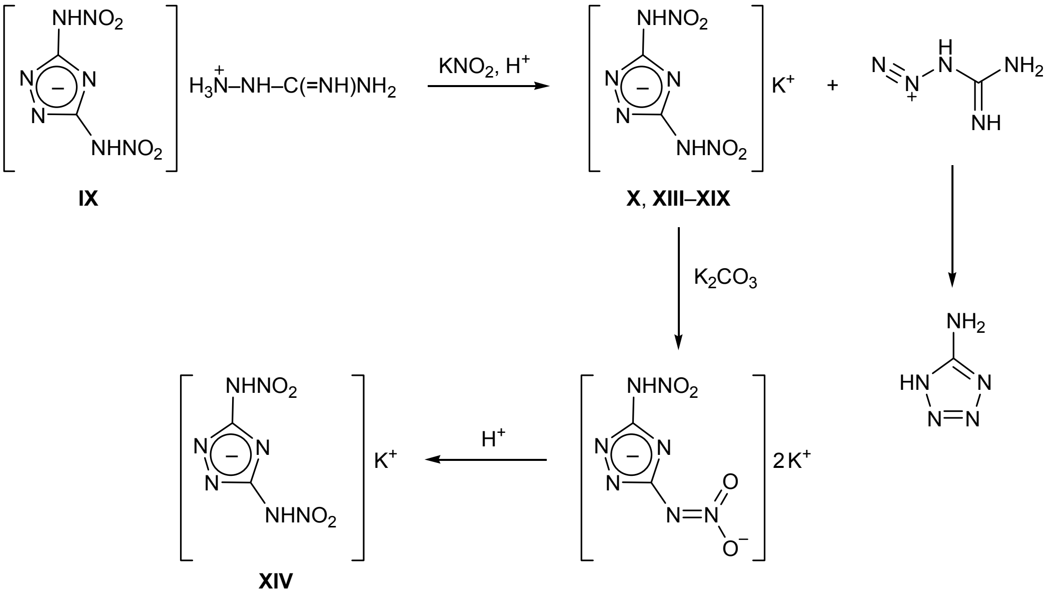
X, Cat = $NH_3C(=NH)NH_2$; **XIII**, Cat = Na; **XIV**, Cat = K; **XV**, Cat = Ba; **XVI**, Cat = N_2H_5; **XVII**, Cat = Pb; **XVIII**, Cat = Ag; **XIX**, Cat = Hg; A = Cl, SO_4, CO_3, HCO_3, NO_3.

product prepared as described in [2]. This intermediate was identified [2] as 1,6-dinitro(2-aminoguanyl)biguanidine ammonium salt. Acidification of an aqueous solution of double salt **XX** to pH 2.5–3.0 yields initial 3,5-bis(nitroamino)-1,2,4-triazole aminoguanidinium salt **IX**. Likewise, treatment of salts **XI**, **XIV**, and **XVI** with 6–8 equiv of bases gave the corresponding double salts **XXI**–**XXIII**.

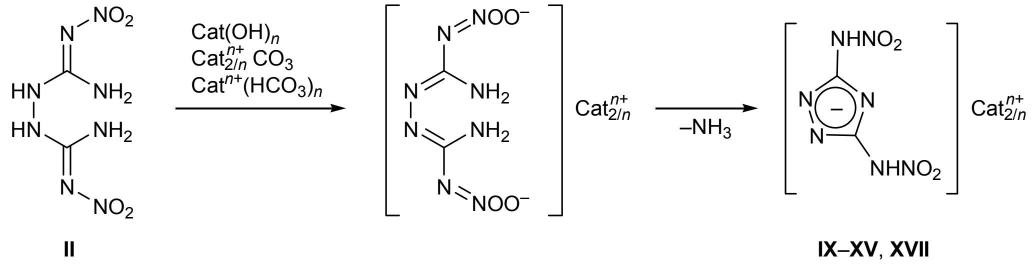
Thus the results of the present study show that the reaction described in [2] as a method of synthesis of 1,6-dinitro(2-aminoguanyl)biguanidine through its ammonium salt is in fact cyclization of hydrazine-1,2-bis(N^2-nitrocarboximidamide) bis(aminoguanidinium) salt (**I**), leading to 3,5-bis(nitroamino)-1,2,4-triazole aminoguanidinium salt (**IX**). Heating of the latter with 6–8 equiv of ammonium chloride gives double 3,5-bis(nitroamino)-1,2,4-triazole ammonium–aminoguanidinium salt (**XX**). In addition, the formation of potassium salt **XIV**, which was presumed [2] to arise from diazotization of 1,6-dinitro(2-aminoguanyl)biguanidine, should be regarded as the result of two concurrent reactions involving 3,5-bis(nitroamino)-1,2,4-triazole aminoguanidinium salt (**IX**). On the one hand, diazotization of aminoguanidinium cation leads to 5-aminotetrazole through intermediate formation of azido derivative [7, 8]. On the other hand, exchange reaction of aminoguanidinium salt **IX** with potassium nitrite gives the corresponding potassium salt **XIV** whose further transformations are shown in Scheme 3.

