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Reaction of 5-methyl-1,3,4-thiadiazoline-2-thione with molecular iodine

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The formation of the n—σ* complex of 5-methyl-1,3,4-thiadiazoline-2-thione with molecular iodine of the composition $C_3H_4N_2S_2 \cdot I_2$ in dilute chloroform solutions was studied by UV-Vis spectroscopy. The crystal and molecular structure of the new salt bis(5-methyl-1,3,4-thiadiazol-2-ylthio)iodonium pentaiodide $[(C_3H_4N_2S_2)_2I^+]I_5^-$ was determined by X-ray diffraction. This salt is formed by the chemical reaction of thione with elemental iodine. In the crystal structure of the salt, the molecules are linked by hydrogen bonds into chains along the [011] diagonal direction. The crystalline salt is characterized by the presence of chains of dimers formed through S...S (3.587(2) Å) and I...I (4.0729(7) Å) contacts corresponding to the interactions between the sulfur atom of the heterocycle and the thione sulfur atom and between the central iodine atoms, respectively. The mixed supramolecular layers are linked by short contacts between the thione sulfur atoms (3.645(3) Å). The behavior of 5-methyl-1,3,4-thiadiazoline-2-thione, which is a potential antithyroid drug, toward molecular iodine was investigated.

Key words: 5-methyl-1,3,4-thiadiazoline-2-thione, bis(5-methyl-1,3,4-thiadiazol-2-ylthio)iodonium pentaiodide, stability constant, X-ray diffraction study.

Heteroaromatic thioamide derivatives are widely known as drugs with various pharmacological activities, such as antiviral, antibacterial, antifungal, and antituberculosis (pyridine derivatives).[1] These compounds are used for the treatment of hyperthyreosis (imidazole and pyrimidine derivatives),[2] leukemia (purine derivatives),[3] and cerebrovascular diseases.[4] The thioamide group, which is present in imidazole-, oxazole-, thiazole-, hydantoin-, thiadiazole-, and barbiturate- and uracil-based compounds, is believed to be a pharmacophore responsible for the antithyroid activity,[5,6] with the result that these compounds exhibit antithyroid and goitrogenic properties.

It was noted[7,8] that in organisms antithyroid drugs can play a role of iodine sponges that trap molecular iodine, I^+, or HOI. The results of *in vitro* studies of the reaction products of thioamides with active forms of iodine, which differ in the composition and structure, were published.[9—15]

In the last decade, the structural diversity and criteria for the search for new substances having a thyrostatic action were discussed.[16—21] Theoretical investigations of complexes of heteroaromatic thioamides with iodine are of interest primarily because of their diverse and unusual structures, as well as due to the thermodynamic stability of these compounds.[7,22,23] The coordination ability of thioamide depends on the σ-donor properties of the molecule determined by the nature of the heteroaromatic moiety and the type of the hybridization of the orbitals of the sulfur atom.[24] The tendency of heteroaromatic thiones to oxidize and the ability of the iodine molecule to undergo heterolysis when present in charge transfer complexes (CTC) or in contact with solvents result in the formation of a wide spectrum of iodine-containing compounds.

The adiabatic ionization potentials of heteroaromatic thiols (thiones) are rather low due to which these compounds are readily oxidized to form radical cations or thiyl radicals as a result of the loss of the hydrogen atom from thiols.[25] The thiyl radicals are dimerized to form disulfides

$$\mathrm{RS}^{\cdot} + {}^{\cdot}\mathrm{SR} \longrightarrow \mathrm{RSSR}.$$

This mechanism is observed in the reaction of pyrimidine-2-thione with iodine.[26] Pyridine-2-thione, which has properties of a potential antithyroid drug, reacts with molecular iodine in a molar ratio of 1 : 1 and is oxidized to 2,2´-dithiobis(2-mercaptopyridinium) triiodide. The crystal structure of the oxidation product of *N*-methylimidazoline-2-thione with molecular iodine

