

N-Nitroimines: I. Synthesis, Structure, and Properties of 3,5-Diamino-1-nitroamidino-1,2,4-triazole

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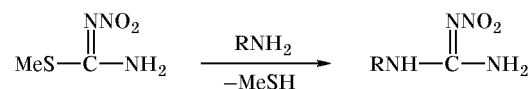
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Abstract—The reaction of 3,5-diamino-1,2,4-triazole with 2-methyl-1-nitroisothiourea gives 3,5-diamino-1-nitroamidino-1,2,4-triazole instead of the expected 1-[5(3)-amino-1,2,4-triazol-3(5)-yl]-2-nitroguanidine. Almost planar structure of the molecule of 3,5-diamino-1-nitroamidino-1,2,4-triazole gives rise for direct polar conjugation which is responsible for the low basicity of the amino groups.

Both 1,2,4-triazole and nitroguanidine derivatives attract interest as high-energy compounds [1–4]. We expected that combination of a nitroguanidine fragment and a 1,2,4-triazole ring in a single molecule should give rise to new high-energy compounds possessing a set of useful properties inherent to substances of the two series, specifically high density and thermal stability and low sensitivity to mechanical action.

A known method for preparation of nitroguanidine derivatives is based on the reaction of 2-methyl-1-nitroisothiourea with amines [5–7]:



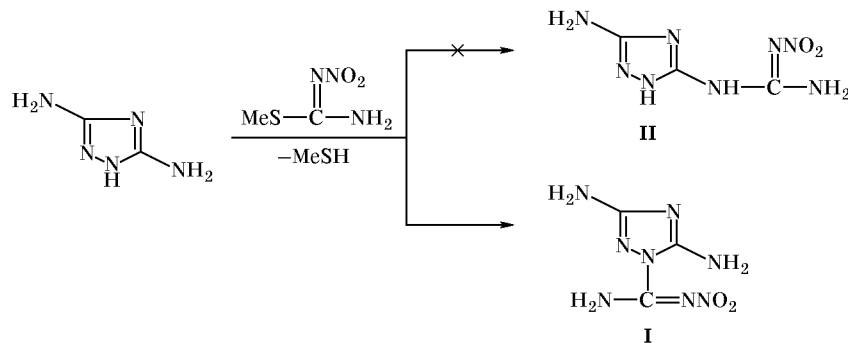
A great number of nitroguanidines having various aliphatic and aromatic substituents were synthesized according to the above procedure [4–7]. However, we have found no published data on analogous reactions with amino-substituted 1,2,4-triazoles. Taking into account the known data on the reactivity of guanazole, it was difficult to predict *a priori* the reaction direction so as to whether will it occur at the amino group or at the triazole ring. Electrophilic species can attack both exo- and endocyclic nitrogen atoms. For instance, picryl chloride reacts with guanazole at the amino group [1, 8], whereas acylation of guanazole involves the pyrrole-like nitrogen atom in the heteroring [1, 9].

Formerly, we believed that the reaction with 2-methyl-1-nitroisothiourea will occur at one of the amino groups of the guanazole molecule, so that the product should be 1-[5(3)-amino-1,2,4-triazol-3(5)-yl]-2-nitroguanidine (**II**). In fact, guanazole relatively readily reacted with 2-methyl-1-nitroisothiourea in an alcoholic solution on heating, and elemental composition of the product was similar to that expected for compound **II**. The data of electronic and vibrational spectra did not contradict structure **II**. Moreover, further chemical transformations of the product, in particular formation of salts **III** and **IV** with nitric and perchloric acids, respectively, are also consistent with the triazolylguanidine structure.

Taking into account that compounds **I** and **II** have the same formula $\text{C}_3\text{H}_6\text{N}_8\text{O}_2$ and possess similar functional groups, the results of elemental analysis and UV and IR spectral data did not allow us to identify the real structure of the product. Likewise, the ^1H , ^{13}C , and ^{15}N NMR spectra cannot be interpreted unambiguously. The product structure was unequivocally established by X-ray analysis which showed that the reaction occurs at the endocyclic nitrogen atom rather than at the amino group (which was initially presumed to be the most nucleophilic). Thus the product has the structure of 3,5-diamino-1-nitroamidino-1,2,4-triazole (**I**) (Scheme 1).

