STRUCTURE OF 2,4-DIMERCAPTO[4,2,1]TRIAZOLO[3,4-b][1,3,4]-THIADIAZOLE

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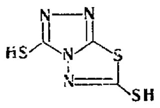
A thione-thiol structure was established for 2-mercapto-5-thiono[4,2,1]triazolino[3,4-b][1,3,4]thiadiazole in accordance with calculations of the π-bonding and solvation energies by the Pariser-Parr-Pople method and also on the basis of a study of the IR and UV spectra. It follows from a determination of the ionization constants that this compound is a strong acid.

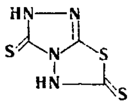
The condensed two-ring [4,2,1]thiazolo[3,4-b][1,3,4]thiadiazole system is of considerable interest, inasmuch as it has two annelated heterorings — 1,2,4-triazole and 1,3,4-thiadiazole. As a rule, derivatives of these compounds are capable of interconversion. Thus, a 1,2,4-triazole with one exocyclic sulfur atom is thermodynamically more stable than the isomeric thiadiazole derivative [1], whereas a 1,2,4-triazole with two exocyclic sulfur atoms is isomerized to a thiadiazole compound on heating [2].

The problems of transmission of an electronic effect, the dual reactivity, and thione-thiol tautomerism of sulfur derivatives of 1,2,4-triazole and 1,3,4-thiadiazole have been studied in detail [3, 4]. These problems have not been studied for two-ring systems, although it is evident that annelation of triazole and thiadiazole has an appreciable effect on both the properties of each of the heterocyclic components of the two-ring system and on the properties of the system as a whole.

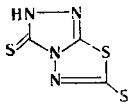
Compounds with two-ring system I were first obtained by Sandström [5], and dimercapto structure Ia was assigned to this compound without proof, although tautomeric structures — dithione Ib and two different thione-thiol structures (Ic and Id) — can be assigned to it with equal probability.



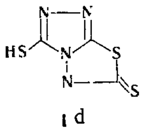
Ia



Ib



Ic



Id

In order to select the most probable of these four structures we calculated their energy characteristics by the Pariser—Parr—Pople (PPP) method. The geometry of the two-ring compound was constructed from fragments of rings with similar structures [6, 7]. The ionization potentials (I_μ) and one-center coulombic integrals ($\gamma_{\mu\mu}$) are presented in Table 1. The two-center coulombic integrals ($\gamma_{\mu\gamma}$) were calculated by the Mataga—Nishimoto method, and the resonance integrals ($\beta_{\mu\gamma}$) of the C—N bonds were determined by the method in [8] and were assumed to be —1.159 and —1.623 eV, respectively, for carbon—sulfur single and double bonds [9, 10].

The π-bonding energy is considered to be the most effective characteristic of the energic stability of tautomers [11]. It follows from the data in Table 2 that dithione structure Ib has the greatest stability in the gas phase. However, allowance for the solvation effect in accordance with the formula of Hoijtink and co-workers [12] predicts

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TABLE 1. Ionization Potentials and One-Center Coulombic Integrals

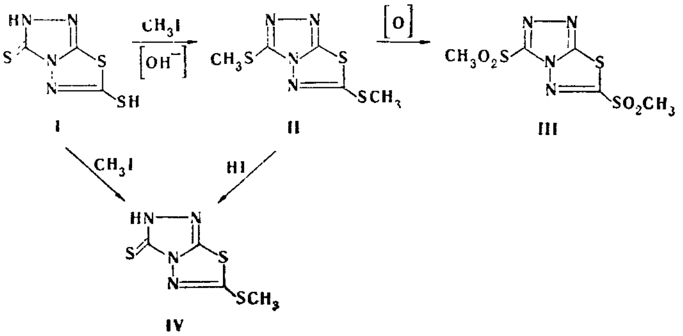
Integrals	Atoms				
	C	$\dot{N}$	$\ddot{N}$	$\dot{S}$	$\ddot{S}$
I_{μ}, eV	11,16	14,12	28,71	12,86	21,00
$\gamma_{\mu\mu}$, eV	11,13	12,34	16.75	9,92	10.84

