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2-Nitroguanidine Derivatives: VI.* Synthesis and Chemical Properties of Hydrazo- and Azobis(nitroformamidine)

E. L. Metelkina

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

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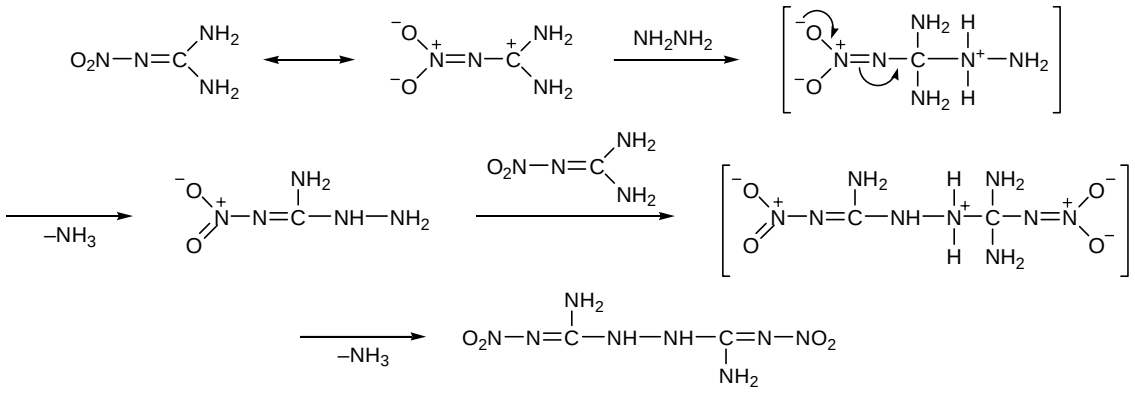
Abstract—New methods have been proposed for the synthesis of hydrazobis(nitroformamidine), and its reactions with electrophilic reagents, formaldehyde and glyoxal, have been studied. Oxidation of hydrazobis(nitroformamidine) with atmospheric oxygen in glacial acetic acid in the presence of a catalytic amount of N_2O_4 gives crystalline azobis(nitroformamidine). Ionization constants of the oxidation product, determined by potentiometric titration (pK_a^1 = 3.50, pK_a^2 = 7.93), indicate considerable increase in the NH acidity as compared to 2-nitroguanidine. Reactions of azobis(nitroformamidine) with β-dicarbonyl compounds lead to formation of 1-diacylmethyl-N'^1,N'^2-dinitrohydrazine-1,2-dicarboximidamides.

Two methods for the preparation of hydrazobis(nitroformamidine) (**I**) are known [2]. One of these includes initial synthesis of hydrazobis(nitroformamidine) bis(aminoguanidinium) salt (**II**) by hydrazinolysis of 2-nitroguanidine in anhydrous methanol or ethanol, followed by acidification; it is characterized by a poor yield (4.5%). The second procedure is multistep, and the overall yield of hydrazo compound **I** is also low (7%). Moreover, the final step in the second procedure (reaction of 1-amino-2-nitroguanidine with 1-methyl-2-nitro-1-nitrosoguanidine at room temperature) takes two months and is fairly laborious. By varying the conditions of this reaction we succeeded in shortening the reaction time to 7 days and raising the yield from 20 to 45%. Taking into account that the first procedure for the synthesis of hydrazobis(nitroformamidine) (**I**) is simpler, the study of hydrazinolysis of 2-nitroguanidine was continued with a view to increase the yield of bis(aminoguanidinium) salt **II**.

Comparison of the conditions for reactions of 2-nitroguanidine with hydrazine hydrate in anhydrous methanol (or ethanol) [2] and in water [3], which lead, respectively, to both bis(aminoguanidinium) salt **II** and 1-amino-2-nitroguanidine, allowed us to presume that the results of the process should strongly depend on pH of the medium. In keeping with the above assumption, experiments showed that hydrazinolysis of 2-nitroguanidine according to the procedure described in [3] but with a smaller amount of water (by a factor of 2.5) gives a 1:1 mixture of 1-amino-2-nitroguani-

Scheme 1.



I

* For communication V, see [1].

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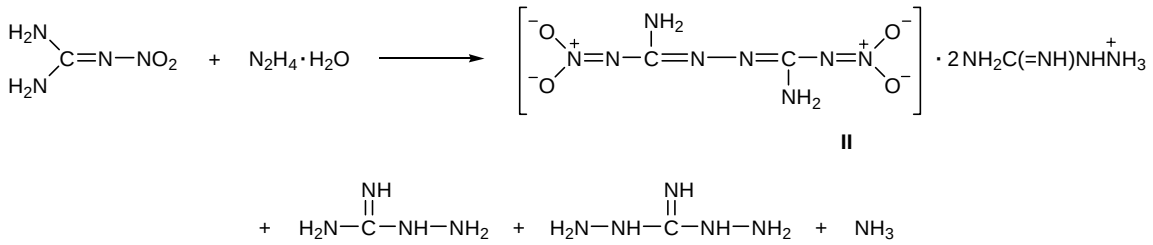
Scheme 2.



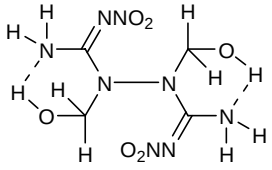
dine and hydrazobis(nitroformamidine) bis(aminoguanidinium) salt (**II**) in an overall yield of 35–36%. Presumably, compound **II** is formed due to increase of pH in a certain step, which favors reaction of 1-amino-2-nitroguanidine with 2-nitroguanidine as shown in Scheme 1.

