

Nitroimines: II.* Structure of Nitroamino-1,2,4-triazoles

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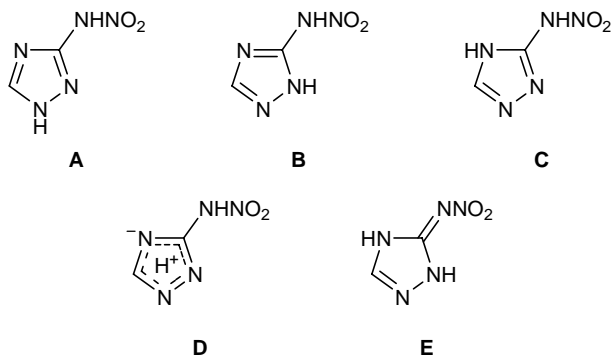
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Abstract—According to the X-ray diffraction data, compounds formerly known as 3(5)-nitroamino-1,2,4-triazoles are in fact *N*-nitroimines rather than primary *N*-nitroamines. Their chemical properties and UV and NMR spectra indicate their nitroimine structure in solution as well.

3(5)-Nitroamino-1,2,4-triazole (**I**) and its derivatives attract interest as energy-rich compounds [2–5]. Although these substances were reported for the first time as early as 1950 [6] and, as it would seem, were extensively studied in the recent years, their structure still remains a matter of discussion. In most publications, e.g., in review [2], compound **I** was assigned the primary *N*-nitroamine structure. However, it is not clear which nitrogen atom in the triazole ring is attached to hydrogen.



According to some authors, compound **I** is 3-nitroamino-1,2,4-triazole (structure **A**) [3, 7–9], while the others believe that it has the structure of 5-nitroamino-1,2,4-triazole (**B**) [6, 10], or it is referred to as 3(5)-nitroamino-1,2,4-triazole [2, 11]. Bonner and Lockhart [12] and Gao *et al.* [13] presumed that the hydrogen atom in molecule **I** is located at N⁴ (structure **C**). Moreover, structure **D** was also proposed to be possible on the basis of the IR spectral data [13] (we believe that this assumption was insufficiently substantiated). Finally, Licht *et al.* [4] presumed the existence

in solution of a tautomeric equilibrium between primary nitroamine and nitroimine structures **B** and **E**, respectively.

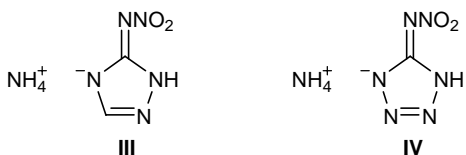
Assignment of the nitroamine structure to nitroamino-1,2,4-triazoles is based mainly on the data on their acidity, as well as on the UV and IR spectra [7, 14]. However, in such cases spectroscopic data could be treated with ambiguity [15, 16], and no rigorous conclusions concerning the structure of nitroamino-1,2,4-triazoles could be drawn.

We previously proposed nitroimine structure for compound **I** on the basis of its physical and chemical properties and quantum-chemical calculations [17]. Taking into account that the structure of nitroamino-1,2,4-triazoles is the key point in understanding their reactivity and mechanism of thermal decomposition and correctly interpreting their spectral parameters, in the present work we made an attempt to unambiguously determine their structure by X-ray analysis. Probably, the structure of **I** has not been determined so far, for it is difficult to obtain its single crystals suitable for X-ray analysis. Compound **I** is almost insoluble in most common organic solvents, sparingly soluble in water, and readily soluble in acids. We failed to obtain suitable crystalline samples by crystallization from water or nitric acid. The X-ray powder pattern of **I** contains a relatively small number of peaks, some of which are broadened, so that it was impossible to determine the unit cell parameters from the X-ray powder patterns. No single crystals were obtained by crystallization from DMF or aqueous dioxane. On the other hand, compound **I** crystallized from DMSO to give colorless transparent crystals of a complex with DMSO, which seemed to be suitable for X-ray analysis. Unfortunately, the complex **I**–DMSO is unstable.

* For communication I, see [1].

It decomposes during separation from the solution upon washing on a filter with water or some other solvent. Loss of DMSO also occurs upon drying on a filter in air for a short time (without preliminary washing). In both cases, compound **I** is isolated as a white fine powder unsuitable for X-ray analysis.

