

## Structure of the Molecule of 1,2-Bis(1-ethyl-1*H*-1,2,3-triazol-4-yl)diazene 1-Oxide in the Crystal and in Solutions

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**Abstract**—Reduction of 4-nitro-1-ethyl-1*H*-1,2,3-triazole with aluminum in alkaline medium resulted in a *syn*-isomer of 1,2-bis(1-ethyl-1*H*-1,2,3-triazol-4-yl)diazene 1-oxide. The latter according to the data of X-ray diffraction analysis existed in the crystal as the most stable *s-cis,s-trans*-conformer, and in solution, as showed NMR data, as a mixture of *s-cis,s-trans*- and *s-trans,s-trans*-conformers. The data of quantum-chemical calculations are in agreement with the results of the structural studies.

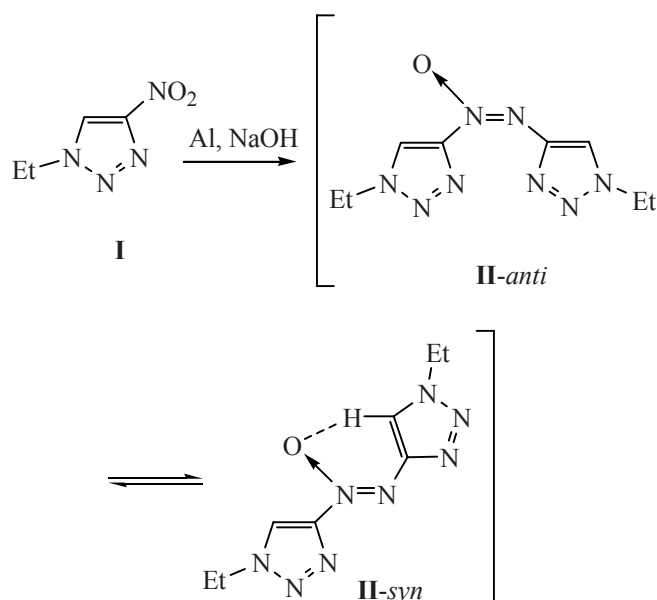
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We formerly found that the reduction of 4-nitro-1-ethyl-1*H*-1,2,3-triazole (**I**) with aluminum in alkaline medium did not give 1-ethyl-1*H*-1,2,3-triazol-4-amine but stopped at the stage of formation of 1,2-bis(1-ethyl-1*H*-1,2,3-triazol-4-yl)diazene 1-oxide (**II**) [1]. Compound **II** was shown to exist in two mutually convertible forms: from the alcoholic reaction mixture a yellow substance was isolated that on dissolution in chloroform quickly decolorized, and on evaporation of the solvent turned into colorless crystals. The reverse transition occurred on

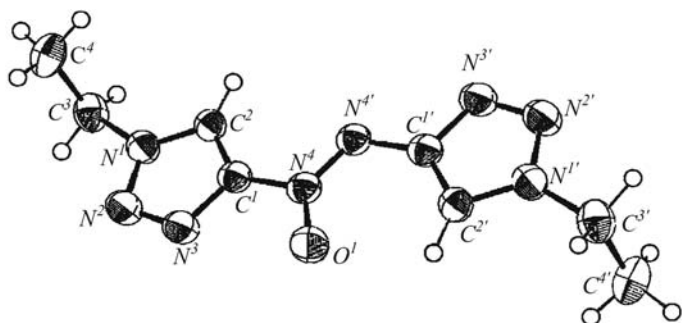
dissolution of the crystals in DMSO. The <sup>1</sup>H NMR spectra of compound **II** in CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> are considerably different: in CDCl<sub>3</sub> the protons of the triazole rings appear as two signals at 8.36 and 8.80 ppm, whereas in DMSO-*d*<sub>6</sub> these signals virtually coincide (9.10 and 9.12 ppm). To the yellow substance a structure of *anti*-isomer was assigned, to the colorless compound, of *syn*-isomer with an intramolecular hydrogen bond [1].