The salt-like structure of compounds **IX**–**XXIII** is additionally confirmed by the results of physicochemical studies; previously synthesized compounds [2] were characterized only by the data of elemental analysis and by the synthesis of benzylidene derivatives. The ^1H NMR spectra of compound **IX** and that prepared by the procedure described in [2] were identical; the spectra contained only one broadened signal at δ 7.24 ppm due to NH protons. In the

Scheme 3.



Scheme 4.



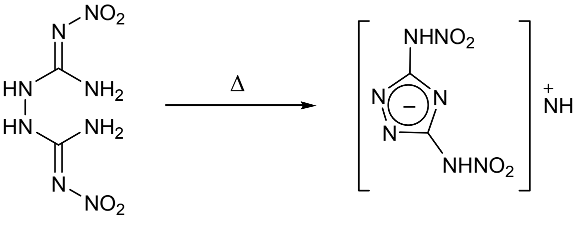
IX, Cat = $NH_3NHC(=NH)NH_2$; **X**, Cat = $NH_3C(=NH)NH_2$; **XI**, Cat = NH_4; **XII**, Cat = Li; **XIII**, Cat = Na; **XIV**, Cat = K; **XV**, Cat = Ba; **XVII**, Cat = Pb.

^{13}C NMR spectra of **IX–XXIII**, the signal at δ_C 119.4 ppm, as well as in the spectrum of hydrazine-1,2-bis-(N^2-nitrocarboximidamide) bis(aminoguanidinium) salt (**I**) (δ_C 119.4, 116.4 ppm) [6], corresponds to resonance of the carbon atom in the cation, and the signal at δ_C 111.5 ppm should be assigned to the triazole ring carbon atoms. The above assignment is supported by the ^{1}H and ^{13}C NMR spectra of monopotassium salt **XIV**, which contain only proton and carbon signals belonging to the anion, δ 7.47 ppm (NH) and δ_C 110.4 ppm. As might be expected, the spectral parameters of 3,5-bis(nitroamino)-1,2,4-triazole potassium salt **XIV** obtained by both cyclization of **VII** and diazotization of **IX** were identical.

The vibrational spectra of 3,5-bis(nitroamino)-1,2,4-triazole salts **IX**, **XI**, **XIII–XV**, and **XX–XXIII** are fairly complex. It is difficult to identify absorption bands unambiguously, for the anion is a conjugated system. The observed strong bands at 1590, 1550, 1500–1480, 1400, 1340, and 1320 cm^{-1} may be attributed to both triazole ring vibrations [9–14] and conjugated bond system in the nitroamidine fragments. Moreover, the whole set of the above absorption bands may be considered to arise from the conjugated bond system of the entire molecule. Absorption bands in the region 1230–1000 cm^{-1} are likely to belong to skeletal vibrations of the triazole ring [9, 10]. The electron absorption spectra of aqueous solutions of 3,5-bis-(nitroamino)-1,2,4-triazole salts **IX**, **XI**, and **XIII–XV** are characterized by the presence of strong bands at λ_{max} 315–318 nm (logε 4.20–4.25), which arise from electron transitions in the triazole ring conjugated with the nitroamino groups in positions *3* and *5*.

Further study of the heterocyclization showed that 3,5-bis(nitroamino)-1,2,4-triazolium salts can be obtained not only from hydrazine-1,2-bis(N^2-nitrocarboximidamide) salts **I** and **III–VIII** but also from hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) itself by heating in aqueous medium in the presence of 2 equiv of the corresponding base (Scheme 4). Furthermore, heating of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) in boiling water for 2.5 h afforded ammonium 3,5-bis(nitroamino)-1,2,4-triazolide (**XI**) (Scheme 5).

Scheme 5.



Spectrophotometric monitoring (Fig. 1) of the behavior of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) in aqueous medium on heating showed that the strong absorption band with its maximum at λ 271 nm appreciably decreased with time. Simultaneously, sharp increase in the optical density at λ 300–310 nm was observed, indicating the transformation of **II** into ionized cyclic structure.

Attempts to isolate free 3,5-bis(nitroamino)-1,2,4-triazole were unsuccessful. Heating of salt **XI** with concentrated nitric acid resulted in separation of a crystalline product which was a solvate complex formed by the initial salt and HNO_3. This solvate completely decomposed to give initial salt **IX** after triple recrystallization.