Unlike compound **I**, crystallization of 3(5)-methyl-5(3)-nitroamino-1,2,4-triazole (**II**) [6] from an aqueous solution afforded quite suitable crystals of the corresponding monohydrate, **II**·H₂O. X-Ray analysis of these crystals unambiguously showed that compound **II** has the nitroimine structure (Fig. 1). Monoammonium salt **III** derived from **I** also readily crystallizes from water, yielding needle-shaped crystals. According to the X-ray diffraction data, the anion in **III** has the nitroimine structure (Fig. 1). Presumably, the same structure is also intrinsic to initial compound **I**. This assumption is supported by the fact that both monoammonium salt of 5-nitroaminotetrazole (**IV**) [18] and 5-nitroaminotetrazole (**V**) [13, 19] were found to exist as nitroimines, i.e., proton abstraction does not change the nitroimine structure.



Thus compounds **I** and **V** are converted into the corresponding anions via abstraction of proton from the nitrogen atom in position 4 of the heteroring. However, the negative charge in the resulting anion is delocalized over the entire molecule, as in other NH acids having nitroimine structure [20]. Therefore, the above given formulas of salts **III** and **IV** are speculative. As shown in [18], it is difficult to draw a structural formula strictly corresponding to the experimental geometric parameters or even represent molecule **IV** as a resonance hybrid of several structures with separated charges. The same applies to compound **III**. Moreover, the formally double C=NNO₂ bond in compounds **II**–**V** (as well as in other nitroimines for which X-ray diffraction data are available [21]) is neither a double bond nor even the shortest bond among the other C–N bonds.

The C–N and N–O bonds in the nitroimine fragment of the monoanions are longer while the N–N bond is shorter than the corresponding bonds in the neutral molecules (see [18] and Table 1). Variations in bond angles are insignificant [18]. These data indicate

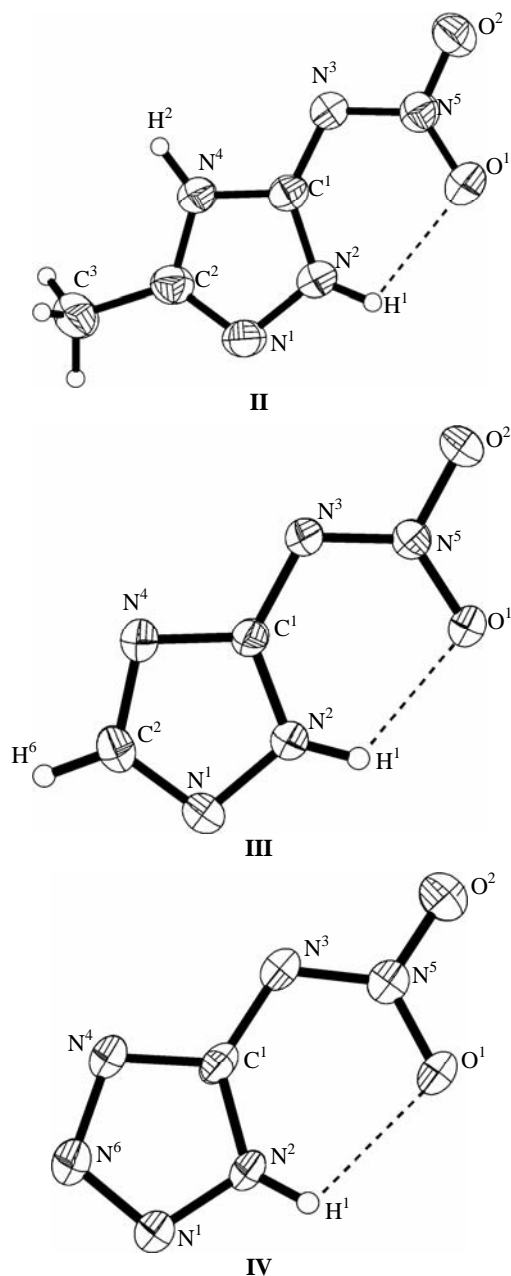


Fig. 1. Molecular structure of compounds **II**, **III** (anion), and **IV** (anion). Intramolecular hydrogen bonds are shown as dashed lines.

that conjugation of *p* electrons on the imino nitrogen atom in the anion with π electrons of the nitro group is stronger than with the π -electron system of the heteroring. Nevertheless, as in other nitroimines [21], the C–N, N–N, and N–O bond lengths are intermediate between those typical of the corresponding single and double bonds (Table 1), i.e., π -electron density is delocalized over the whole molecule. In keeping with the experimental bond lengths, the structures of compounds **II** and **III** may be represented as shown below.