According to the X-ray diffraction data (see figure and Tables 1–3), a unit cell of **I** contains two

Scheme 1.



independent molecules. In the two molecules, the nitroamidine fragment, triazole ring, and amino groups attached thereto lie in one plane: the mean-square deviations are 0.031 (2) and 0.040 (2) Å, and the maximal deviations are 0.036 (3) and 0.068 (3) Å.

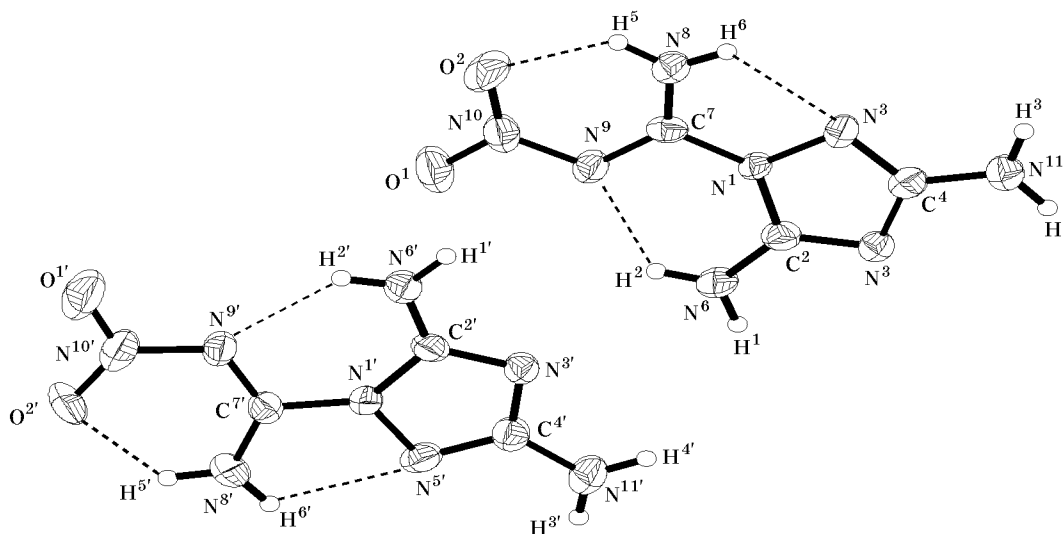
The geometric parameters of the *N*-nitroimino fragment in **I** are similar to those found for the other structurally related compounds [10]. The oxygen atom of the nitro group O² (O^{2'}) and hydrogen atom of the amino group H⁵ (H^{5'}) are involved in intramolecular hydrogen bond, which is typical of nitroimino compounds. In addition, two shortened intramolecular contacts N⁵...H⁶ (N^{5'}...H^{6'}) and N⁹...H² (N^{9'}...H^{2'}) were observed (see figure; Table 3). Molecules of **I**

in crystal are packed through intermolecular hydrogen bonds N–H...O and N–H...N. The geometric parameters of the triazole ring are similar to those found for the other 1,2,4-triazole derivatives [10].

Almost planar structure of molecule **I** gives rise to direct polar conjugation between the triazole ring, amino groups, and nitroamidine fragment. As a result, the electron density is displaced toward the acceptor nitroamidino group. Therefore, the electron density on the amino groups is reduced, and they are characterized by low nucleophilicity and basicity. Despite the presence of two free amino groups (the third amino group in the nitroamidine fragment is strongly deactivated), we succeeded in obtaining only 1:1 salts