The structure of salts **IX–XXIII** suggests that 3,5-bis(nitroamino)-1,2,4-triazole is a polyfunctional compound. Its molecule contains two symmetrically located nitroamino groups whose electronic nature and

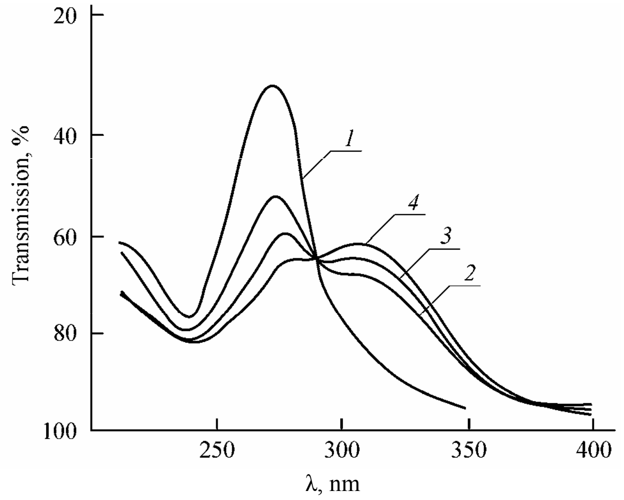


Fig. 1. UV spectra of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) in water at (*1*) 20°C and after heating at 75°C for (*2*) 30 min, (*3*) 1.5 h, and (*4*) 2.5 h.

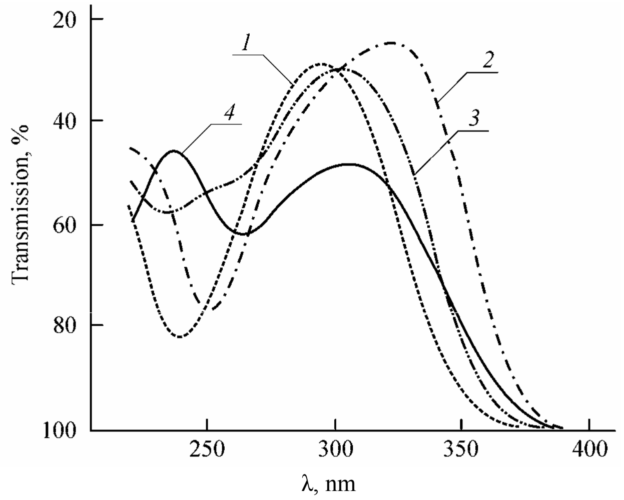
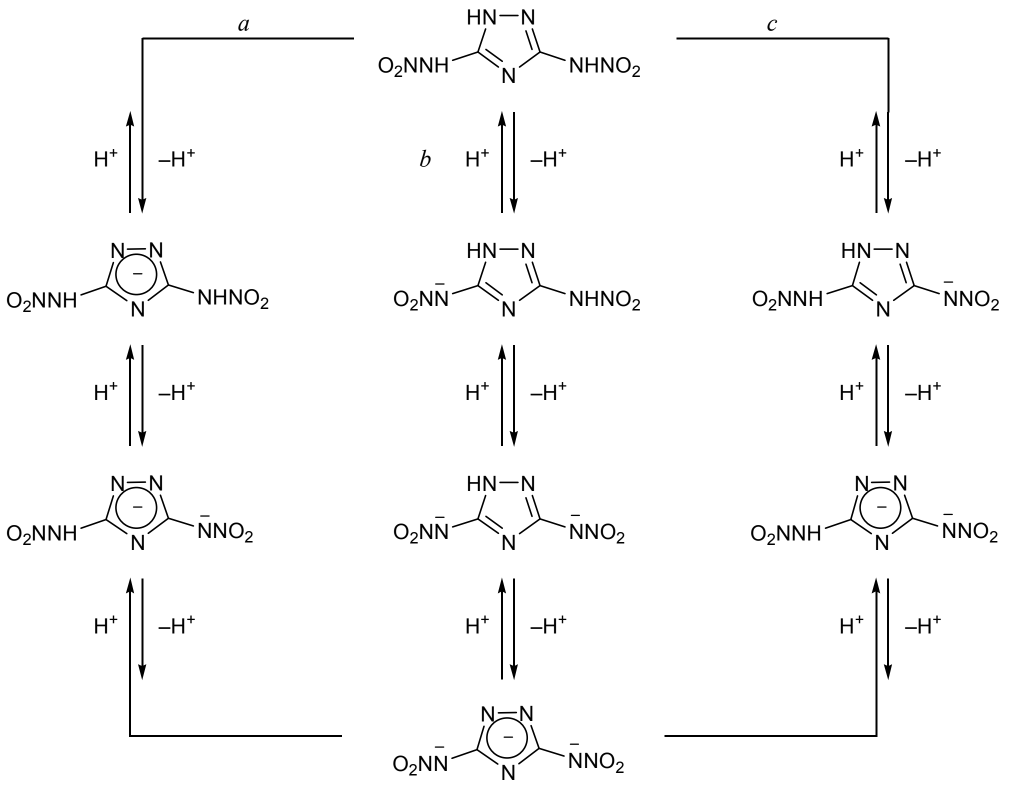