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($[C_4H_6N_2S]_2(I_3)_2I_2$) consists of $[C_4H_6N_2S]_2^{2+}$ dications, I_3^- anions, and a iodine molecule.[8,15] 5,5´-Dimethyl-2,2´-dithiodi-1,3,4-thiadiazole is formed by the oxidation of 5-methyl-1,3,4-thiadiazoline-2-thione, which is the object of our study, in the presence of hydrogen peroxide[27] or copper(I) bromide.[28]

There are a few known iodonium salts, which are formed through the full charge transfer in the iodine molecule coordinated by thioamide followed by the formation of the dimeric thioamide moiety with the bridging iodine atom. The ionic salts based on thiazolidine-2-thione were characterized by X-ray diffraction.[10] The structure of $[(C_3H_3NS_2)_2I^+]I_3^- \cdot 2I_2$ consists of the cationic moiety $(C_3H_3NS_2)_2I^+$ containing the S—I$^+$—S linker, the I_3^- counterion, and two independent iodine molecules. Previously,[13] a mixture of the reaction products of benzimidazoline-2-thione with iodine of the composition $[(C_7H_6N_2S)_2I^+]I_3^- \cdot (C_7H_6N_2S)I_2$ containing a molecular adduct and triiodide of the iodonium salt has been described. The reaction products of thiourea and its dimethylated analog with molecular iodine in ratios of 2 : 1 and 1 : 1, *viz.*, iodide and triiodide of the iodonium cations, respectively, were studied by X-ray diffraction.[29]

The structures and the reactivities of the iodonium salts $Ar(R)I^+X^-$ (R is the alkynyl, alkenyl, or fluoroalkyl group) were presented in the review.[29] The geometry of these iodonium structures is characterized by the Ar—I—R angle close to 90°.

The aim of the present study was to investigate the complexation of the potential antithyroid drug, 5-methyl-1,3,4-thiadiazoline-2-thione, with elemental iodine and to determine the molecular and crystal structure of the chemical reaction product. The ability of 5-methyl-1,3,4-thiadiazoline-2-thione to form the outer-sphere charge-transfer complex with molecular iodine of the composition $C_3H_4N_2S_2 \cdot I_2$ in dilute solutions of nonpolar solvents was estimated by spectrophotometry with the use of the average iodine number ($\bar{n}_{I_2}$).

The reaction product of 5-methyl-1,3,4-thiadiazoline-2-thione with iodine was obtained for the first time. This product was isolated in the crystalline state by slowly evaporating chloroform in air followed by recrystallization with the replacement of the solvent. The reaction of 5-methyl-1,3,4-thiadiazoline-2-thione with molecular iodine in a ratio of 2 : 3 gave the iodonium salt as a result of the full charge transfer in the iodine molecule coordinated to thioamide to form bis(5-methyl-1,3,4-thiadiazol-2-ylthio)iodonium pentaiodide ($[(C_3H_4N_2S_2)_2I^+]I_5^-$) containing the linear S—I$^+$—S linker.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker DPX-600 instrument in $CDCl_3$. The mass spectrum (ESI, the ionization electron energy was 1—3 eV) was obtained on a Thermo Finnigan Surveyor MSQ spectrometer.

5-Methyl-1,3,4-thiadiazoline-2-thione (98%, Alfa Aesar) was used without additional purification. The ^{1}H NMR spectrum of 5-methyl-1,3,4-thiadiazoline-2-thione (δ): 2.50 (s, 3 H, Me); 11.37 (br.s, 1 H, NH). The solvents were purified according to known procedures.[30]

The electronic absorption spectra of chloroform solutions containing thione and molecular iodine in different ratios were measured on a Cary 100 spectrophotometer in cells with a 1.0 cm light path in the 250—650 nm region. Isomolar series of solutions of thione and iodine ($2.0 \cdot 10^{-3}$ mol L^{-1}) in chloroform were used as the starting solutions. The precise value of the molar absorption coefficient of iodine (ε_{510}) was estimated in advance. In the reaction series, the concentration of molecular iodine was varied from a deficient amount to a 30-fold excess, the concentration of thione remaining constant ($4.0 \cdot 10^{-5}$ mol L^{-1}).