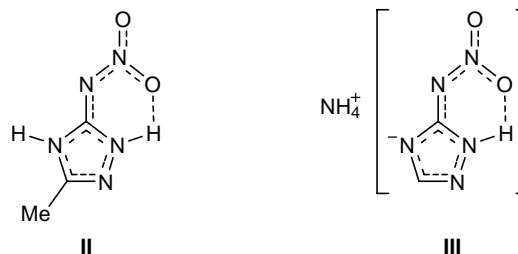
Table 1. Bond lengths and bond angles in molecules **II–IV**

Bond	<i>d</i> , Å		
	II ·H ₂ O	III	IV ^a
N ¹ –N ²	1.377(2)	1.360(2)	1.343(2)
N ² –C ¹	1.327(2)	1.342(2)	1.339(2)
C ¹ –N ⁴	1.345(2)	1.335(2)	1.327(2)
N ⁴ –C ² (N ⁶)	1.360(2)	1.350(2)	1.350(2)
C ² (N ⁶)–N ¹	1.302(2)	1.313(2)	1.297(2)
C ¹ –N ³	1.354(2)	1.386(2)	1.374(2)
N ³ –N ⁵	1.331(2)	1.295(2)	1.305(2)
N ⁵ –O ¹	1.236(2)	1.259(2)	1.254(2)
N ⁵ –O ²	1.246(2)	1.276(2)	1.254(2)
C ² –C ³	1.480(2)	–	–
N ² –H ¹	0.87(1)	0.86 ^b	0.83(2)
N ⁴ –H ²	0.89(1)	–	–
C ³ –H	0.96 ^b	–	–
C ² –H ⁶	–	0.93 ^b	–
Angle	ω, deg		
N ¹ N ² C ¹	111.0(1)	109.6(1)	108.9(2)
N ² C ¹ N ⁴	105.8(1)	109.3(1)	107.8(2)
C ¹ N ⁴ C ² (N ⁶)	107.8(1)	103.5(1)	106.3(1)
N ⁴ C ² (N ⁶)N ¹	110.5(1)	114.5(1)	110.9(1)
C ² (N ⁶)N ¹ N ²	104.8(1)	103.1(1)	106.2(2)
N ² C ¹ N ³	135.4(1)	131.0(1)	132.4(2)
N ⁴ C ¹ N ³	118.7(1)	119.6(1)	119.7(2)
C ¹ N ³ N ⁵	116.7(1)	116.7(1)	116.8(1)
N ³ N ⁵ O ¹	122.7(1)	123.9(1)	123.6(1)
N ³ N ⁵ O ²	115.0(1)	116.9(1)	116.5(1)
O ¹ N ⁵ O ²	122.3(1)	119.2(1)	119.9(1)
N ¹ C ² C ³	125.6(1)	–	–
N ⁴ C ² C ³	123.8(1)	–	–
N ¹ N ² H ¹	119(1)	125 ^b	117(2)
C ¹ N ² H ¹	130(1)	125 ^b	133(2)
N ¹ (N ⁴)C ² H ⁶	–	123 ^b	–

^a Data of [18].^b Interatomic distances and bond angles were calculated for idealized positions of hydrogen atoms.

It is unlikely that transition of compounds **I** and **II** from the crystalline state to solution would give rise to tautomeric primary nitroamines. Their nitroimine structure in solution is evidenced by the following [17]:

(1) Absorption maxima ($n \rightarrow \pi^*$ transition) in the electron spectra of aqueous solutions of **I** and **II** are located at λ 284 (log ϵ 4.10) and 287 nm (log ϵ 4.13), respectively. The electron absorption spectrum of



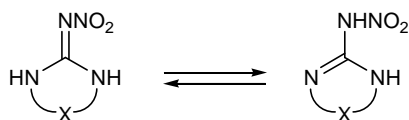
5-nitroamino-3-nitro-1,2,4-triazole (**VI**) resembles those of **I** and **II**, the long-wave maximum being located at λ 286 nm (log ϵ 4.13) (Fig. 2). This spectral region (λ 265–290 nm) is typical of nitroimines rather than primary nitroamines which absorb at shorter wavelengths (λ 230±10 nm) [22, 23]. Pevzner *et al.* [14] assigned the nitroamine structure to compound **VI** on the basis of comparison of its acidic properties and UV and IR spectra with the corresponding parameters of **I** and **II** which were considered *a priori* to be primary nitroamines; this conclusion seems to be erroneous;