Fig. 2. UV spectra of aqueous solutions of potassium 3,5-bis(nitroamino)-1,2,4-triazolide (**XIV**): (*1*) 40% H_2SO_4 (*2*) pH 3.3, (*3*) pH 7.0, (*4*) 0.1 N NaOH.

mesomeric effect should enhance the acidity as compared to monosubstituted 3(5)-nitroamino-1,2,4-triazole. Presumably, 3,5-bis(nitroamino)-1,2,4-triazole in aqueous solution is capable of dissociating like a trihydric acid. Scheme 6 shows three possible ionization paths. The pK_a values of 3,5-bis(nitroamino)-1,2,4-triazole were determined by spectrophotometric and potentiometric titration (25°C): pK_a^1 = –2.0, pK_a^2 = 4.8, pK_a^3 = 10.6). Obviously, the anomalously high acidity of 3,5-bis(nitroamino)-1,2,4-triazole (among nitro compounds [15] and *N*-nitroamines [16]) and the observed red shift of the absorption maximum from

Scheme 6.



λ 290 to 320 nm in going to the monoanion (Fig. 2) are explained by proton abstraction from the endocyclic nitrogen atom, for in this case the conjugation in the resulting anion should be the strongest. Therefore, dissociation paths *b* and *c* (Scheme 6) can be ruled out.

In the UV spectrum of 3,5-bis(nitroamino)-1,2,4-triazole dianion, the main absorption band is displaced by 12–15 nm toward shorter wavelengths relative to the spectrum of the monoanion, and a new weak band appears in the short-wave region (λ 250–255 nm) as a shoulder on the short-wave flank of the long-wave band. Ionization of one nitroamino group at the second step of acid dissociation of 3,5-bis(nitroamino)-1,2,4-triazole ($pK_a^2 = 4.8$) changes the character of conjugation in the molecule, resulting in blue shift of the absorption maximum and hypochromic effect observed in the spectra of double salts **XX–XXIII**.

Increase in pH to 10–12 is accompanied by further decrease in the intensity of the main absorption band (λ_{max} 305 nm). In the short-wave region, the band observed as a shoulder in the spectrum of the dianion (which was assigned to electron transitions in the ionized nitroamino group) is transformed into a separate band with its maximum at λ 235 nm. This pattern may be interpreted in terms of formation of a triple anion via proton abstraction from the second nitroamino group ($pK_a^3 = 10.6$). In keeping with the obtained ionization constants, the acidity of 3,5-bis-(nitroamino)-1,2,4-triazole is greater by six orders of magnitude than the acidity of its mononitroamino analog [17], which is the result of cross-conjugation between the anionic fragments.

EXPERIMENTAL

The IR spectra were recorded in KBr on a UR-20 spectrometer. The electron absorption spectra were measured from aqueous solutions using an SF-9 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained on Tesla BS-487C (80 MHz) and Bruker WH-360 (90 MHz) instruments using DMSO-d_6 as solvent and HMDS as external reference. The ionization constants were determined by potentiometric titration with the aid of a Model 340 pH-meter following standard procedure [18]. Spectrophotometric measurements were performed with a series of H_2SO_4 solutions whose acidities were determined by titration [19]. Hydrazine-1,2-bis(N^2-nitrocarboximidamide) salts **I** and **III–VIII** were synthesized as described in [6].

Aminoguanidinium 3,5-bis(nitroamino)-1,2,4-triazolide (IX). *a*. A solution of 7.08 g (0.02 mol) of hydrazine-1,2-bis(N^2-nitrocarboximidamide) bis-(aminoguanidinium) salt (**I**) in 160 ml of water was stirred for 15 min on heating under reflux (until ammonia no longer evolved). The solution gradually changed from orange–red to light yellow. The mixture was cooled to 18–20°C and acidified to pH 3.0–3.5 with concentrated nitric acid. After 1 h, the precipitate was filtered off, washed with water until neutral washings, recrystallized from water, and dried in air. Yield 4.82 g (93%), decomposition point 172°C. IR spectrum, cm^{-1}: 1400 ($\nu_{as}NO_2$), 1320 (ν_sNO_2), 3420–3320 (νNH). UV spectrum, λ_{max}, nm (logε): 317 (4.25). ^{1}H NMR spectrum, δ, ppm: 7.27 br.s (NH). ^{13}C NMR spectrum, δ_C, ppm: 119.4 s (HN=C–NH), 111.5 s (C, triazole). Found, %: C 13.69; H 3.04; N 58.30. $C_3H_9N_{11}O_4$. Calculated, %: C 13.68; H 3.42; N 58.55.