Bis(5-methyl-1,3,4-thiadiazol-2-ylthio)iodonium pentaiodide. 5-Methyl-1,3,4-thiadiazoline-2-thione (1 mmol, 0.1152 g) was mixed with I_2 (2 mmol, 0.5080 g) in chloroform (20 mL). After evaporation of the solvent, red-brown rectangular plate-like crystals were obtained. The product was recrystallized by the slow saturation of the chloroform solution with petroleum ether, m.p. 98 °C (with sublimation). ^{1}H NMR, δ: 2.61 (s, 6 H, Me); 10.90 (br.s, 2 H, NH). Found (%): I, 74.14. $C_6H_8I_6N_4S_4$. Calculated (%): I, 74.22 (redoximetry with sodium thiosulfate). Positive-ion MS, m/z (I_{rel} (%)): 262.3 $[M - 2\,H - 3\,I_2]^{\cdot +}$ (100). Negative-ion MS, m/z (I_{rel} (%)): 126.3 $[I]^-$ (100).

X-ray diffraction study. The X-ray diffraction data for the salt $[(C_3H_4N_2S_2)_2I^+]I_5^-$ were collected on a Bruker SMART 1000 CCD diffractometer equipped with a CCD detector (Mo-Kα radiation, graphite monochromator, 120(2) K, ω-scanning technique). A total of 9582 reflections were measured, among which 4203 reflections were independent. The hkl ranges were $-10 \le h \le 10$, $-13 \le k \le 13$, $-16 \le l \le 16$, $2\theta_{max} = 52.00°$. The crystal structure was solved by direct methods. All nonhydrogen atoms were located in difference electron density maps and refined based on F^2_{hkl} with anisotropic displacement parameters (hydrogen atoms were refined isotropically using a riding model). The absorption correction ($\mu = 8.983$ mm^{-1}) was applied with the use of the SADABS program;[31] the transmission coefficients T_{min} and T_{max} were 0.0779 and 0.1657, respectively. All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[32]

Principal crystallographic parameters are as follows: $C_6H_8I_6N_4S_4$, M = 1025.80, triclinic, space group $P\bar{1}$, a = = 8.1626(6) Å, b = 11.1420(8) Å, c = 13.1255(9) Å, α = = 104.0650(10)°, β = 95.8600(10)°, γ = 107.6340(10)°, V = 1083.42(13) Å^3, Z = 2, d_{calc} = 3.144 g cm^{-3}, R_1 = 0.0363 (calculated based on F_{hkl} for 3999 reflections with $I > 2\sigma(I)$), wR_2 = 0.0912 (calculated based on F^2_{hkl} for all 4203 independent reflections), the number of refined parameters was 184. The maximum and minimum residual electron density peaks are 1.346 and −1.554 e Å^{-3}, respectively.

Results and Discussion

Since there is a good correlation between the *in vivo* antithyroid activity of heteroaromatic thioamides and the formation constants of the charge transfer complexes with iodine,[33] it was interesting to estimate the stability of the outer-sphere complex of 5-methyl-1,3,4-thiadiazoline-2-thione with molecular iodine. The composition and the stability constant of this complex in a chloroform solution were determined spectrophotometrically by the equilibrium-shift method

$$\mathrm{Het{=}S} + n\,\mathrm{I_2} \rightleftharpoons \mathrm{Het{=}S}\cdot n\mathrm{I_2}$$

(Het=S is 5-methyl-1,3,4-thiadiazoline-2-thione) according to the equation

$$\beta = [\mathrm{Het{=}S}\cdot n\mathrm{I_2}]/([\mathrm{Het{=}S}][\mathrm{I_2}]^n).$$

The electronic absorption spectra of solutions containing 5-methyl-1,3,4-thiadiazoline-2-thione at a constant concentration and iodine, whose concentration was varied from $2\cdot10^{-5}$ to $1.2\cdot10^{-3}$ mol L^{-1}, are shown in Fig. 1.