Table 1. Relative coordinates of atoms ($\times 10^4$) and their equivalent thermal parameters ($U \times 10^4$, Å²) in two independent molecules of 3,5-diamino-1-nitroamidino-1,2,4-triazole (**I**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
N ¹	2556 (1)/589 (1)	534 (4)/2191 (4)	2259 (1)/4949 (1)	263 (8)/279 (7)
C ²	2871 (2)/884 (2)	–153 (5)/2838 (5)	2836 (2)/4348 (2)	300 (10)/290 (9)
N ³	3497 (1)/1505 (1)	–35 (4)/2446 (4)	2745 (2)/4370 (1)	303 (8)/317 (8)
C ⁴	3561 (2)/1583 (2)	761 (5)/1560 (5)	2110 (2)/4988 (2)	300 (10)/330 (10)
N ⁵	3027 (1)/1065 (1)	1153 (4)/1361 (4)	1777 (1)/5367 (2)	323 (8)/349 (8)
N ⁶	2566 (1)/580 (1)	–852 (4)/3701 (4)	3386 (2)/3841 (2)	393 (9)/411 (9)
H ¹	0.279/0.079	–0.129/0.407	0.373/0.348	520 (40)
H ²	0.215/0.017	–0.087/0.390	0.340/0.387	520 (40)
N ¹¹	4154 (1)/2164 (2)	1100 (4)/971 (5)	1831 (2)/5216 (2)	440 (10)/510 (10)
H ³	0.419/0.220	0.159/0.045	0.142/0.562	520 (40)
H ⁴	0.450/0.250	0.083/0.111	0.206/0.496	520 (40)
C ⁷	1918 (2)/–31 (2)	801 (5)/2297 (5)	2098 (2)/5191 (2)	270 (10)/300 (10)
N ⁸	1809 (1)/–120 (2)	1662 (4)/1642 (4)	1528 (2)/5820 (4)	364 (9)/422 (9)
H ⁵	0.142/–0.050	0.189/0.164	0.140/0.600	520 (40)
H ⁶	0.213/0.020	0.202/0.121	0.127/0.605	520 (40)
N ⁹	1513 (1)/–449 (1)	109 (4)/3020 (4)	2585 (2)/4742 (1)	325 (8)/329 (8)
N ¹⁰	871 (2)/–1080 (2)	298 (4)/3137 (4)	2459 (2)/4939 (2)	408 (9)/426 (9)
O ¹	524 (1)/–1431 (1)	–310 (5)/3804 (5)	2916 (2)/4499 (2)	640 (10)/750 (10)
O ²	645 (1)/–1293 (1)	999 (4)/2617 (4)	1929 (2)/5511 (1)	578 (9)/542 (9)



Mutual arrangement of two independent molecules of 3,5-diamino-1-nitroamidino-1,2,4-triazole (**I**) in crystal. Intramolecular hydrogen bonds are shown as dashed lines.

of **I** with strong mineral acids. Moreover, the salts were hydrolytically unstable: recrystallization from water resulted in their complete hydrolysis with formation of a dilute aqueous solution of the corresponding acid and initial compound **I**.

Signals at δ 7.18 (2H) and 5.49 ppm (2H) in the ^1H NMR spectrum of **I** were assigned to protons of the amino groups attached to the triazole ring. An appreciable difference in the chemical shifts suggests different reactivities of these amino groups. Protons of

Table 2. Bond lengths and bond angles in the structure of 3,5-diamino-1-nitroamidino-1,2,4-triazole (**I**) (data for two independent molecules)

Bond	<i>d</i> , Å	Angle	ω , deg
N ¹ -C ²	1.381 (4)/1.390 (4)	N ¹ C ² N ³	109.6 (3)/109.2 (3)
N ¹ -N ⁵	1.418 (4)/1.406 (4)	C ² N ³ C ⁴	104.1 (3)/104.2 (3)
N ¹ -C ⁷	1.369 (4)/1.366 (4)	N ³ C ⁴ N ⁵	116.9 (3)/116.3 (3)
C ² -N ³	1.309 (5)/1.316 (5)	C ⁴ N ⁵ N ¹	101.0 (3)/102.0 (3)
C ² -N ⁶	1.333 (5)/1.318 (4)	N ¹ C ⁷ N ⁹	112.8 (3)/114.3 (3)
N ³ -C ⁴	1.358 (5)/1.362 (5)	N ¹ C ⁷ N ⁸	115.7 (3)/115.2 (3)
N ⁵ -C ⁴	1.307 (4)/1.304 (5)	N ⁸ C ⁷ N ⁹	131.6 (3)/130.5 (3)
C ⁴ -N ¹¹	1.361 (5)/1.349 (5)	C ⁷ N ⁹ N ¹⁰	116.3 (3)/117.9 (3)
C ⁷ -N ⁸	1.281 (4)/1.314 (4)	N ⁹ N ¹⁰ O ¹	114.2 (3)/113.8 (3)
C ⁷ -N ⁹	1.354 (5)/1.330 (4)	N ⁹ N ¹⁰ O ²	124.2 (3)/124.5 (3)
N ⁹ -N ¹⁰	1.356 (4)/1.361 (4)	O ¹ N ¹⁰ O ²	121.6 (3)/121.7 (3)
N ¹⁰ -O ¹	1.218 (4)/1.216 (4)	N ¹ C ² N ⁶	123.6 (3)/124.5 (3)
N ¹⁰ -O ²	1.232 (4)/1.244 (4)	N ³ C ² N ⁶	126.8 (3)/126.3 (3)
		N ⁵ C ⁴ N ¹¹	121.9 (3)/121.0 (3)
		N ³ C ⁴ N ¹¹	121.2 (3)/122.6 (3)