b. Aminoguanidinium hydrogen carbonate, 2.5 g (0.02 mol), was added to a suspension of 2.06 g (0.01 mol) of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) in 50–70 ml of water. The mixture was heated for 15 min at the boiling point until ammonia no longer evolved, cooled to room temperature, and acidified with concentrated nitric acid to pH 3.0–3.5. After 2 h, the precipitate was filtered off, washed with cold water until neutral washings, and dried in air. Yield 2.26 g (86%), decomposition point 172°C. Found, %: C 13.73; H 3.12; N 58.83. $C_3H_9N_{11}O_4$. Calculated, %: C 13.68; H 3.42; N 58.55. Samples of **IX** obtained by the two methods (*a* and *b*) had identical physical constants.

Guanidinium 3,5-bis(nitroamino)-1,2,4-triazolide (X). *a*. Compound **X** was isolated from a solution of 6.4 g (0.02 mol) of diguanidinium salt **III** in 120 ml of water. Yield 4.5 g (90%), decomposition point 176°C. IR spectrum, ν, cm^{-1}: 1590 (C=N), 1550 (δNH), 1400 ($\nu_{as}NO_2$), 1320 (ν_sNO_2), 3420–3320 (NH). UV spectrum, λ_{max}, nm (logε): 318 (4.24). ^{1}H NMR spectrum, δ, ppm: 7.27 br.s (NH). Found, %: C 14.80; H 3.34; N 56.99. $C_3H_8N_{10}O_4$. Calculated, %: C 14.51; H 3.22; N 56.45.

b. Compound **X** was obtained from a solution of 0.412 g (2 mmol) of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) in 10 ml of water and 0.445 g (0.02 mol) of guanidinium carbonate. Yield 0.44 g (88.7%), decomposition point 176°C. Found, %: C 14.73; H 3.36; N 56.75. $C_3H_8N_{10}O_4$. Calculated, %: C 14.51; H 3.22; N 56.45.

c. Guanidinium chloride, 1.05 g (0.012 mol), or guanidinium carbonate, 1.08 g (6 mmol), was added with stirring to a solution of 2.63 g (0.01 mol) of salt **IX** in 50 ml of water, heated to 50–60°C. The mixture was stirred for 25–30 min at 80–85°C, slowly cooled to 15°C, and acidified with concentrated nitric acid to pH 3.5–3.0. The precipitate was filtered off, washed with ice water, and recrystallized from water. Yield 2.24 g (90%), decomposition point 176°C. Found, %: C 14.63; H 3.28; N 56.60. $C_3H_8N_{10}O_6$. Calculated, %: C 14.51; H 3.22; N 56.45.

Ammonium 3,5-bis(nitroamino)-1,2,4-triazolide (XI). *a.* Salt **XI** was isolated from a solution of 2.4 g (0.01 mol) of diammonium salt **IV** in 45 ml of water. Yield 1.55 g (90%), decomposition point 186°C. IR spectrum, ν, cm^{-1}: 1680, 1595, 1550, 1500, 1450, 1390, 1300, 1280, 1220. UV spectrum, λ_{max}, nm (logε): 315 (4.20). ^1H NMR spectum, δ, ppm: 7.23 br.s (NH). ^{13}C NMR spectrum, δ_C, ppm: 110.6 s (C, triazole). Found, %: C 11.83; H 3.06; N 54.37. $C_2H_6N_8O_4$. Calculated, %: C 11.66; H 2.95; N 54.36.

b. Salt **XI** was prepared from a solution of 0.206 g (1 mmol) of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) in 8 ml of water and 0.28 ml (2 mmol) of aqueous ammonia or 0.114 g (1 mmol) of ammonium carbonate. Yield 0.16 g (76%), decomposition point 186°C. Found, %: C 11.72; H 3.10; N 54.31. $C_2H_6N_8O_4$. Calculated, %: C 11.66; H 2.95; N 54.36.

c. Salt **XI** was prepared from a solution of 0.263 g (1 mmol) of salt **IX** in 15 ml of water and 0.12 g (1.5 mmol) of ammonium nitrate. Yield 0.207 g (98%), decomposition point 186°C. Found, %: C 11.88; H 3.23; N 54.47. $C_2H_6N_8O_4$. Calculated, %: C 11.66; H 2.95; N 54.36.