The number of iodine molecules coordinated to 5-methyl-1,3,4-thiadiazoline-2-thione and the stability constant of the molecular adduct were evaluated with the use of the average iodine number $\bar{n}_{I_2}$.[34] The equilibrium concentration of iodine ($[I_2]$) was calculated from the absorbance at the maximum of the individual absorption band of elemental iodine (A_{max}) according to the equation

$$[\mathrm{I_2}] = A_{max}/(l\varepsilon_{I_2}).$$

For each equilibrium concentration of iodine, the corresponding value of $\bar{n}_{I_2}$ was calculated according to the equation

$$\bar{n}_{I_2} = (C_{I_2} - [\mathrm{I_2}])/C_{\mathrm{Het=S}},$$

where $C_{\mathrm{Het=S}}$ and C_{I_2} are the analytical concentrations of 5-methyl-1,3,4-thiadiazoline-2-thione and molecular iodine, respectively.

The stability constant β for $0 < \bar{n}_{I_2} < 1$ was calculated by the least-squares method according to the equation

$$\bar{n}_{I_2}/\{(1 - \bar{n}_{I_2})\} = \beta[\mathrm{I_2}]$$

($\log\beta = 2.9\pm0.1$ ($\rho = 0.993$)).

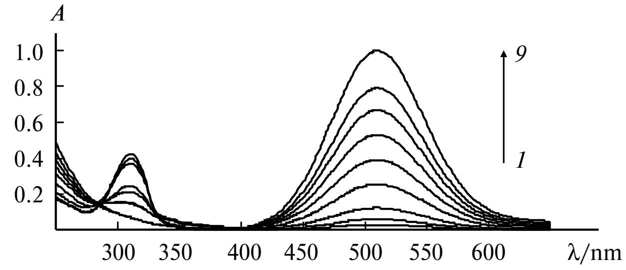

Fig. 1. Electronic absorption spectra of solutions of 5-methyl-1,3,4-thiadiazoline-2-thione ($4.0\cdot10^{-5}$ mol L^{-1}) and molecular iodine at a concentration of $2.0\cdot10^{-5}$ (*1*), $4.0\cdot10^{-5}$ (*2*), $1.6\cdot10^{-4}$ (*3*), $3.2\cdot10^{-4}$ (*4*), $4.8\cdot10^{-4}$ (*5*), $6.4\cdot10^{-4}$ (*6*), $8.0\cdot10^{-4}$ (*7*), $9.6\cdot10^{-4}$ (*8*), and $1.2\cdot10^{-3}$ mol L^{-1} (*9*).

Taking into account the stability constant of the molecular complex of thione with iodine, 5-methyl-1,3,4-thiadiazoline-2-thione would be expected to exhibit the *in vivo* pharmacological activity similar to that of thiouracil derivatives.[35]

The reaction of 5-methyl-1,3,4-thiadiazoline-2-thione with molecular iodine with the account for the heterolytic disproportionation of I_2 and the formation of the complex anion I_5^- in solution can be represented by the equation

$$2\,\mathrm{Het{=}S} + 3\,\mathrm{I_2} = [\mathrm{Het{=}S{\to}I{\leftarrow}S{=}Het}]^+\cdot\mathrm{I_5}^-.$$

5-Methyl-1,3,4-thiadiazoline-2-thione involved in the n—σ* complex with molecular iodine initiates the full charge transfer in the molecule of the latter and forms the iodonium salt through the formation of the three-center 10-electron molecular orbital by the linear S—I$^+$—S linker.

The formation of bis(5-methyl-1,3,4-thiadiazol-2-ylthio)iodonium pentaiodide is accompanied by the downfield shifts of the signals for the protons of the Me groups by 0.11 ppm and by the upfield shifts of the signals for the protons of the NH groups by 0.47 ppm in the ^{1}H NMR spectrum recorded in $CDCl_3$.

The crystal structure of the reaction product of thione with molecular iodine (Fig. 2) consists of the iodonium cations $(C_3H_4N_2S_2)_2I^+$ and the pentaiodide anions I_5^-, which are linked by the intermolecular N(4)...H—N(1′) and I(1)...H—N(3′) hydrogen bonds into chains running along the *c* axis (Fig. 3).