Thus in aqueous medium, as well as in anhydrous methanol (ethanol) [2], the reaction direction should be determined by the initial concentration of hydrazine hydrate. In fact, addition of hydrazine hydrate to a suspension of 2-nitroguanidine in water and subsequent heating of the resulting mixture afforded salt **II** in a yield exceeding that obtained in anhydrous methanol [2] by a factor of 10. Analysis of the reaction mixture showed formation of aminoguanidine, diaminoguanidine, and ammonia as by-products (Scheme 2).

The rate of hydrazinolysis of 2-nitroguanidine in water was found to strongly depend on the temperature conditions. Reduction of the temperature to 45–50°C leads to increase in the reaction time by 4 h, while the reaction at room temperature in 12 days also gives compound **II** in a similar yield. Hydrazinolysis of 2-nitroguanidine in water at 60°C and higher results in formation of aminoguanidine. Acidification of bis(aminoguanidinium) salt **II** with 4 equiv of concentrated nitric acid at 0–5°C yields hydrazobis(nitroformamidine) (**I**). The structure of compounds **I** and **II** was confirmed by the data of elemental analysis and IR, UV, and ^{1}H NMR spectroscopy, which were consistent with those reported in [4, 5].

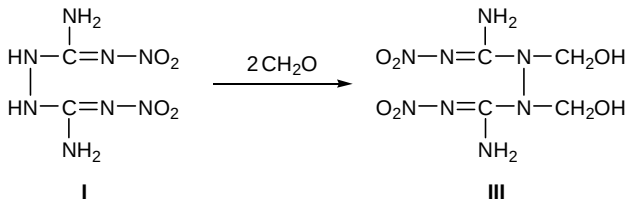
Nitrogen atoms of the hydrazo group in hydrazobis(nitroformamidine) (**I**) participate in specific conjugation with the nitroformamidine moieties (Y-aromaticity) [6], which increases their nucleophilicity as compared to 1,2-disubstituted hydrazines [7] and hence enhances the reactivity toward electrophilic reagents.

Heating of hydrazo compound **I** with 5 equiv of formaldehyde for 40 min at 60°C afforded bis(hydroxymethyl) derivative **III** (Scheme 3) whose structure was confirmed by the IR, UV, and ^{1}H NMR spectra. Unlike hydrazo(bisformamidine) (**I**), 1,2-bis(hydroxymethyl)-*N*′^{1},*N*′^{2}-dinitrohydrazine-1,2-bis(carboximidamide) (**III**) displayed in the IR spectrum a broad absorption band in the region 3000–3600 cm^{-1}, which arises from stretching vibrations of the N–H, C–H, and O–H bonds. The spectral pattern in that region indicates formation of intra- and intermolecular hydrogen bonds. In the ^{1}H NMR spectrum of **III**, signals from the magnetically nonequivalent methylene protons appear as a typical *AB* quartet at δ 4.93 and 5.40 ppm. The hydroxy protons give a signal at δ 6.61 ppm, and broadened downfield signals centered at δ 8.03 and 9.09 ppm belong to protons of the primary amino groups in the nitroguanidine fragments. The presence of intramolecular hydrogen bonds and magnetic nonequivalence of the methylene protons suggest that the hydroxymethyl (nitro)guanidine moieties in **III** exist as six-membered H-chelate rings.

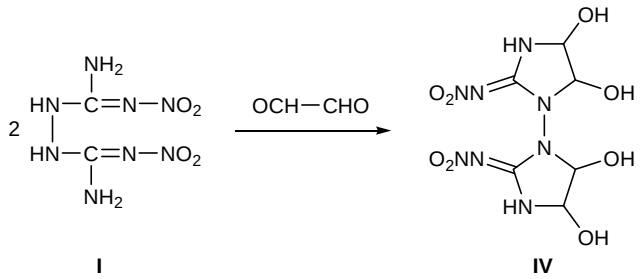


Unlike 2-nitroguanidine [8], hydrazobis(nitroformamidine) (**I**) reacts with glyoxal at a higher temperature both in water at pH 8–9 and in an acetate buffer. The product is 1,1'-bi(4,5-dihydroxy-2-nitroiminoimidazolidine) (**IV**) (Scheme 4). Its structure was confirmed by the ^{1}H NMR data. In the ^{1}H NMR spectrum of **IV**, protons at C^4 and C^5 appear as

Scheme 3.



Scheme 4.

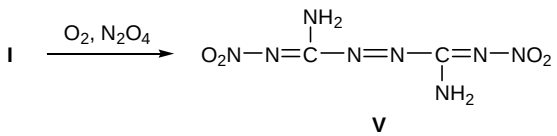


I IV

a broadened singlet at δ 5.19 ppm, and the OH protons give two signals at δ 7.04 and 7.15 ppm due to their magnetic nonequivalence. A broadened poorly resolved triplet in a weak field (δ 10.04 ppm) belongs to the NH proton. The observed spectral pattern suggests the presence of stereoisomers.