Lithium 3,5-bis(nitroamino)-1,2,4-triazolide (XII). *a.* Lithium salt **XII** was isolated from a solution of 2.2 g (0.01 mol) of dilithium salt **V** in 45 ml of water. Yield 1.72 g (87%), decomposition point 211°C. Found, %: C 11.03; H 1.20; N 44.76. $C_2H_2LiN_7O_4$. Calculated, %: C 10.91; H 0.91; N 44.54.

b. Salt **XII** was prepared from 0.206 g (1 mmol) of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) and 0.064 g (1 mmol) of lithium carbonate. Yield 1.76 g (88%), decomposition point 211°C. Found, %: C 10.98; H 1.22; N 44.68. $C_2H_2LiN_7O_4$. Calculated, %: C 10.91; H 0.91; N 44.54.

Sodium 3,5-bis(nitroamino)-1,2,4-triazolide (XIII). *a.* Sodium salt **XIII** was isolated from a solution of 5 g (0.02 mol) of disodium salt **VI** in 65 ml of water. Yield 3.17 g (75%), decomposition point 230°C. IR spectrum, ν, cm^{-1}: 1600, 1550, 1490, 1420, 1400, 1350, 1320, 1260, 1220, 1050. UV spectrum, λ_{max}, nm (logε): 315 (4.21). ^1H NMR spectrum, δ, ppm: 7.45 s (NH). ^{13}C NMR spectrum, δ_C, ppm: 110.8 s (C, triazole). Found, %: C 11.84; H 2.33; N 52.54. $C_2H_2N_7NaO_4$. Calculated, %: C 11.37; H 1.88; N 52.82.

b. Salt **XIII** was obtained from a solution of 0.206 g (1 mmol) of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) and 0.08 g (2 mmol) of sodium hydroxide or 0.106 g (1 mmol) of sodium carbonate in 10 ml of water. Yield 0.16 g (76%), decomposition point 230°C. Found, %: C 11.56; H 2.12; N 52.68. $C_2H_2N_7NaO_4$. Calculated, %: C 11.37; H 1.88; N 52.82.

c. Salt **XIII** was obtained from 0.526 g (2 mmol) of salt **IX** in 15 ml of water and 0.14 g (2.2 mol) of sodium chloride or 0.2 g (2.2 mmol) of sodium hydrogen carbonate. Yield 0.35 g (82%), decomposition point 230°C (from H_2O). Found, %: C 11.63; H 2.06; N 52.74. $C_2H_2N_7NaO_4$. Calculated, %: C 11.37; H 1.88; N 52.82.

Potassium 3,5-bis(nitroamino)-1,2,4-triazolide (XIV). *a.* Potassium salt **XIV** was isolated from a solution of 5.64 g (0.02 mol) of dipotassium salt **VII** in 80 ml of water. Yield 4.1 g (90%), decomposition point 202°C. IR spectrum, ν, cm^{-1}: 1600, 1550, 1490, 1400, 1420, 1350, 1320, 1260, 1220, 1050. UV spectrum, λ_{max}, nm (logε): 318 (4.21). ^1H NMR spectrum, δ, ppm: 7.47 s (NH). ^{13}C NMR spectrum, δ_C, ppm: 110.4 s (C, triazole). Found, %: C 10.48; H 1.49; N 42.74. $C_2H_2KN_7O_4$. Calculated, %: C 10.52; H 1.31; N 42.98.

b. Salt **XIV** was synthesized from 0.412 g (2 mmol) of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) and 0.138 g (1 mmol) of potassium carbonate or 0.092 g (2 mmol) of potassium hydroxide. Yield 0.4 g (88%), decomposition point 202°C. Found, %: C 10.66; H 1.58; N 42.88. $C_2H_2KN_7O_4$. Calculated, %: C 10.52; H 1.31; N 42.98.

c. Salt **XIV** was obtained from a solution of 0.263 g (1 mmol) of salt **IX** in 10 ml of water and 0.1 g (1 mmol) of potassium hydrogen carbonate or 0.122 g (1.2 mmol) of potassium nitrate. Yield 0.21 g (82%), decomposition point 202°C (from H_2O). Found, %: C 10.68; H 1.38; N 42.86. $C_2H_2KN_7O_4$. Calculated, %: C 10.52; H 1.31; N 42.98.

Barium 3,5-bis(nitroamino)-1,2,4-triazolide (XV). *a.* Barium salt **XV** was isolated from a solution of 0.341 g (2 mmol) of salt **VIII** in 12 ml of water. Yield 0.232 g (50%), decomposes above 320°C.