The pentaiodide anions have a V-shaped conformation, which is energetically more favorable than the linear and T-shaped conformations.[36] The pentaiodide ion can be considered as the iodide ion (the central I(1) atom), which coordinates two iodine molecules. An analysis of the I—I bond lengths shows that the iodine molecule I(4)—I(5) (d_{I-I} = 2.8402(6) Å) interacts with the central I(1) ion (d(I(1)—I(4)) = 3.0069(5) Å) much stronger than the iodine molecule I(2)—I(3) (d(I(1)—I(2)) = 3.1499(6) Å), in the former the distance between the atoms being closer to the bond length in the free iodine molecule (d_{I-I} = 2.7662(6) Å). The angle between the iodine mole-

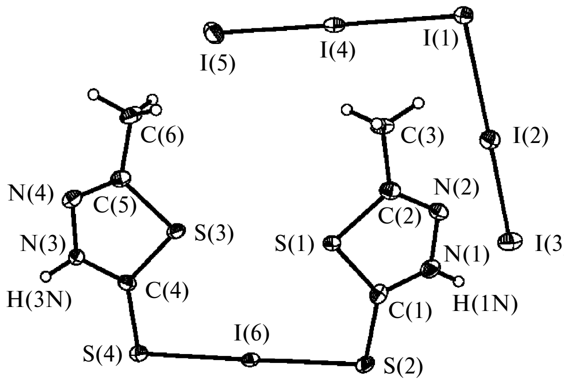

Fig. 2. Structure of the compound $[(C_3H_4N_2S_2)_2I^+]I_5^-$.

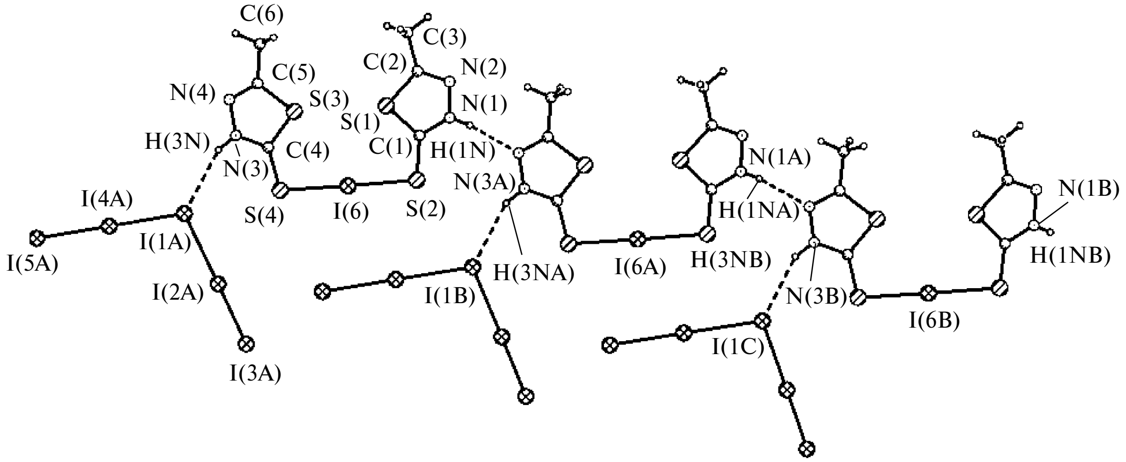

Fig. 3. Chains of the molecules in the crystal structure of the salt $[(C_3H_4N_2S_2)_2I^+]I_5^-$ formed through hydrogen bonds (N(4)...H—N(1´), 2.16 Å; I(1)...H—N(3´), 2.74 Å).

cules in the pentaiodide (I(2)—I(1)—I(4)) is 98.593(14)°. The $(C_3H_4N_2S_2)_2I^+$ cation has the *cis* configuration. The S—I$^+$—S linker is almost linear.

The crystalline salt is characterized by the presence of double chains (Fig. 4) formed through different dipole-dipole interactions between the iodine and sulfur atoms.