Oxidation of hydrazobis(nitroformamidine) (**I**) gives azobis(nitroformamidine) (**V**) [2]. However, in this case difficultly accessible calcium permanganate is used, and product **V** is isolated as an amorphous substance. Therefore, it seemed reasonable to search for other oxidants ensuring preparation of crystalline azobis(nitroformamidine) (**V**) in high yield. The oxidation of **I** with potassium permanganate in 1.5–3.5 N nitric acid over a wide temperature range (20–45°C) afforded amorphous but analytically pure compound **V** in high yield. By oxidation of **I** with halogens in aqueous medium at 0–3°C finely crystalline azobis(nitroformamidine) (**V**) was obtained in a good yield but with reduced decomposition point. The above drawbacks were eliminated by the use of atmospheric oxygen as oxidant in the presence of a catalytic amount of nitrogen oxides [9]. Variation of the conditions showed that the best results were obtained by carrying out the reaction in glacial acetic acid containing N_2O_4 at a volume ratio of 36:1 in a stream of air, gradually raising the temperature from 20 to 75°C (Scheme 5). Azobis(nitroformamidine) (**V**) was thus isolated in the crystalline state and was analytically pure. The structure of product **V** obtained by different methods was confirmed by elemental analysis and IR and ^{1}H NMR spectroscopy. The N=N bond in **V** was identified by the Raman spectra. Due to symmetric *trans* configuration of the nitroformamidine fragments

Scheme 5.

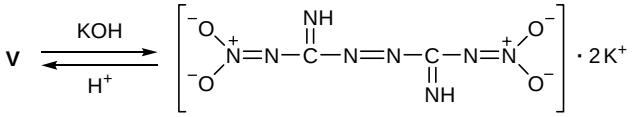


V

with respect to the azo groups, the N=N vibrations are not active in the IR spectra. Stretching vibrations of the N–NO_2 group in **V** (1325, 1290, and 1265 cm^{-1}) appear at lower frequencies than those observed for hydrazobis(nitroformamidine) (**I**) and 2-nitroguanidine [4]; presumably, this is the result of concurrent p–π conjugation between the nitroformamidine fragments and nitrogen atoms of the azo group. A strong unresolved absorption was observed in the region 1640–1615 cm^{-1}; this composite band is likely to arise from vibrations of the C=N and N–H bonds. The ^{1}H NMR spectrum of **V** confirms the previous conclusion [10] that this compound has a symmetric nitroimino structure: the spectrum contains only one signal from the amino protons at δ 10.01 ppm.

The presence of a nonconjugated electron-acceptor azo group in molecule **V** considerably increases the NH acidity of the amino groups, as compared to 2-nitroguanidine. Azo compound **V** readily reacts with an aqueous solution of potassium hydroxide at room temperature to give dipotassium salt **VI** (Scheme 6).

Scheme 6.



VI

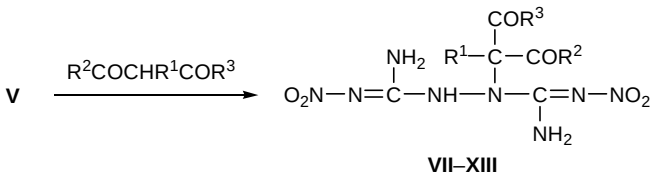
The structure of azobis(nitroformamidine) dianion was examined by UV and ^{1}H NMR spectroscopy. The UV spectrum of **VI** is characterized by increased intensity of the band at λ 265 nm (ε = 8700) and broadening of the long-wave flank of that band in the range from 305 to 320 nm, indicating ionization of the nitroformamidine fragments. The ^{1}H NMR spectrum of **VI** does not contradict the assumed structure: the NH_2 signal typical of the neutral species disappears, while a signal from the imino group appears in a stronger field (δ 7.4 ppm).

Good solubility of potassium salt **VI** made it possible to quantitatively estimate acid–base properties of azobis(nitroformamidine) (**V**) by potentiometric titration. The values pK_a^1 = 3.50 and pK_a^2 = 7.93 (20°C) indicate considerably reduced basicity of the anions derived from **V**, as compared to 2-nitroguanidine (pK_a = 12.20) [5], due to the presence of an acceptor azo group.

The absence of continuous conjugation and reduced electron density on the nitrogen atoms of the azo group

in molecule **V** make the latter more electrophilic, thus favoring its reactions with nucleophilic reagents. Azobis(nitroformamidine) (**V**) was found to react with β-dicarbonyl compounds under milder conditions than those reported for azodicarboxylic acid ester [9]. As a result, the corresponding diacylmethyl derivatives **VII**–**XIII** were obtained (Scheme 7). Presumably, the reaction is initiated by nucleophilic centers of azo compound **V**, which facilitate deprotonation of the CH acid.

Scheme 7.



VII, R^1 = H, R^2 = R^3 = Me; **VIII**, R^1 = R^2 = R^3 = Me; **IX**, R^1 = H, R^2 = Me, R^3 = OEt; **X**, R^1 = Et, R^2 = Me, R^3 = OEt; **XI**, R^1 = H, R^2 = EtOCO, R^3 = OEt; **XII**, R^1 = H, R^2 = Ph, R^3 = Me; **XIII**, R^1 = H, R^2 = R^3 = Ph.

The structure of compounds **VII**–**XIII** was confirmed by the data of elemental analysis and spectral methods. The UV spectra of condensation products **VII** and **VIII** (Fig. 1) contain a strong band at λ 250–265 nm (ε = 20000–30000) which is typical of *p*–π and π–π* transitions in nitroformamidines, and much less intense absorption at λ 310–370 nm (a shoulder for compounds **IX** and **XI**), which may be assigned to π–π* transitions in the β-dicarbonyl fragment.

In the ^{1}H NMR spectra of **VII**–**XIII**, NH protons give rise to five separate signals, four of which are grouped in pairs (Fig. 2). Each signal corresponds to one proton. Presumably, magnetic nonequivalence of protons in the amino groups originates from the presence of a bulky electron-acceptor substituent which is capable of stabilizing rotational isomers [11]. Magnetically anisotropic groups in the β-dicarbonyl fragment exert a strong shielding effect on the NH proton in the hydrazo moiety, and its signal shifts upfield (δ ~7 ppm) relative to the corresponding signal in the spectrum of hydrazobis(nitroformamidine) (**I**).