TABLE 2. π-Bonding and Solvation Energies of Tautomeric Forms of I

Energy characteristic	Tautomeric form			
	Ia	Ib	Ic	Id
E_{π}^{bond}, eV	−12,90	−30,62	−25,88	−18,03
E_{solv}, eV	$-3{,}926\left(1-\frac{1}{\varepsilon}\right)$	$-6{,}456\left(1-\frac{1}{\varepsilon}\right)$	$-7{,}498\left(1-\frac{1}{\varepsilon}\right)$	$-5{,}482\left(1-\frac{1}{\varepsilon}\right)$

maximum stabilization of the solvation of thione-thiol tautomer Ic. Moreover, the difference in the solvation energies of Ic and the other tautomers is so great that the gain in the energy of Ic as compared with the next most stable tautomer Ib is 13 kcal even in nonpolar dioxane ($\varepsilon = 2.2$).

Experimental confirmation of these conclusions was obtained by a study of the IR and UV spectra. A distinct ν_{SH} band characteristic for the thiol group at 2500 cm^{-1} is observed in the IR spectrum of the compound in the crystalline state, and this excludes structure Ib from consideration. In addition, the spectrum contains intense bands at 1500 and 1375 cm^{-1}, which are usually assigned to the stretching vibrations of thione and thioamide groupings. However, this absorption region is not characteristic because superimposition of the absorption bands of C—N and other bonds is possible [13]. It is therefore difficult to make an unambiguous choice from among structures Ia, Ic, and Id on the basis of these data.



In order to make the selection, we obtained di-S-methyl derivative II [5], which has known fixed structure Ia. The structure of this compound was proved by oxidation to disulfone III. As seen from Fig. 1, the UV spectra of the starting compound and its di-S-methyl derivative II in dioxane solutions do not coincide either with respect to the form of the curve or with respect to the position of the absorption maxima, and structure Ia can consequently be excluded from consideration. Mono-S-methyl derivative IV* is the fixed analog of structure Ic, thanks to the absence of a band at 2500 cm^{-1} in the IR spectrum of IV. The agreement between the UV spectra of the investigated compound and IV in dioxane indicates that I has structure Ic in dioxane solution and in the crystalline state.

The UV spectra I in aqueous and alcohol solutions differ considerably from the spectrum in a dioxane solution both with respect to the position of the maxima and with respect to the intensities between the maxima; this can be explained by ionization of I in aqueous

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*We proved the location of the methyl group in IV at the exocyclic sulfur atom of the thiadiazole ring by cyclic cleavage of the two-ring system [15].

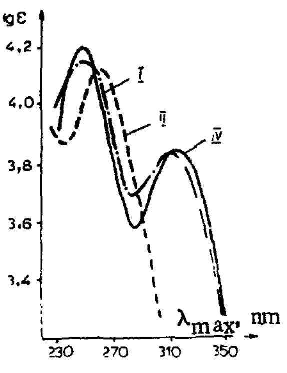


Fig. 1

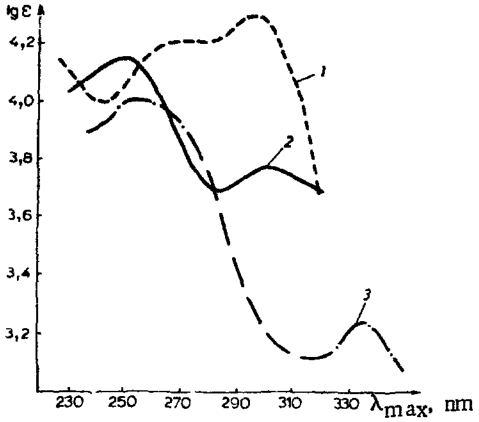
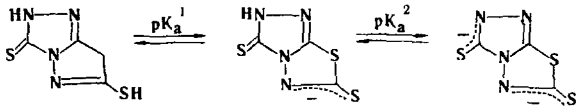


Fig. 2

Fig. 1. UV spectra of I, II, and IV in dioxane.