the amino group in the nitroamidino fragment appear in a weaker field as two broadened singlets at δ 8.28 and 8.82 ppm. Analogous nonequivalence of the nitroguanidyl protons was observed previously in the spectra of 1-alkylamino-2-nitroguanidine [11] and 1-hydroxymethylamino-2-nitroguanidine [12]. Most other nitroguanidine derivatives show in the ^1H NMR spectra one broadened singlet from the same protons [11–14]. The ^{13}C NMR spectrum of **I** contains three signals, at δ_{C} 153.5 and 156.0 ppm from the triazole ring carbon atoms and at δ_{C} 162.9 ppm from the nitroamidino carbon atom. In the ^{15}N NMR spectrum, the chemical shifts of the amino nitrogen atoms attached to the triazole ring are δ_{N} -324.4 and -308.0 ppm. The amino group of the nitroamidino fragment gives a signal at δ_{N} -282.7 ppm. The signal at δ_{N} -15.8 ppm belongs to nitrogen atom of the nitro group, and signal from the imino nitrogen atom appears at δ_{N} -142.6 ppm. The chemical shifts of the endocyclic nitrogen atoms are δ_{N} -208.4, -185.6, and -171.1 ppm. On the whole, the ^{15}N chemical shifts of **I** are comparable with the corresponding published data for nitroguanidine [14] and 1,2,4-triazole derivatives [15].

To conclude, it should be noted that compound **I** is a starting material for preparation of new high-energy nitro and nitroamino derivatives of 1-nitroamidino-1,2,4-triazole [16].

EXPERIMENTAL

The IR spectra were recorded on a Nicolet IMPACT-400 Fourier spectrometer coupled with a Spectra-Tech Inspect IR⁺ IR microscope. The ^1H ,

Table 3. Geometric parameters of intramolecular hydrogen bonds in two independent molecules of 3,5-diamino-1-nitroamidino-1,2,4-triazole (**I**)

D-H	A	$d(\text{D-H}), \text{\AA}$	$d(\text{H}\cdots\text{A}), \text{\AA}$	Angle DHA, deg	$d(\text{D}\cdots\text{A}), \text{\AA}$
N ⁸ -H ⁵	O ²	0.86/0.86	2.00/2.02	123/124	2.573(4)/2.594(4)
N ⁶ -H ²	N ⁹	0.86/0.86	2.17/2.21	126/125	2.759(4)/2.789(4)
N ⁸ -H ⁶	N ⁵	0.86/0.86	2.19/2.22	108/107	2.591(4)/2.610(4)

¹³C, and ¹⁵N NMR spectra were obtained on a Bruker AVANCE 200 spectrometer (200 MHz) in DMSO-*d*₆; the chemical shifts were measured relative to tetramethylsilane (¹H, ¹³C) or nitromethane (¹⁵N). The UV spectra were recorded on an SF-26 spectrophotometer in water. The elemental compositions were determined on a Karlo Erba 1106 CHN-analyzer. Thermal gravimetric analysis was performed using a Q-1500D derivatograph.