Analysis of the IR spectra confirms the existence of rotational isomers of compounds **VII**–**XIII**, which are stabilized by strong intramolecular hydrogen bonds: The most conformationally sensitive stretching vibrations of the carbonyl groups appear as a weak unresolved band. The available data are insufficient to rigorously estimate conformational heterogeneity of

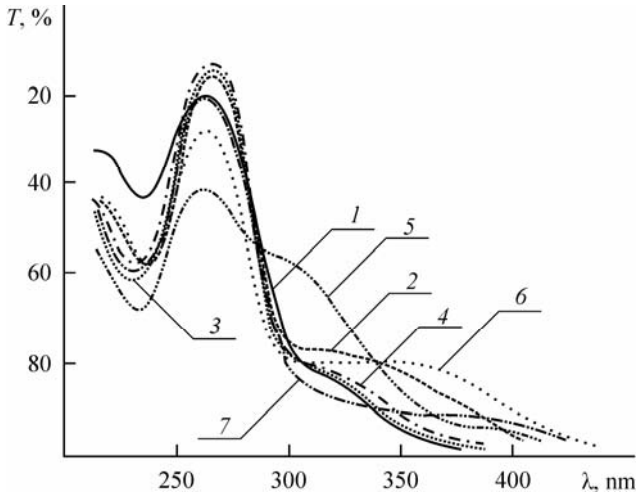


Fig. 1. UV spectra in water: (*1*) **VII**, (*2*) **VIII**, (*3*) **IX**, (*4*) **X**, (*5*) **XI**, (*6*) **XII**, (*7*) **XIII**.

these compounds, but the observed variations in the vibrational spectra of **VII**–**XI** provide some information on the effect of substituents in the β-dicarbonyl fragments on the contribution of the carbonyl and amino groups to intra- and intermolecular hydrogen bonding. A considerable decrease in the C=O absorption intensity in the spectra of **VIII** and **X** (Fig. 3), as well as analogous reduction in the intensity and broadening of N–H stretching vibration bands, as compared to the spectra of **VII** and **IX** (Fig. 4), indicate enhancement of intra- and intermolecular interactions between the C=O and N–H groups upon introduction of a bulky substituent.

Successive replacement of acetyl groups (compound **VII**) by benzoyl (**XII**, **XIII**) (Figs. 3–5) is accompanied by gradual shift of the C=O stretching vibration bands to lower frequencies and decrease in

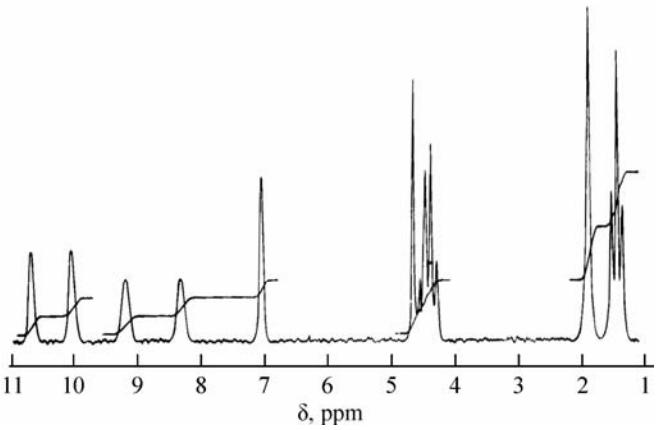


Fig. 2. ^{1}H NMR spectrum of ethyl 2-{1,2-bis[amino(nitroimino)methyl]hydrazino}-3-oxobutanoate (**IX**) in DMSO-d_6.

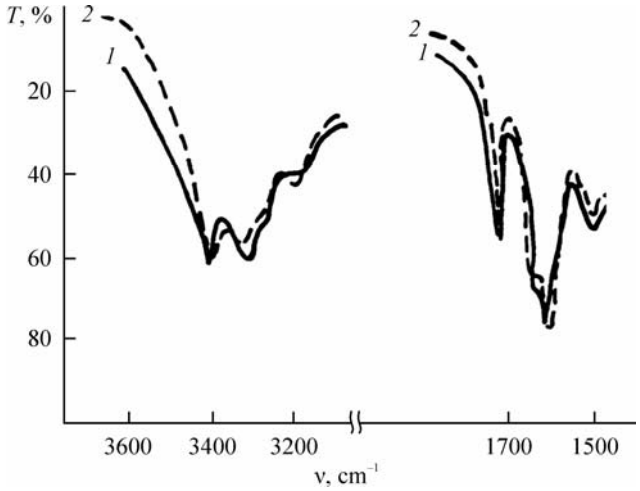


Fig. 3. IR spectra (KBr) of compounds (*1*) **VII** and (*2*) **VIII**.

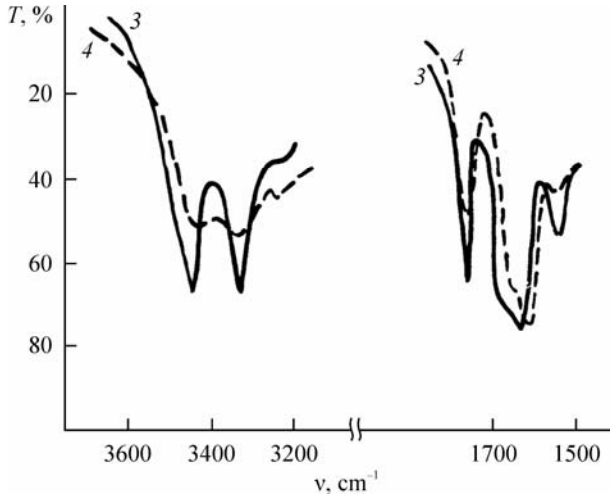


Fig. 4. IR spectra (KBr) of compounds (*3*) **IX** and (*4*) **X**.