Fig. 2. UV spectra of 2-mercapto-5-thiono[4,2,1]triazolino-[3,4-b][1,3,4]thiadiazole (I): 1) in water; 2) in dioxane; 3) in sulfuric acid.

and alcohol solutions. This was confirmed by a determination of the ionization constants. Theoretically, I can split out two protons:



The first ionization constant was obtained by spectrophotometry ($pK_a^1 = -1.13$), and the second ionization constant was obtained by potentiometry ($pK_a^2 = 8.02$). Thus I is a strong acid. 2,5-Dimercapto-1,3,4-thiadiazole has the same high acidity [4].

The potentiometrically determined pK_a value for mono-S-methyl compound IV is 6.68. The ranges of pH values over which one or another form exists can be determined from the magnitudes of the ionization constants of Ic: at pH 1-8 the compound is a monoanion, whereas it is a dianion at pH values above 10.

The pK_a values obtained explain the difference in the spectra of aqueous and alcohol solutions of mercaptothione Ic from the spectrum of a dioxane solution. The spectra of aqueous and alcohol solutions are due to the absorption of the monoanion, whereas the spectrum of the dioxane solution is due to the absorption of the nonionized form. When the spectra of Ic in dioxane and in water–sulfuric acid are compared (Fig. 2) it is easy to note that the spectrum of Ic in dioxane occupies an intermediate position between the spectrum in water (the monoanion) and the spectrum in sulfuric acid (the neutral form). This can be explained either by the fact that the monoanion is partially present in dioxane solutions of I or by the stronger solvation effect of sulfuric acid as compared with dioxane.

Thus it was established that a thione group (attached to the triazole ring) and a thiol group (attached to the thiadiazole ring) coexist in the two-ring [4,2,1]triazolo[3, 4-b]-[1,3,4]thiadiazole system with two exocyclic sulfur atoms in the crystalline state and in dioxane solutions.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of alcohol, water, and dioxane solutions of the compounds were recorded with an SF-4 spectrophotometer. The pK_a values were determined spectrophotometrically and potentiometrically by the methods in [14]. The pH values of the solutions were measured with an LPU-01 pH-meter, and the optical densities were measured with an SF-4 spectrophotometer. The measurements were made at 20 ± 1°. Solutions with concentrations of $3 \cdot 10^{-3}$ M in 50% aqueous alcohol were used for the potentiometric titrations. Compound IV is only slightly soluble in alcohol, and it was therefore dissolved in alcohol with the addition of an equivalent amount of KOH and slight heating, after which water was added. The cooled solution was titrated with 0.1 M HCl. The spectrophotometric determination of the pK_a values was carried out in water and in aqueous alcohol (1:1) at a I concentration of $4 \cdot 10^{-5}$ M.

2,5-Dimethylsulfonyl [4,2,1]triazolo[3,4-b][1,3,4]thiadiazole (III). A 0.5-g (2.3 mmole) sample of II [5] was dissolved in 14 ml of acetic acid, and a 7% solution of $KMnO_4$ was added dropwise to the mixture until filter paper dipped into the mixture retained a rose color. The mixture was then treated with sodium hydrosulfite, and the resulting colorless precipitate was removed by filtration to give 0.4 g (62%) of a product with mp 150-151° (needles, from water). Found: C 20.9; H 2.2; S 34.4%. $C_5H_6N_4S_3O_4$. Calculated: C 21.2; H 2.1; S 34.5%.

2-Methylthio-5-thiono[4,2,1]triazolo[3,4-b][1,3,4]thiadiazole (IV). A) A solution of 0.1 g (4.6 mmole) of II in 10 ml of hydriodic acid (sp. gr. 1.5) was heated: the compound dissolved during the first 5-10 min, after which a colorless precipitate formed. The precipitate was removed by filtration to give 0.87 g (92%) of IV with mp 241-242° (needles, from alcohol). Found: C 23.6; H 1.9; S 47.7%. $C_4H_4N_4S_3$. Calculated: C 23.3; H 1.9; S 47.6%.

B) A 1-g (2.8 mmole) sample of the pyridinium salt of Ib was dissolved in water, and an alcohol solution containing 0.6 ml of methyl iodide was added. The mixture was cooled, and the resulting precipitate was removed by filtration to give 0.59 g (51%) of IV. No melting-point depression was observed for a mixture of this product with the compound obtained by method A.

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