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Spectroscopic Study of Interaction of 1*H*-1,2,4-Triazoline-3-thione with Molecular Iodine

M. S. Chernovyants[a], N. V. Aleshina[a], I. N. Shcherbakov[a], and Z. A. Starikova[b]

[a] *Southern Federal University, ul. Zorge 7, Rostov-on-Don, 344090 Russia*
e-mail: chernov@sfedu.ru

[b] *Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

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Abstract—The formation by 1*H*-1,2,4-triazoline-3-thiones in dilute chloroform solution of *n*–σ*-complex with molecular iodine of the composition $C_2H_2N_3S \cdot I_2$ was studied by electronic spectroscopy in the UV and visible regions (log β = 2.14±0.05). By the XRD method the crystal and molecular structure of the product of chemical interaction of the thione with molecular iodine in ethanol, 1,2-di(1*H*-1,2,4-triazol-3-yl) disulfide, was determined.

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Derivatives of 1,2,4-triazoline-5-thione have a broad spectrum of biological activity, including analgesic [1], anti-inflammatory [2], bacteriostatic [3, 4], and antifungal [5] action. In [6] a synthesis was described of a series of new derivatives of 1,2,4-triazoline-5-thione with a potential pharmacological activity. Biological activity of 1,2,4-triazoline-5-thione is correlated with their ability to form complexes with transition metal ions [7]. In [8] the synthesis conditions were described and the results of research on chemosensory properties of 5-amino-3,4-dihydro-2*H*-1,2,4-triazolyl-3-thiones. The 3(5)-sulfhydryl-1,2,4-triazoles unsubstituted at the S and N atoms have been used successfully in organic synthesis of bicyclic 1,2,4-triazoles [9–11]. Besides these compounds have antithyroid action and interact with molecular iodine like *N*-methylimidazoline-2-thione (methimazole) and 3-methyl-2-thioxo-4-imidazoline-1-carboxylate (carbimazole) [12, 13].

The aim of our work was to study the interaction of 1*H*-1,2,4-triazoline-3-thione with elemental iodine in chloroform and ethanol solutions.

In chloroform solutions reversible complexation of 1*H*-1,2,4-triazoline-3-thione with elemental iodine was observed, which we studied by UV/vis spectroscopy:

$$L + nI_2 \rightleftarrows L \cdot nI_2$$

The number of I_2 molecules coordinated by the thione (L) in solution and the stability constant of the molecular adduct of the thione (L) with elemental iodine was evaluated by the spectroscopic method of shifting the reaction equilibrium:

$$\beta = \frac{L \cdot nI_2}{[L][I_2]^n}. \quad (1)$$

Electronic spectra of solutions with constant concentration of 1*H*-1,2,4-triazoline-3-thione and the concentration of iodine varied from 4×10^{-5} to 1.2×10^{-3} M, are shown in Fig. 1.

The stability constant was calculated by the method of least squares using the Eq. (2), the linearized form of Eq. (1):

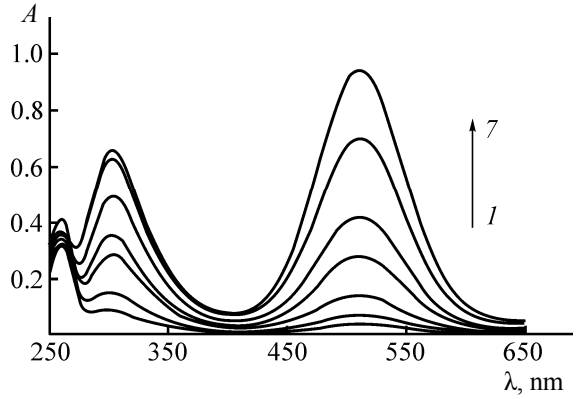

Fig. 1. Electron absorption spectra of solutions of thione (4.0×10^{-5} M) with molecular iodine at concentrations of the latter 4.0×10^{-5} (*1*), 8.0×10^{-5} (*2*), 1.6×10^{-4} (*3*) 3.2×10^{-4} (*4*), 4.8×10^{-4} (*5*), 8.0×10^{-4} (*6*), 1.2×10^{-3} (*7*).