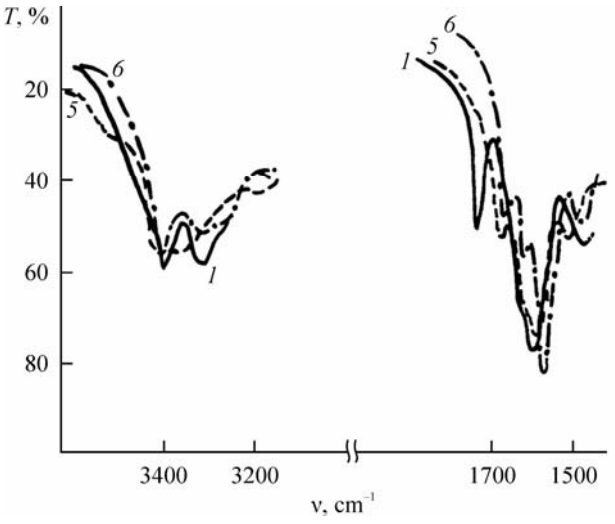


Fig. 5. IR spectra (KBr) of compounds (*1*) **VII**, (5) **XII**, and (*6*) **XIII**.

their intensity (Fig. 5), in agreement with the electronic effect of phenyl groups on the C=O bond. In addition, considerable reduction of the carbonyl absorption intensity in the spectrum of **XIII** relative to **XII** is likely to result from steric effect of two bulky phenyl groups. Presumably, distortion of the planar structure for steric reasons favors formation of intra- and intermolecular hydrogen bonds.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr. The Raman spectra were obtained on a DFS-12 instrument with a laser excitation source from pelleted samples. The UV spectra were measured on an SF-9 spectrophotometer from solutions in water. The ^{1}H NMR spectra were recorded on Tesla BS-487C (80 MHz) and Bruker WH-360 (90 MHz) spectrometers using DMSO-d_6 as solvent and HMDS as external reference. The ionization constants were determined by potentiometric titration [12] using a 340 pH-meter.

***N′*^{1},*N′*^{2}-Dinitrohydrazine-1,2-bis(carboximidamide) (I).** *a*. Bis(aminoguanidinium) salt **II**, 17.5 g (0.05 mol), was dissolved in 200 ml of an ice–water mixture, and 25 ml of 58% nitric acid was added with stirring. After 40 min, the colorless precipitate was filtered off, washed with water, and dried in air. Yield 5.8 g (91%), mp 189°C (decomp.). IR spectrum, ν, cm^{-1}: 3370 (NH), 3310 (NH), 3250 (NH), 1680, 1610, 1550, 1440 ($\nu_{as}NO_2$), 1390 ($\nu_{as}NO_2$), 1290 (ν_sNO_2), 1050. UV spectrum, λ_{max}, nm (logε): 218 (3.96), 271 (4.50). ^{1}H NMR spectrum, δ, ppm: 8.67 (2H, NH_2), 10.01 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 121.97 s. Found, %: C 11.56; H 2.99; N 54.38. $C_2H_6N_8O_4$. Calculated, %: C 11.65; H 2.91; N 54.32.

b. A solution of 1.47 g (0.01 mol) of 1-methyl-2-nitro-1-nitrosoguanidine in 5 ml of water was added with stirring to a suspension of 1.19 g (0.01 mol) of 1-amino-2-nitroguanidine in 20 ml of water. The mixture was stirred for 7 days at 45–50°C until it became colorless. The colorless precipitate was filtered off, washed with alcohol and diethyl ether, and dried in air. Yield 0.93 g (45%), decomposition point 198°C (from water). Found, %: C 11.68; H 3.02; N 54.43. Calculated, %: C 11.65; H 2.91; N 54.32.

***N′*^{1},*N′*^{2}-Dinitrohydrazine-1,2-bis(carboximidamide) bis(aminoguanidinium) salt (II).** Hydrazine hydrate, 19 ml (0.75 mol), was added with stirring to a suspension of 52 g (0.5 mol) of 2-nitroguanidine in

220 ml of water. The mixture was stirred for 2 h 40 min at 57–58°C and cooled to 18–20°C while stirring. The precipitate was filtered off, washed with cold water (3–5°C) until colorless washings, and dried in air. Yield 17.5 g (45%), mp 166–167°C (decomp.). IR spectrum, ν, cm^{-1}: 3470 (NH), 3370 (NH), 1650, 1595, 1570, 1400 (ν_{as} NO_2), 1340 (ν_s NO_2), 1070. UV spectrum, λ_{max}, nm (log ε): 253 (4.09), 322 (3.86). ^{1}H NMR spectrum, δ, ppm: 4.82 br.s (NH). ^{13}C NMR spectrum, δ_C, ppm: 119.3 s [H_2N–C(=NH)$NHNH_3^+$], 116.4 s [$^-$OON=N(NH_2)C=N–]. Found, %: C 13.71; H 5.24; N 62.92. $C_2H_6N_8O_4 \cdot 2CH_6N_4$. Calculated, %: C 13.56; H 5.12; N 63.26.