Additional data obtained by means of X-ray diffraction analysis and quantum-chemical calculations and also <sup>1</sup>H NMR and UV spectra of compound **II** measured in various solvents compelled us to revise partly the previous conclusions.\*

The X-ray diffraction study confirmed that compound **II** existed in the crystal as a planar (save the ethyl groups) *syn-s-cis,s-trans*-isomer with an intramolecular hydrogen bond (see the table, Fig. 1). The molecule possesses a center of symmetry with the inversion center in the middle of the N–N bond. The oxygen atom has an occupancy factor 0.5, with total occupancy after inversion. The maximum deviation from the least-squares plane is 0.013(2) Å for C<sup>1</sup> atom. The length of intramolecular hydrogen bond equals O⋯H 2.29(2) Å, of intermolecular hydrogen bonds, O⋯H 2.40(2) Å. The



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**Fig. 1.** Structure of the molecule of 1,2-bis(1-ethyl-1H-1,2,3-triazol-4-yl)diazene 1-oxide (**II**).

bond distances and bond angles of molecule **II** are presented in the table.

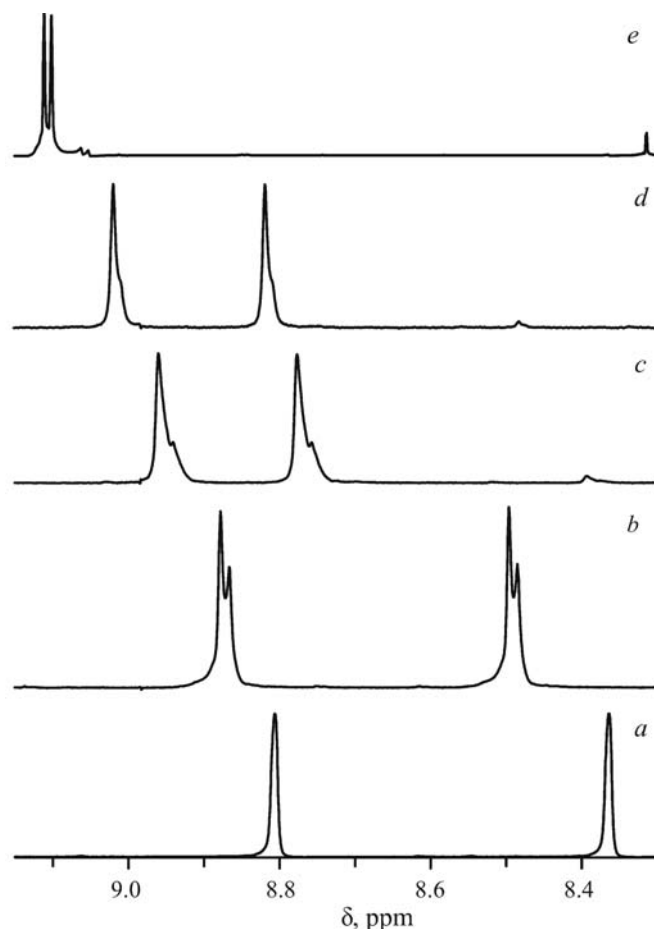
The conclusion on the existence of oxide **II** in solutions in two forms remains valid. Moreover, the measurement of its  $^1\text{H}$  NMR spectra in the solvents of various polarity and basicity clearly demonstrated the simultaneous presence of the two forms in methanol, acetone, and acetonitrile solutions, whereas in the other solvents only one type signals were observed (Fig. 2). The assignment of the upfield and downfield signals (Fig. 2, spectra *a-d*) to CH protons of triazole rings linked to different nitrogen atoms in the  $\text{N}=\text{N}-\text{O}$  moiety was possible by comparison with the spectrum of initial nitrotriazole **I**. The upfield signal of the CH proton in the spectrum of compound **II** nearly coincided with the signals of CH proton in compound **I**, therefore it was

Bond lengths ( $l$ ) and bond angles ( $\varphi$ ) in the molecule of 1,2-bis(1-ethyl-1H-1,2,3-triazol-4-yl)-diazene 1-oxide (**II**) (bond lengths and bond angles in the ethyl group are not shown)