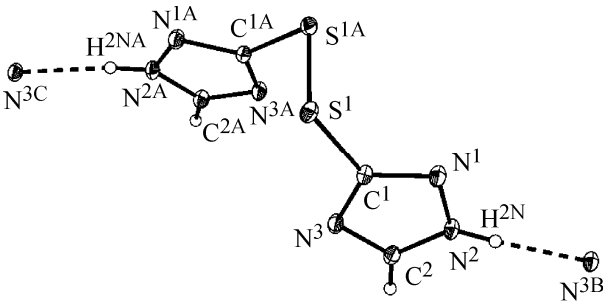

Fig. 2. The molecular structure of 1,2-di(1*H*-1,2,4-triazole-3-yl) disulfide.

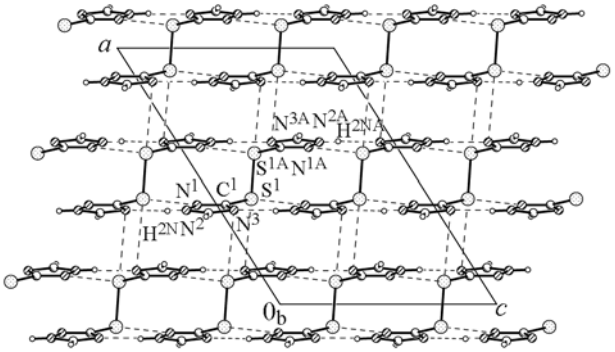

Fig. 3. The crystal packing the layers of 1,2-di(1*H*-1,2,4-triazole-3-yl) disulfide parallel to the 0*yz* plane.

$$\log\frac{A_i}{A_{\max}-A_i} = \log\beta + n\log\left[c_{I2} - n\frac{A_i}{A_{\max}}c_L\right], \qquad (2)$$

where A_{max} is the optical density of the solution in which the thione L is fully bound in the adduct (λ_{max} = 303 nm); A_i is the optical density of solutions containing L and the molecular adduct; β is the stability constant; n is the number of iodine molecules coordinated by the thione, c_{I2}, c_L are analytical concentrations of molecular iodine and the thione, respectively.

From the equation of strait line (2) $y = 1.04x + 2.14$ (ρ = 0.992), it follows that in the chloroform solution the thione is coordinated with one molecule of iodine, and the stability constant is log β = 2.14 ± 0.05.

The interaction of 1*H*-1,2,4-triazoline-3-thione with elemental iodine in ethanol leads to irreversible oxidation of thione to form 1,2-di(1*H*-1,2,4-triazol-3-yl) disulfide, whose molecular and crystal structure we studied using X-ray diffraction method (Figs. 2 and 3). Hydrogen bonds NH···N and weak dipole–dipole S···N interactions stabilize the crystal structure of 1,2-di(1*H*-1,2,4-triazole-3-yl) disulfide.

Previously [14] a similar product of autoxidation of 1*H*-1,2,4-triazoline-3-thione was obtained in the presence of sodium hydroxide in boiling ethanol. In the table comparative geometric parameters (bond lengths, bond and torsion angles) of the crystal structure of 1,2-di(1*H*-1,2,4-triazole-3-yl) disulfide are presented synthesized by us and described in [14].

It should be noted that we have achieved a high degree of refinement of molecular and crystal structure of 1,2-di(1*H*-1,2,4-triazole-3-yl) disulfide (R_1 = 0.0237, wR_2 = 0.0573, S = 1.008). The refinement parameters in [14] are as follows: R_1 = 0.029, wR_2 = 0.081, S = 1.09).

EXPERIMENTAL

1,2,4-Triazoline-3-thione (98%, Aldrich) was used without further purification. 1,2-Di(1*H*-1,2,4-triazol-3-yl) disulfide was synthesized by mixing 1,2,4-triazoline-3-thione) (1 mmol, 0.1011 g) with I_2 (2 mmol, 0.5076 g) in ethanol (15 ml). Solvents were purified by known methods [15].