1,2-Bis(hydroxymethyl)-*N′*^{1},*N′*^{2}-dinitrohydrazine-1,2-bis(carboximidamide) (III). A suspension of 2.06 g (0.01 mol) of hydrazobis(nitroformamidine) (**I**) in 10 ml of a 32% formaldehyde solution was heated for 20 min at 60°C, and the resulting solution was filtered and cooled to 20°C. After 15–20 h, the precipitate was filtered off and dried in air. Yield 2.3 g (87%), mp 142°C. UV spectrum, λ_{max}, nm (log ε): 2.73 (4.50). Found, %: C 18.34; H 4.04; N 42.04. $C_4H_{10}N_8O_6$. Calculated, %: C 18.04; H 3.76; N 42.10.

1,1′-Bis(4,5-dihydroxy-2-nitroiminoimidazolidine) (IV). *a*. A suspension of 2.06 g (0.01 mol) of hydrazobis(nitroformamidine) (**I**) in 10 ml of water was added with stirring to 5 ml of a 30% aqueous solution of glyoxal adjusted to pH 8–9 by adding 20% aqueous potassium hydroxide. The mixture was heated for 8 h at 40–45°C and cooled, and the crystalline product was filtered off. Yield 2.98 g (93%), mp >260°C. Found, %: C 23.59; H 3.21; N 34.85. $C_6H_{10}N_8O_8$. Calculated, %: C 23.60; H 3.16; N 34.78.

b. A suspension of 1.5 g (0.0073 mol) of hydrazobis(nitroformamidine) (**I**) in an acetate buffer (a mixture of 12 ml of a 2 M solution of acetic acid and 6 ml of a 4 N solution of sodium acetate) was added to 3.7 ml of a 30% aqueous solution of glyoxal adjusted to pH 9 by adding 20% potassium hydroxide. The mixture was stirred for 7 h at 54–56°C, slowly cooled, and left overnight, and the colorless crystals were filtered off. Yield 2.2 g (90%), mp >260°C. Found, %: C 23.57; H 3.24; N 34.86. $C_6H_{10}N_8O_8$. Calculated, %: C 23.60; H 3.16; N 34.78.

***N′*^{1},*N′*^{2}-Dinitrodiazene-1,2-bis(carboximidamide) (V).** *a*. A stream of chlorine was passed over a period of 25 min through a suspension of 3.09 g (0.015 mol) of hydrazobis(nitroformamidine) (**I**) in 30 ml of water under stirring at 0–5°C. The yellow precipitate was filtered off, washed with cold water until neutral washings, and dried in air. Yield 1.72 g (56%), mp 154°C (from nitromethane).

b. A suspension of 4.12 g (0.02 mol) of hydrazobis(nitroformamidine) (**I**) in 50 ml of water was cooled to 0–5°C, and 1.4 ml of bromine was slowly added under vigorous stirring. The mixture was stirred for 10–15 min, and the bright yellow precipitate was filtered off, washed with cold water until neutral washings, and dried in air. Yield 3.55 g (89%), mp 157°C.

c. Bromine, 2.5 ml, was quickly added at 0–3°C to an aqueous solution of hydrazobis(nitroformamidine) (**I**) monoammonium salt which was prepared by addition of 6.5 ml of 22% aqueous ammonia to a suspension of 10.3 g (0.05 mol) of hydrazobis(nitroformamidine) (**I**) in 980 ml of water. The bright yellow finely crystalline precipitate was filtered off, washed with cold water until neutral washings, and dried in air. Yield 8.2 g (80%), decomposition point 159°C. Found, %: C 11.72; H 1.94; N 54.94. $C_2H_4N_8O_4$. Calculated, %: C 11.76; H 1.96; N 54.90.

d. A 5% aqueous solution of potassium permanganate, 42 ml, was added in portions under vigorous stirring at 20–22°C to a suspension of 4.12 g (0.02 mol) of hydrazobis(nitroformamidine) (**I**) in 100 ml of 1.5–2.5 N nitric acid. Each next portion of the potassium permanganate solution was added after complete decoloration of the mixture. The reaction was assumed to be complete when addition of one drop of the $KMnO_4$ solution induced precipitation of brown MnO_2. The latter was removed by adding sodium pyrosulfite. The orange solid was filtered off, washed with cold water until neutral washings, and dried in air. Yield 3.3 g (80%), decomposition point 160°C. ^{1}H NMR spectrum, δ, ppm: 10.01 s (NH_2). Found, %: C 11.80; H 1.98; N 54.91. $C_2H_4N_8O_4$. Calculated, %: C 11.76; H 1.96; N 54.90.

e. A flask equipped with a reflux condenser which was connected to a trap was charged with a solution of 10 ml of dinitrogen tetraoxide in 360 ml of glacial acetic acid, and a stream of air was passed through the solution over a period of 5 min at 20–23°C. The flow rate of air was reduced, and 15.4 g (0.074 mol) of hydrazobis(nitroformamidine) (**I**) was added to the transparent solution in five portions over a period of 20 min. The flow rate of air was raised, and the mixture spontaneously warmed up to 40–45°C. It was then heated to 75–80°C at a rate of 1–2 deg/min. Initially, hydrazo compound **I** dissolved, and bright

yellow crystalline azobis(nitroformamidine) (**V**) began to separate from the solution. When the temperature reached 80°C, the mixture was cooled to 15–20°C while continuously passing air, and air supply was turned off. The precipitate was filtered off and washed with cold water (5–7°C) until neutral washings. Yield 11.1 g (72%), decomposition point 158°C.