Bond	$l$ , Å	Bond	$l$ , Å
$\text{N}^4-\text{O}$	1.222(3)	$\text{N}^2-\text{N}^3$	1.309(2)
$\text{N}^4-\text{N}^{4'}$	1.289(2)	$\text{N}^3-\text{C}^1$	1.353(2)
$\text{N}^4-\text{C}^1$	1.408(2)	$\text{N}^1-\text{C}^3$	1.465(3)
$\text{C}^1-\text{C}^2$	1.369(3)	$\text{C}^3-\text{C}^4$	1.502(3)
$\text{C}^2-\text{N}^3$	1.343(2)	$\text{C}^2-\text{H}^2$	1.00(2)
$\text{N}^1-\text{N}^2$	1.344(2)		
Angle	$\varphi$ , deg	Angle	$\varphi$ , deg
$\text{ON}^4\text{N}^{4'}$	129.3(2)	$\text{N}^2\text{N}^3\text{C}^1$	107.87(16)
$\text{O}^1\text{N}^4\text{C}^1$	115.8(2)	$\text{N}^3\text{C}^1\text{N}^4$	117.21(16)
$\text{N}^4\text{N}^4\text{C}^1$	114.91(16)	$\text{N}^3\text{C}^1\text{C}^2$	109.80(16)
$\text{N}^4\text{C}^1\text{C}^2$	132.97(17)	$\text{C}^2\text{N}^1\text{C}^3$	128.59(18)
$\text{C}^1\text{C}^2\text{N}^1$	103.47(18)	$\text{C}^3\text{N}^1\text{N}^2$	119.97(17)
$\text{C}^2\text{N}^1\text{N}^2$	111.31(17)	$\text{C}^1\text{C}^2\text{H}^2$	132.6(13)
$\text{N}^1\text{N}^2\text{N}^3$	107.55(16)	$\text{N}^1\text{C}^2\text{H}^2$	123.9(13)

possible to assign it to the triazole ring linked to the oxidized nitrogen of the  $-\text{N}(\text{O})=\text{N}-$  moiety, and then the downfield signal in the spectrum of compound **II** at 8.80 ppm belonged to CH proton involved into the intramolecular hydrogen bond with the oxygen of the diazene oxide fragment.

The possibility of *anti*-isomer formation and the easy transitions between *syn*- and *anti*-isomers provokes objection. Actually, the calculations in the basis B3LYP/6-311G(d,p) showed that compared to the *syn*-isomer the *anti*-isomer was less energetically feasible by 12.8 kcal mol $^{-1}$ , and due to the sterical hindrance the triazole rings could not be located in the plane of the diazene oxide fragment  $\text{N}=\text{N}-\text{O}$  and are placed to the plane at the angle  $>40$  deg and at the angle  $>80$  deg with respect to each other. At the same time in the planar *syn*-isomer as a result of the rotation around the bonds between the diazene oxide fragment and the triazole rings various *s-cis*- and *s-trans*-isomers existed (Fig. 3). High values of



**Fig. 2.**  $^1\text{H}$  NMR spectra of 1,2-bis(1-ethyl-1H-1,2,3-triazol-4-yl)-diazene 1-oxide (**II**) registered in  $\text{CDCl}_3$  (*a*),  $\text{CD}_3\text{CN}$  (*b*), acetone- $d_6$  (*c*),  $\text{CD}_3\text{OD}$  (*d*),  $\text{DMSO}-d_6$  (*e*).

$E_{\text{rel}}$  for conformers **IIc** and **II d** indicate that the rupture of the intramolecular hydrogen bond requires high energy expenditure [5.5–7.9 kcal mol<sup>-1</sup> (Fig. 3)], therefore it is logical to presume that the intramolecular hydrogen bond should be retained in both forms existing in the solution. This conclusion is also confirmed by the experimentally observed close values of the chemical shifts of the same ring in both forms (Fig. 2, spectra *b–d*). If in one of the forms the intramolecular hydrogen bond would be broken, the chemical shift should considerably change. Therefore it is possible to conclude that the second form of compound **II** in solution is *syn-s-trans,s-trans*-isomer

**IIb** (Fig. 3). If this conclusion is true, then the close energy value of forms **IIa** and **IIb** at the large difference in the dipole moments suggests, that their relative stabilities in the polar environment may be reversed. Actually, the calculation with the use of Onsager model gave a result for energy in a polar environment of  $\epsilon$  36 for form **IIb** by 3.24 kcal mol<sup>-1</sup> lower than for form **IIa**. Therewith in the polar environment the intramolecular hydrogen bond of form **IIa** virtually remained the same as in the gas phase ( $\Delta l$  was only 0.003 E), whereas in form **IIb** it shortened by 0.035 E and was 2.281 E.