3,5-Diamino-1-nitroamidino-1,2,4-triazole (I). 2-Methyl-1-nitroisothiourea, 2 g (0.15 mol), was added to a solution of 2 g (0.20 mol) of 3,5-diamino-1,2,4-triazole in 30 ml of ethanol, and the mixture was heated to the boiling point. Depending on the reaction time (1–12 h), the yield of **I** ranged from 1.6 to 2.5 g (58–91%). The precipitate was filtered off, washed with water, and dried in air. The product had no definite melting point: it decomposed at 270–275°C without melting. Compound **I** is poorly soluble in common organic solvents and cold water. It can be recrystallized from boiling water (150 ml/g). IR spectrum, ν , cm⁻¹: 3461, 3418, 3398, 3360, 3307, 3234, 3081, 1674, 1614, 1564, 1517, 1431 [$\nu_{\text{as}}(\text{NO}_2)$], 1259 [$\nu_{\text{s}}(\text{NO}_2)$], 1240, 1204, 1161, 1114, 1054, 943, 860, 803, 779, 756, 689. UV spectrum, λ_{max} , nm (log ϵ): 265 (4.09), 325 (3.87). Found, %: C 19.63, 19.66; H 3.25, 3.13; N 60.61, 60.32. C₃H₆N₈O₂. Calculated, %: C 19.36; H 3.25; N 60.20.

X-Ray diffraction data. C₃H₆N₈O₂. Orthorhombic crystals. Unit cell parameters: $a = 20.678(1)$, $b = 7.2493(5)$, $c = 19.251(1)$ Å; $V = 2885.7(3)$ Å³, $d_{\text{calc}} = 1.714$ g/cm³; $Z = 16$; space group *Pbca*; $R^1 = 0.0413$, $wR^2 = 0.1086$, GOF = 1.001. The intensities of 1452 independent reflections were measured on a KM-4 KUMA-Diffraction four-circle automatic diffractometer ($\lambda\text{CuK}\alpha$, graphite monochromator, variable $\theta/2\theta$ -scanning, $2\theta_{\text{max}} 120^\circ$). The structure was solved by the direct methods and was refined with the use of SHELX-97 software [17]. Hydrogen atoms were visualized by difference synthesis of electron density, and their positions were refined in

the bound group approximation with a single isotropic thermal parameter.

3,5-Diamino-1-nitroamidino-1,2,4-triazolium nitrate (III). Nitric acid ($d = 1.4$ g/cm³), 3 ml, was added to 35 ml of boiling water, and 1 g of compound **I** was added in small portions under stirring. The solution was cooled, and thin nacrous leaflets separated. The precipitate was filtered off and dried in air. Yield 1.27 g (95%). The product had no definite melting point. According to the thermal analysis data, loss of weight is observed above 160°C in the solid phase (elimination of HNO₃); the initial temperature of vigorous decomposition (270–275°C) corresponds to that of initial compound **I**. IR spectrum, ν , cm⁻¹: 3493, 3370, 3335, 3275, 3204, 3137, 2869, 2685, 1713, 1677, 1635, 1512, 1440 [$\nu_{\text{as}}(\text{NO}_2)$], 1334 (NO₃), 1264 [$\nu_{\text{s}}(\text{NO}_2)$], 1201, 1135, 1077, 1057, 1017, 950, 820, 768, 727. Found, %: C 13.89, 13.62; H 3.05, 3.08; N 50.10, 51.08. C₃H₇N₉O₅. Calculated, %: C 14.46; H 2.83; N 50.60.

3,5-Diamino-1-nitroamidino-1,2,4-triazolium perchlorate (IV). Perchloric acid ($d = 1.5$ g/cm³), 5 ml, was added to 10 ml of boiling water, and 1 g of compound **I** was added in small portions under stirring. After cooling, colorless leaflets separated. The precipitate was filtered off and dried in air. Yield 1.54 g (~100%), mp 240°C (decomposes with a flash). IR spectrum, ν , cm⁻¹: 3474, 3404, 3374, 3312, 3292, 3277, 3246, 1681, 1634, 1578, 1523, 1497, 1446 [$\nu_{\text{as}}(\text{NO}_2)$], 1419, 1276 [$\nu_{\text{s}}(\text{NO}_2)$], 1206, 1183, 1084 (ClO₄), 1027, 996, 949, 861, 802, 780, 703, 690. Found, %: C 12.67, 12.55; H 2.46, 2.45; N 39.07, 39.35. C₃H₇N₈ClO₆. Calculated, %: C 12.57; H 2.46; N 39.10.

Taking into account hydrolytic instability of salts **III** and **IV**, they should not be washed with water or alcohol on a filter. The UV spectra of aqueous solutions of **III** and **IV** were identical to the spectrum of **I** because of their complete hydrolysis.

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