(2) Compounds **I** and **II** differ in chemical properties from primary nitroamines [23]: they are relatively stable in acid medium, they do not give hydroxymethyl derivatives, and they do not undergo aminomethylation;

(3) Structural analogs of **I** and **II**, such as nitroguanidine [24–27] and 2-nitroiminoimidazolidine derivatives [28, 29] and primarily compound **V** [13, 19] were shown to have nitroimine structure both in the crystalline state [21] and in solution.

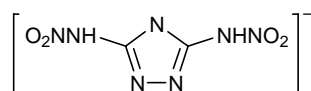
In order to get an additional information on the structure of nitroamino-1,2,4-triazoles in solution we examined the ¹H and ¹³C NMR spectra of compounds **I–VI**. The spectral parameters and probable signal assignments are given in Table 2. On the whole, the ¹H NMR spectra are low informative, and resonance signals appear as broadened singlets. Identification of signals from particular NH protons is difficult due to exchange, especially when the solvent (DMSO-*d*₆) contains traces of water. The ¹³C NMR spectra also did not allow us to distinguish between nitroamino and nitroimino structures. However, the data in Table 2 show that all compounds are characterized by similar chemical shifts of the nitroimino carbon atom. Taking into account previously established nitroimine structure of compound **V** in solution [19], we believe that compounds **I–IV** and **VI** have a similar structure. Nevertheless, rigorous conclusion on the structure of nitroamino-1,2,4-triazoles in solution requires ¹⁵N NMR spectra to be recorded for both compounds **I–III** and **VI** and their *N*-methyl derivatives [30, 31].

At present, the possibility for nitroimine–nitroamine tautomerism of compounds possessing a nitroguanidine fragment remains hypothetical.



No rigorous experimental proof for the existence of such tautomerism has been reported so far. On the other hand, it cannot be ruled out for compounds belonging to other classes. For example, the nitroimine structure in the crystalline state was found for nitroaminopyridines by X-ray analysis [32–34], while ^{15}N NMR spectra of some compounds in solution are interpreted better from the viewpoint of their nitroamine structure [35, 36].

Zhuji *et al.* [37] performed X-ray analysis of monoammonium and monopotassium salts derived from 3,5-bis(nitroamino)-1,2,4-triazole (**VII**) and concluded that the anion of **VII** has primary nitroamine structure.



However, no data were given in [37] on the position of hydrogen atoms. It remained unclear whether their location was determined from the experimental data or hydrogen atoms were localized on the basis of theoretical considerations *a priori* assuming the nitroamine structure of the anion. The coordinates of hydrogen atoms were given in [37] without standard deviations and thermal parameters, whereas the corresponding data were presented for the other atoms. Therefore, the planar anion of **VII** could equally be assigned the nitroimine structure. Obviously, the structure of compound **VII** and its derivatives requires further study.

EXPERIMENTAL

Compounds **I–VI** were synthesized and purified by known methods [2, 3, 14, 18, 38].

The X-ray diffraction data for compounds **II**· H_2O and **III** were acquired on a KM-4 KUMA-Diffraction automatic diffractometer at room temperature using standard technique (CuK_α irradiation, graphite monochromator, variable $\theta/2\theta$ scanning). The structures were solved by the direct methods and were refined by the full-matrix least-squares procedure in anisotropic approximation (isotropic for hydrogen atoms) using