Electronic spectra of chloroform solutions with different ratios of thione and molecular iodine were obtained on a Cary 100 spectrophotometer in the region of 250–650 nm using the cells with a thickness of the absorbing layer 1.0 cm,. As the initial solutions

Selected geometric parameters of the crystal structure of 1,2-di(1*H*-1,2,4-triazole-3-yl) disulfide obtained by oxidation with I_2 and by autoxidation

Geometrical parameters (Å, deg)	The oxidation with molecular iodine	Autoxidation [14]
S^1–S^{1A}	2.0718(6)	2.0693(11)
S^1–C^1	1.7587(13)	1.7541(15)
N^1–C^1	1.3268(15)	1.3225(19)
N^1–N^2	1.3600(15)	1.3549(18)
N^2–H(^{2}N)	0.88(2)	0.89(2)
C^1–N^3	1.3677(16)	1.3653(19)
C^2–N^2	1.3335(16)	1.324(2)
C^2–N^3	1.3303(16)	1.322(2)
$C^1S^1S^{1A}$	101.64(4)	101.72(5)
$N^1C^1S^1$	123.1(1)	123.30(12)
$N^3C^1S^1$	122.24(9)	122.40(11)
$C^1S^1S^2C^3$	83.70(4)	83.69 (8)

isomolar chloroform solutions of the thione and iodine (2.0×10^{-3} M) were used. Prior to the measurements the exact value of molar absorption coefficient ε_{510} of iodine was determined. In the reaction series the concentration of molecular iodine was changed from the deficit up to 30-fold excess at a constant concentration of thione (4.0×10^{-5} M).

The 1,2-di(1*H*-1,2,4-triazole-3-yl) disulfide crystals were prepared by mixing ethanol solutions of molecular iodine and the thione in a molar ratio of 1:2, followed by slow evaporation of the solvent in air. The resulting light-brown oil was crystallized from ethanol to colorless needles.

Mass spectrum (ESI, the ionization energy 1–3 eV) of 1,2-di(1*H*-1,2,4-triazole-3-yl) disulfide was registered on a Thermo Finnigan Surveyor MSQ instrument at the positive and negative ionization. The *m/z* (I_r, %) parameters are as follows: ESI(+)-MS, 200.9 $[M + H^+]^+$ (100), ESI(–)-MS 198.9 $[M - H^+]^-$ (100).

XRD study. The experimental set of the reflection intensities for the compound $C_4H_4N_6S_2$ were obtained on a Bruker SMART 1000 CCD diffractometer equipped with CCD-detector (MoK_α, graphite monochromator, temperature 120(2) K, ω-scanning). 4145 reflections were measured, including 988 independent ones. Interval of measurement indices: $-18 \le h \le 18$, $-8 \le k \le 8$, $-13 \le l \le 13$, $2\theta_{max} = 58.00°$. The crystal structure was solved by the direct method with subsequent calculation of the Fourier maps. All non-hydrogen atoms were located in difference electron density syntheses and refined with respect to F^2_{hkl} in the anisotropic approximation. The extinction (μ = 0.666 mm^{-1}) is taken into account by using the SADABS software [16], the transmission coefficients of T_{min} and T_{max} are 0.810 and 0.878, respectively. All calculations were performed using a software package SHELXTL-97 [17].

The main crystallographic data are as follows: $C_4H_4N_6S_2$, M = 200.25, monoclinic crystal system, space group C2/*c*, a = 13.8827(13) Å, b = 6.3594(6) Å, c = 9.9190(9) Å, β = 122.4920(10)° , V = 738.63(12) $Å^3$, Z = 4, d_{calc} = 1.801 g cm^{-3}, R_1 = 0.0237 [calculated with respect to F_{hkl} for 884 reflections with $I > 2\sigma(I)$], wR_2 = 0.0553, number of refined parameters 59. The values of maximum and minimum residual peaks are 0.532 and –0.227 e $Å^{-3}$, respectively.

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