Found, %: C 9.52; H 1.23; N 38.10. $C_4H_4BaN_{14}O_8$. Calculated, %: C 9.30; H 1.14; N 38.05.

b. Salt **XV** was obtained from a solution of 0.206 g (1 mmol) of hydrazine-1,2-bis(N^2-nitrocarboximidamide) (**II**) and 0.315 g (1 mmol) of barium hydroxide in 10 ml of water. Yield 0.24 g (92%), decomposes above 320°C. Found, %: C 9.48; H 1.21; N 38.12. $C_4H_4BaN_{14}O_8$. Calculated, %: C 9.30; H 1.14; N 38.05.

c. Salt **XV** was obtained from a solution of 0.263 g (1 mmol) of salt **IX** in 10 ml of water and 0.313 g (1.2 mmol) of barium nitrate or 0.236 g (1.2 mol) of barium carbonate. Yield 0.22 g (85%), decomposes above 320°C. Found, %: C 9.58; H 1.26; N 38.08. $C_4H_4BaN_{14}O_8$. Calculated, %: C 9.30; H 1.14; N 38.05.

Hydrazinium 3,5-bis(nitroamino)-1,2,4-triazolide (XVI) was synthesized from a solution of 2.63 g (0.01 mol) of salt **IX** in 50 ml of water and 1.74 g (0.012 mol) of hydrazinium sulfate. Yield 2.3 g (95%), decomposition point 181°C. Found, %: C 11.00; H 3.18; N 57.12. $C_2H_2N_9O_4$. Calculated, %: C 10.84; H 3.16; N 57.01.

Lead 3,5-bis(nitroamino)-1,2,4-triazolide (XVII). *c*. Salt **XVII** was synthesized from a solution of 0.263 g (1 mmol) of salt **IX** in 10 ml of water and 0.134 g (0.5 mmol) of lead carbonate or 0.166 g (0.5 mmol) of lead nitrate (without preliminary acidification). Yield 0.29 g (99%), vigorously decomposes above 250°C.

Silver 3,5-bis(nitroamino)-1,2,4-triazolide (XVIII). *c*. Salt **XVIII** was synthesized from a solution of 0.526 g (2 mmol) of salt **IX** in 20 ml of water and 0.34 g (2 mmol) of silver nitrate in 10 ml of water (withouth acidification). Yield 0.58 g (98%), vigorously decomposes above 250°C.

Mercury 3,5-bis(nitroamino)-1,2,4-triazolide (XIX). *c*. Salt **XIX** was synthesized from a solution of 0.526 g (2 mmol) of salt **IX** in 20 ml of water and 0.34 g (1 mmol) of mercury nitrate (without preliminary acidification). Yield 0.57 g (98%), vigorously decomposes above 250°C.

3,5-Bis(nitroamino)-1,2,4-triazole ammonium–aminoguanidinium salt (XX). Ammonium chloride, 3.2 g (0.6 mol), was added under stirring to a suspension of 2.63 g (0.01 mol) of salt **IX** in 50 ml of water, heated to 40–45°C. After 3 h, the precipitate was filtered off, washed with water, alcohol, and ether, and dried in air. Yield 2.5 g (89%), decomposition point 178°C. IR spectrum, ν, cm^{-1}: 1580 (C=N), 1400 ($\nu_{as}NO_2$), 1320 (ν_sNO_2), 3420–3320 (NH). UV spectrum, λ_{max}, nm (logε): 302 (7.31). ^1H NMR spectrum, δ, ppm: 7.31 br.s (NH). ^{13}C NMR spectrum, δ_C, ppm: 119.2 s (HN=C–NH), 111.0 s (C, triazole). Found, %: C 13.01; H 4.13; N 59.86. $C_3H_{12}N_{12}O_4$. Calculated, %: C 12.85; H 4.28; N 60.00.

Compounds **XXI–XXIII** were synthesized in a similar way.

3,5-Bis(nitroamino)-1,2,4-triazole diammonium salt (XXI) was prepared from a solution of 2.05 g (0.01 mol) of salt **XI** in 10 ml of water and 10 ml (0.07 mol) of aqueous ammonia. Yield 1.7 g (75%), decomposition point 187°C. IR spectrum, ν, cm^{-1}: 1590 (δNH), 1405 ($\nu_{as}NO_2$), 1335 (ν_sNO_2), 3420–3330 (NH). UV spectrum, λ_{max}, nm (logε): 303 (4.11). ^1H NMR spectrum, δ, ppm: 7.14 br.s (NH). ^{13}C NMR spectrum, δ_C, ppm: 111.5 s (C, triazole). Found, %: C 10.64; H 4.25; N 56.76. $C_2H_9N_9O_4$. Calculated, %: C 10.76; H 4.03; N 6.50.