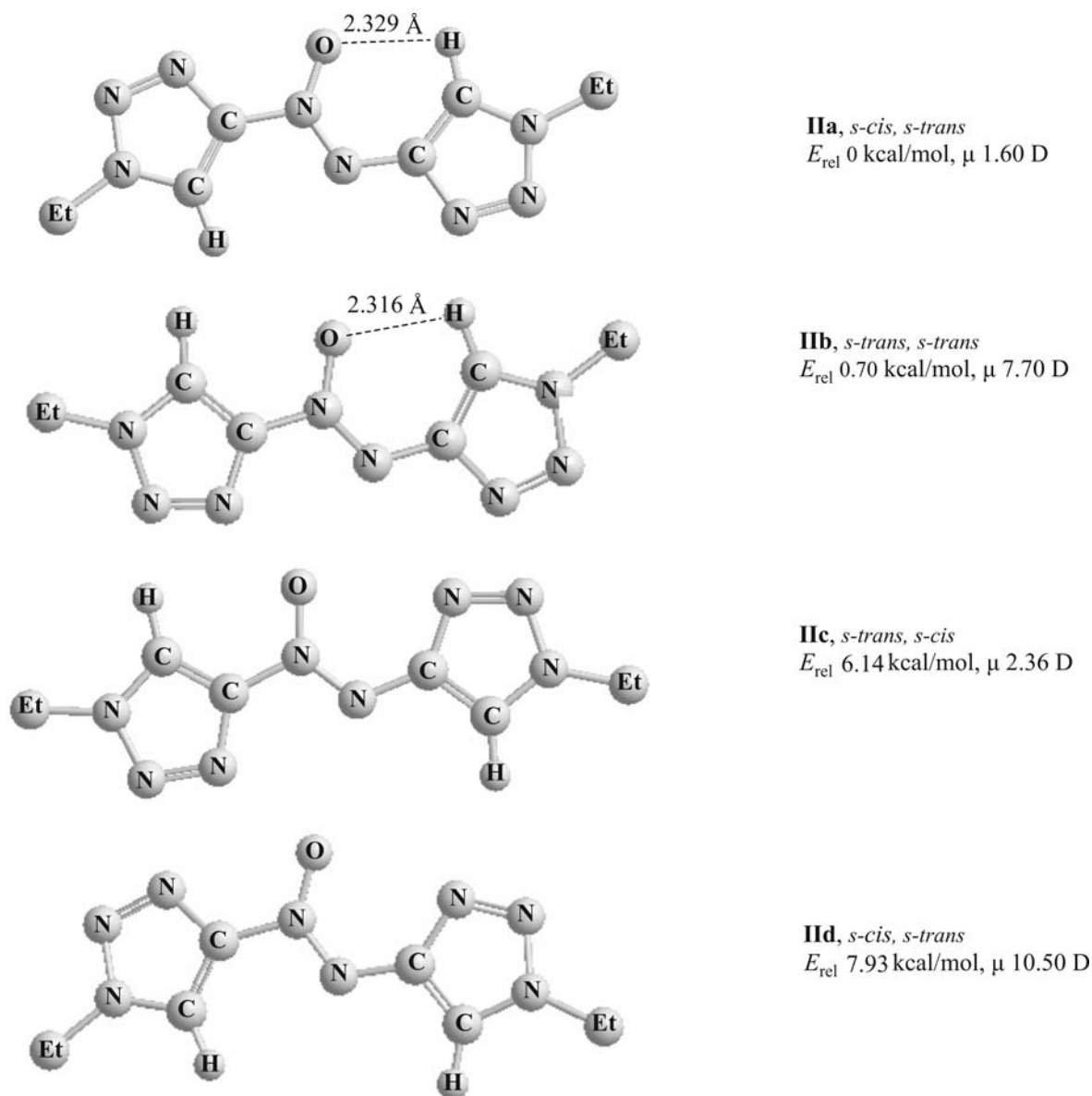
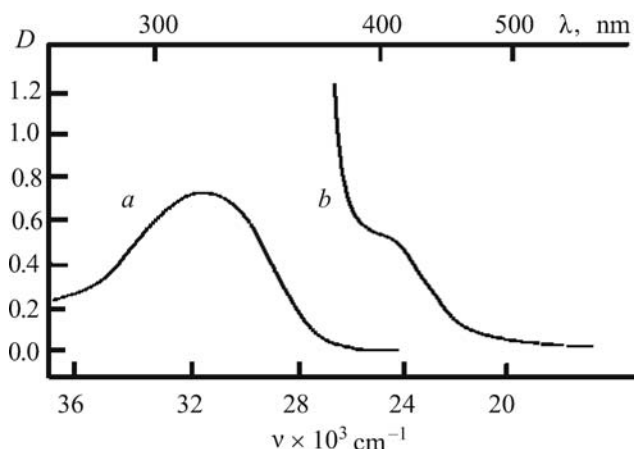