Table 2. NMR spectra of compounds **I–VI**

Comp. no.	Nucleus	Chemical shifts δ , δ_{C} , ppm
I	^1H	3.69 br.s (0.5H, $\text{NH}\cdot\text{H}_2\text{O}$), 8.46 s (1H, CH), 14.05 br.s (1.7H, NH) 8.40, ^a 8.50, ^b 7.70 ^b
	^{13}C	139.0 (CH), 152.2 (C=NNO ₂)
II	^1H	2.29 s (3H, CH ₃), 3.39 br.s (1.7H, $\text{NH}\cdot\text{H}_2\text{O}$), 13.79 br.s (1.7H, NH)
	^{13}C	11.0 (CH ₃), 147.6 (C–CH ₃), 152.5 (C=NNO ₂)
III	^1H	7.33 br.s (>4H, NH_4^+ , NH), 7.64 s (1H, CH)
	^{13}C	148.1 (CH), 156.6 (C=NNO ₂)
IV	^1H	3.47 br.s (1H, NH), 7.71 br.s (4H, NH_4^+)
	^{13}C	157.7 (C=NNO ₂)
V	^1H	10.95 and 11.35 (shoulder) br.s (2H, NH)
	^{13}C	152.6 (C=NNO ₂)
VI	^1H	6.7 br.s (2H, NH)
	^{13}C	151.0 (C–NO ₂), 160.3 (C=NNO ₂)

^a Data of [9].

^b Data of [11].

SHELX-97 software package [39]. All hydrogen atoms were localized by the difference synthesis of electron density; some hydrogen atoms with small displacements were localized in idealized positions (Table 1).

Compound **II**· H_2O . $\text{C}_3\text{H}_5\text{N}_5\text{O}_2\cdot\text{H}_2\text{O}$; monoclinic crystals, space group $P2_1/c$; $Z = 4$; $M = 161.12$; unit cell parameters: $a = 5.1186(2)$, $b = 13.5688(9)$, $c = 10.0630(6)$ Å; $\beta = 99.428(4)^\circ$; $V = 689.47(46)$ Å³; $\rho_{\text{calc}} = 1.552$ g/cm³. Total of 1456 reflections were measured, 1302 of which were independent and 1114 reflections were characterized by $F_{hkl} \geq 4\sigma(F)$; $\mu = 1.19$ mm⁻¹, $2\theta_{\text{max}} = 140^\circ$, $R_1 = 0.0346$ for $F_{hkl} \geq$

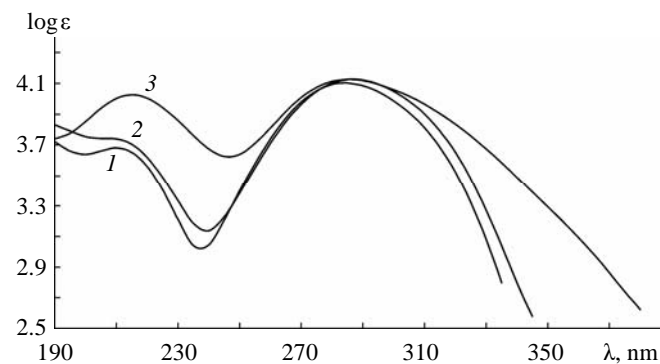


Fig. 2. Electron absorption spectra of nitroamino-1,2,4-triazoles (1) **I**, (2) **II**, and (3) **VI**.

$4\sigma(F)$, $wR_2 = 0.0940$ for $F_{hkl} \geq 4\sigma(F)$; $\text{GooF} = 1.01$ for all reflections.

Compound **III**. $\text{C}_2\text{H}_6\text{N}_6\text{O}_2$; monoclinic crystals, space group Cc ; $Z = 4$; $M = 146.11$; unit cell parameters: $a = 3.8221(2)$, $b = 16.9654(9)$, $c = 9.0963(4)$ Å; $\beta = 95.104(4)^\circ$; $V = 587.50(5)$ Å³; $\rho_{\text{calc}} = 1.652$ g/cm³. Total of 731 reflections were measured, all reflections were independent, and the number of reflections with $F_{hkl} \geq 4\sigma(F)$ was 724; $\mu = 1.25$ mm⁻¹, $2\theta_{\text{max}} = 160^\circ$; $R_1 = 0.0253$ for $F_{hkl} \geq 4\sigma(F)$, $wR_2 = 0.0659$ for $F_{hkl} \geq 4\sigma(F)$; $\text{GooF} = 1.04$ for all reflections.

More detailed experimental data on the crystalline and molecular structure of **II**·H₂O and **III** will be reported elsewhere.

X-Ray powder patterns of compound **I** were obtained on a Bruker D8 Advance automatic diffractometer.

The ¹H and ¹³C NMR spectra were recorded on a Bruker DRX 500 spectrometer (500 MHz) using DMSO-*d*₆ as solvent and tetramethylsilane as reference. The UV spectra were measured on a Shimadzu UV-1601 instrument from aqueous solutions with a concentration of 10⁻⁴ M.

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