3,5-Bis(nitroamino)-1,2,4-triazole dipotassium salt (XXII) was prepared from a solution of 2.25 g (0.01 mol) of salt **XIV** in 10 ml of water and 3.24 g (0.06 mol) of potassium hydroxide in 10 ml of water. Yield 2.52 g (96%), decomposition point 221°C. IR spectrum, ν, cm^{-1}: 1595 (δNH), 1410 ($\nu_{as}NO_2$), 1340 (ν_sNO_2), 3420–3320 (NH). UV spectrum, λ_{max}, nm (logε): 305 (4.00). ^1H NMR spectrum, δ, ppm: 7.20 s (NH). ^{13}C NMR spectrum, δ_C, ppm: 111.3 s (C, triazole). Found, %: C 9.02; H 0.00; N 37.03. $C_2HK_2N_7O_4$. Calculated, %: C 9.06; H 0.38; N 36.98.

3,5-Bis(nitroamino)-1,2,4-triazole dihydrazinium salt (XXIII) was prepared from a solution of 2.2 g (0.01 mol) of salt **XVI** in 10 ml of water and 3 ml (0.07 mol) of hydrazine hydrate. Yield 2.2 g (91%), decomposition point 186°C. IR spectrum, ν, cm^{-1}: 3420–3335 (NH), 1595 (δNH), 1400 ($\nu_{as}NO_2$), 1325 (ν_sNO_2). UV spectrum, λ_{max}, nm (logε): 303 (4.09). ^1H NMR spectrum, δ, ppm: 7.01 br.s (NH). ^{13}C NMR spectrum, δ_C, ppm: 110.8 s (C, triazole). Found, %: C 9.54 H 4.67; N 61.36. $C_2H_{11}N_{11}O_4$. Calculated, %: C 9.49; H 3.50; N 60.86.

The author is grateful to K.V. Varlygo and M.V. Lazareva for their help in this study.

REFERENCES

1. Metelkina, E.L. and Novikova, T.A., *Russ. J. Org. Chem.*, 2000, vol. 36, p. 1568.
2. Henri, R.A., Skolnik, S., and Smith, G.V.I., *J. Am. Chem. Soc.*, 1953, vol. 75, p. 955.

3. Henri, R.A., *J. Am. Chem. Soc.*, 1950, vol. 72, p. 5343.
4. Chipen, G.I., Grinshtein, V.Ya., and Preiman, T.P., *Zh. Obshch. Khim.*, 1962, vol. 32, p. 454.
5. Metelkina, E.L., Varlygo, K.V., Paperno, T.Ya., and Berkova, V.A., *Zh. Obshch. Khim.*, 1995, vol. 65, p. 634.
6. Metelkina, E.L., Varlygo, K.V., and Paperno, T.Ya., *Zh. Obshch. Khim.*, 1995, vol. 65, p. 1693.
7. Beresneva, N.K., Lopyrev, V.A., and Krupin, K.L., *Khim. Geterotsikl. Soedin.*, 1969, p. 118.
8. Lieber, E., Sherman, E., and Patinkin, S.H., *J. Am. Chem. Soc.*, 1951, vol. 73, p. 2329.
9. Mel’nikov, V.V., Stolpakova, V.V., and Pevzner, M.S., *Khim. Geterotsikl. Soedin.*, 1971, p. 414.
10. Slovetskii, V.I., Brusnikina, V.M., Khmel’nitskii, L.I., Lebedev, O.V., and Novikov, S.S., *Khim. Geterotsikl. Soedin.*, 1966, p. 448.
11. Bagal, L.I., Pevzner, M.S., Egorov, A.P., and Somarenko, V.Ya., *Khim. Geterotsikl. Soedin.*, 1970, p. 997.
12. Gehlen, H. and Uteg, K-H., *Arch. Pharm.*, 1969, vol. 302, p. 877.
13. Lopyrev, V.A., Berestova, N.K., and Strelets, B.Kh., *Khim. Geterotsikl. Soedin.*, 1969, p. 732.
14. Gehlen, H., *Z. Chem.*, 1969, p. 338.
15. Bagal, L.I. and Pevzner, M.S., *Khim. Geterotsikl. Soedin.*, 1970, p. 558.
16. Serov, Yu.V., Bazanov, A.G., and Tselinskii, I.V., *Zh. Org. Khim.*, 1980, vol. 16, p. 472.
17. De Vries, J.E. and St. Clair, E.G., *J. Am. Chem. Soc.*, 1954, vol. 76, p. 1008.
18. Albert, A. and Serjeant, E., *Ionization Constants of Acids and Bases*, London: Methuen, 1962.
19. Paul, M.A. and Long, F.A., *Chem. Rev.*, 1957, vol. 57, p. 1.