Fig. 3. Possible conformers of the *syn*-isomer of compound **II**.



**Fig. 4.** UV spectra of 1,2-bis(1-ethyl-1H-1,2,3-triazol-4-yl)diazene-1-oxide (**II**) in chloroform ( $c$   $1.5300 \times 10^{-2}$  mol/l);  $d$ , mm: 0.057 (*a*), 50 (*b*).

The results of the calculations for the polar environment made it possible to assign the signals in the  $^1\text{H}$  NMR spectrum registered in  $\text{CDCl}_3$  (Fig. 2, *a*) and upfield signals in each pair of signals in the spectra recorded in  $\text{CD}_3\text{CN}$ , acetone- $d_6$ , and  $\text{CD}_3\text{OD}$  (Fig. 2, *b*–*d* respectively) to form **IIa**, and the downfield signals in each of these pairs, to form **IIb**. In  $\text{DMSO-}d_6$  owing to the high basicity of the solvent the intramolecular hydrogen bond was broken, and strong intermolecular hydrogen bonds appeared with both hydrogen atoms leading to virtually coinciding signals (Fig. 2, *e*).

In the UV spectra of solutions of isomers **IIa** and **IIb** in  $\text{CHCl}_3$  and  $\text{C}_2\text{H}_5\text{OH}$  an absorption band is present at 318 nm ( $\epsilon$  1455) corresponding to the electron transitions  $\pi \rightarrow \pi^*$  in the triazole fragment. In the UV spectrum of isomer **IIb** another very weak band is observed 400 nm [ $\epsilon$   $1.3 \text{ l mol}^{-1} \text{ cm}^{-1}$ ] corresponding to the  $n \rightarrow \pi^*$  transition (Fig. 4) that is responsible for the yellow color of the compound.

Hence the *syn*-isomer of 1,2-bis(1-ethyl-1H-1,2,3-triazol-4-yl)diazene-1-oxide exists in the crystal as a *s-cis,s-trans*-isomer, and in solution depending on the solvent as a mixture of *s-cis,s-trans*- and *s-trans,s-trans*-conformers.

#### EXPERIMENTAL

Synthesis of compound **II** was performed as described in [1].

UV spectra were recorded on a spectrophotometer Specord UV-Vis.  $^1\text{H}$  NMR spectra were registered on

a spectrometer Bruker DPX-400 at operating frequency 400 MHz, chemical shifts were reported with respect to TMS.

X-ray diffraction analysis was performed on a diffractometer IPDS-2 (Stoe) at 210 K, graphite monochromator,  $\text{MoK}_\alpha$  radiation. Crystals  $0.22 \times 0.71 \times 1.60$  mm (from acetone),  $\text{C}_8\text{H}_{12}\text{N}_8\text{O}$ , monoclinic, space group  $\text{P}2_1/\text{n}$ ,  $Z$  2,  $a$  5.6304(7),  $b$  17.205(2),  $c$  5.7403(8) Å,  $\beta$  95.610(11)°,  $V$  553.41(12) Å<sup>3</sup>,  $\rho$  1.418 g/cm<sup>3</sup>. Cell parameters were established from 5819 reflections with  $2.36^\circ < \theta < 29.33^\circ$ . The structure was solved by the direct method [2] and refined in the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms and in isotropic approximation for hydrogen atoms [3]. The final values of divergence factors are  $R$  0.0435,  $R_w$  0.1166 for 876 reflections with  $I > 2\sigma(I)$ .

Quantum-chemical calculations were carried out with the use of GAUSSIAN-98 software [4].

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