***N'*[1],*N'*[2]-Dinitrodiazene-1,2-bis(carboximidamide) dipotassium salt (VI).** A solution of 1.1 g (0.02 mol) of potassium hydroxide in 5 ml of water was added with stirring at 10–15°C to a suspension of 1.02 g (5 mmol) of azobis(nitroformamidine) (**V**) in 5 ml of water. After 1 h, the colorless precipitate was filtered off and washed with cold water, alcohol, and ether. Yield 1.2 g (85%), decomposition point 124°C. Found, %: C 8.78; H 1.73; N 39.71. $C_2H_4K_2N_8O_4$. Calculated, %: C 8.51; H 1.41; N 39.72.

1-Diacetylmethyl-*N'*[1],*N'*[2]-dinitrohydrazine-1,2-bis(carboximidamide) (VII). Acetylacetone, 0.5 g (5 mmol), was added to a suspension of 1.02 g (5 mmol) of azobis(nitroformamidine) (**V**) in 10 ml of methanol or ethanol. The mixture was stirred for 10–15 min at 50–55°C and cooled, and the precipitate was filtered off and washed with alcohol. Yield 1.46 g (96%), mp 178–179°C. IR spectrum, ν, cm^{-1}: 3420 (NH), 3330 (NH), 3190, 3080, 1740 (C=O), 1660, 1610, 1500, 1445 ($\nu_{as}NO_2$), 1410 ($\nu_{as}NO_2$), 1310 (ν_sNO_2), 1285 (ν_sNO_2), 1150, 1100, 1080. UV spectrum, λ_{max}, nm (log ε): 251 (4.44), 345 (3.59). ^{1}H NMR spectrum, δ, ppm: 1.98 s (3H, CH_3), 2.45 s (3H, CH_3), 4.81 s (1H, CH), 6.91 s (1H, NH), 8.44 and 9.22 s (2H, NH_2), 9.95 s and 10.61 s (2H, NH_2). Found, %: C 27.82; H 4.26; N 37.08. $C_7H_{12}N_8O_6$. Calculated, %: C 27.63; H 3.94; N 36.84.

Compounds **VIII**–**XI** were synthesized in a similar way.

1-(1,1-Diacetylethyl)-*N'*[1],*N'*[2]-dinitrohydrazine-1,2-bis(carboximidamide) (VIII) was obtained from 2.04 g (0.01 mol) of azo compound **V** and 1.14 g (0.01 mol) of 3-methyl-2,4-pentanedione. Yield 2.45 g (77%), mp 161°C. IR spectrum, ν, cm^{-1}: 3400 (NH), 3320 (NH), 3180, 3075, 1725 (C=O), 1660, 1610, 1500, 1445 ($\nu_{as}NO_2$), 1420 ($\nu_{as}NO_2$), 1300 (ν_sNO_2), 1280 (ν_sNO_2), 1130, 1100, 1070. UV spectrum, λ_{max}, nm (log ε): 250 (4.45), 348 (3.60). ^{1}H NMR spectrum, δ, ppm: 1.95 s (3H, CH_3), 2.36 s (3H, CH_3), 2.45 s (3H, CH_3), 7.03 s (1H, NH), 8.27 s and 9.18 s (2H, NH_2), 10.00 s and 10.66 s (2H, NH_2). Found, %: C 30.14; H 4.12; N 35.30. $C_8H_{14}N_8O_6$. Calculated, %: C 30.18; H 4.40; N 35.22.

Ethyl 2-{1,2-bis[amino(nitroimino)methyl]hydrazino}-3-oxobutanoate (IX) was obtained from 1.02 g (5 mmol) of compound **V** and 0.76 g (5 mmol) of ethyl acetoacetate. Yield 1.68 g (98%), mp 149°C. IR spectrum, ν, cm^{-1}: 3440 (NH), 3330 (NH), 1750 (C=O). UV spectrum, λ_{max}, nm (log ε): 265 (4.35), 310 (3.30). ^{1}H NMR spectrum, δ, ppm: 1.28 m (3H, CH_3), 1.96 s (3H, CH_3), 4.43 q (2H, CH_2), 4.70 (1H, CH), 7.01 s (1H, NH), 8.34 and 9.20 s (2H, NH_2), 10.02 s and 10.71 s (2H, NH_2). Found, %: C 29.04; H 4.56; N 33.54. $C_8H_{14}N_8O_7$. Calculated, %: C 28.74; H 4.49; N 33.53.

Ethyl 2-{1,2-bis[amino(nitroimino)methyl]hydrazino}-2-ethyl-3-oxobutanoate (X) was obtained from 1.02 g (5 mmol) of compound **V** and 0.8 g (5 mmol) of ethyl 2-ethyl-3-oxobutanoate. Yield 1.36 g, mp 156°C. UV spectrum, λ_{max}, nm (log ε): 267 (4.50), 320 (3.30). ^{1}H NMR spectrum, δ, ppm: 0.85 m (3H, CH_3), 1.20 m (3H, CH_3), 1.91 s (3H, CH_3), 3.42 q (2H, CH_2), 4.23 q (2H, CH_2), 7.01 s (1H, NH), 8.29 s and 9.15 s (2H, NH_2), 10.00 s and 10.67 s (2H, NH_2). Found, %: C 33.23; H 5.05; N 30.86. $C_{10}H_{18}N_8O_7$. Calculated, %: C 33.14; H 4.97; N 30.94.

Diethyl 2-{1,2-bis[amino(nitroimino)methyl]hydrazino}-3-oxobutanedioate (XI) was obtained from 1.02 g (5 mmol) of compound **V** and 0.94 g (5 mmol) of diethyl 2-oxobutanedioate. Yield 1.77 g, mp 164°C. IR spectrum, ν, cm^{-1}: 3430 (NH), 3330 (NH), 1750 (C=O), 1640, 1620, 1540, 1440 ($\nu_{as}NO_2$), 1400 ($\nu_{as}NO_2$), 1330 (ν_sNO_2), 1300 (ν_sNO_2), 1250, 1220, 1140, 1080. UV spectrum, λ_{max}, nm (log ε): 266 (4.42), 310–340 sh. ^{1}H NMR spectrum, δ, ppm: 1.22 m (3H, CH_3), 1.58 m (3H, CH_3), 4.10–4.60 two q (4H, $2CH_2$), 4.80 (CH), 8.40 s and 9.24 s (2H, NH_2), 10.05 s and 10.75 s (2H, NH_2). Found, %: C 30.39; H 4.01; N 28.49. $C_{10}H_{16}N_8O_9$. Calculated, %: C 30.61; H 4.08; N 28.57.

1-(1-Benzoyl-2-oxopropyl)-*N'*[1],*N'*[2]-dinitrohydrazine-1,2-bis(carboximidamide) (XII). Benzoylacetone, 0.162 g (1 mmol), was added to a suspension of 0.204 g (1 mmol) of azo compound **V** in 6 ml of methanol. The mixture was stirred for 3 h at 30–35°C, and the solvent was distilled off under reduced pressure. The colorless precipitate was recrystallized from methanol. Yield 0.3 g (83%), mp 162°C. IR spectrum, ν, cm^{-1}: 3420 (NH), 3310 (NH), 1690 (C=O). UV spectrum, λ_{max}, nm (log ε): 264 (4.44), 350 (3.71). ^{1}H NMR spectrum, δ, ppm: 2.20 s (3H, CH_3), 5.39 s (1H, CH), 7.00 s (1H, NH), 7.67 m (5H, Ph), 8.20 s and 9.20 s (2H, NH_2), 10.04 s and 10.81 s (2H, NH_2). Found, %: C 42.80; H 4.01; N 33.49. $C_{12}H_{14}N_8O_6$. Calculated, %: C 42.85; H 4.17; N 33.33.

1-Dibenzoylmethyl-*N′*[1],*N′*[2]-dinitrohydrazine-1,2-bis(carboximidamide) (XIII). Dibenzoylmethane, 0.224 g (1 mmol), was added to a suspension of 0.204 g (1 mmol) of azo compound **V** in 35 ml of methanol, and the mixture was stirred for 1 h at 30–35°C. The initial compounds gradually dissolved, and new colorless crystals precipitated. The product was filtered off and recrystallized from ethanol. Yield 0.28 g (65%), mp 180°C (decomp.). IR spectrum, ν, cm^{-1}: 3420 (NH), 3380 (NH), 3180, 1690 (C=O), 1650, 1600, 1520, 1450 ($\nu_{as}NO_2$), 1390 ($\nu_{as}NO_2$), 1300 (ν_sNO_2), 1260 (ν_sNO_2), 1220, 1160, 1080. UV spectrum, λ_{max}, nm (log ε): 265 (4.66), 377 (3.34). ^{1}H NMR spectrum, δ, ppm: 6.00 s (1H, CH), 7.02 s (1H, NH), 7.47 d (5H, H_{arom}), 7.66 d (5H, H_{arom}), 8.53 s and 9.19 s (2H, NH_2), 10.17 s and 10.89 s (2H, NH_2). Found, %: C 47.55; H 3.60; N 26.30. $C_{17}H_{16}N_8O_6$. Calculated, %: C 47.66; H 3.74; N 26.16.

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REFERENCES

1. Metelkina, E.L., *Russ. J. Org. Chem*., 2004, vol. 40, p. 543.
2. Henry, R.A., Skolnik, S., and Smith, G.B.I., *J. Am. Chem. Soc*., 1953, vol. 75, p. 955.
3. Henry, R.A., Mokosky, R.C., and Smith, G.B.I., *J. Am. Chem. Soc*., 1951, vol. 73, p. 474.
4. Metelkina, E.L., Varlygo, K.V., Paperno, T.Ya., and Berkova, G.A., *Zh. Obshch. Khim*., 1995, vol. 65, p. 634.
5. DeVries, J.E. and St. Clair, E.G., *J. Am. Chem. Soc*., 1954, vol. 76, p. 1008.
6. Gund, P., *J. Chem. Educ*., 1972, vol. 49, p. 100.
7. Grekov, A.P. and Sukhorukova, S.A., *Polimery na osnove hydrazina* (Hydrazine-Based Polymers), Kiev: Naukova Dumka, 1976, p. 40.
8. Terpigorev, A.N. and Rudakova, S.B., *Russ. J. Org. Chem*., 1998, vol. 34, p. 1026.
9. Vidal, F.D., Grange, E., and Sarel, V.O., US Patent no. 3192196, 1965.
10. Kumler, W.D., *J. Am. Chem. Soc*., 1953, vol. 75, p. 3092.
11. Ghosh, J.N. and Gula, P.S., *J. Indian Inst. Sci*., 1933, vol. 16, p. 103.
12. Kostyuchenko, N.P., Granin, V.G., Zhidkova, A.M., Glushkov, R.G., and Sheinker, Yu.N., *Khim. Geterotsikl. Soedin*., 1974, p. 1212.
13. Nalimov, V.V., *Teoriya eksperimenta* (Theory of Experiment), Moscow: Nauka, 1971, p. 69.