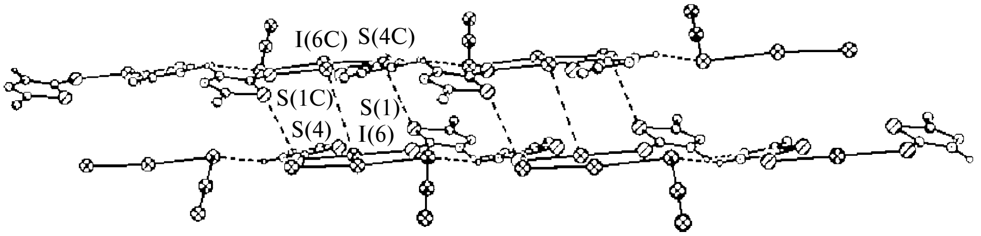

Fig. 4. Double chains in the crystal structure of the salt $[(C_3H_4N_2S_2)_2I^+]I_5^-$. Only the shortest I(6)...I(6´) and S(1)...S(4) contacts are shown.

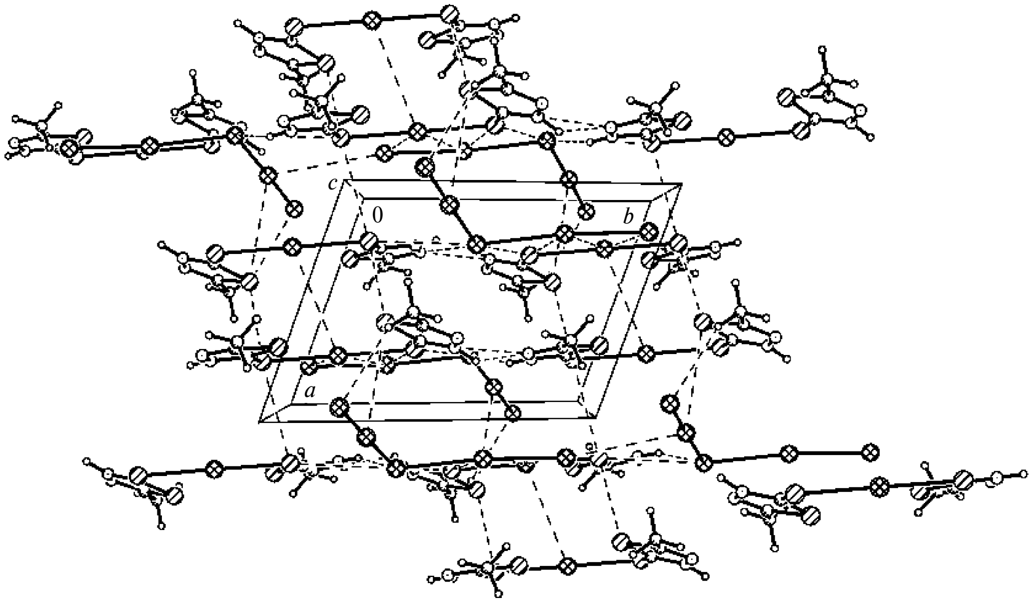

Fig. 5. Layers in the crystal structure of the salt $[(C_3H_4N_2S_2)_2I^+]I_5^-$ formed through iodine...iodine and iodine...sulfur contacts. The shortest S...S and I...S contacts are shown.

The lengths of the shortest I(6)...I(6´) (4.0729(7) Å) and S(1)...S(4) (3.587(2) Å) contacts are smaller than the sums of the corresponding van der Waals radii (4.29 and 3.68 Å, respectively[37]). The double chains are linked into layers parallel to the *ac* plane (Fig. 5) stabilized by numerous iodine—sulfur and sulfur—sulfur contacts. The following contacts are the shortest: I(2)...S(1´) (3.846(2) Å) and S(4)...S(4´) (3.645(2) Å).

The I(1), I(4), and I(5) atoms are coplanar with the plane of the chain, whereas the I(2) and I(3) atoms form an angle of 94.8(1)° with this plane. The I(3) atom forms the shortest contact (I(3)...I(5´), 4.021(1) Å) in the structure.

The bond lengths and bond angles are given in Table 1.

Therefore, the molecular and crystal structure of bis-(5-methyl-1,3,4-thiadiazol-2-ylthio)iodonium pentaiodide ($[(C_3H_4N_2S_2)_2I^+]I_5^-$), which is the reaction product of 5-methyl-1,3,4-thiadiazoline-2-thione with molecular iodine, was determined for the first time. The crystalline salt is characterized by the formation of double layers through the I...I, N—H...I, N—H...N, and I...S contacts comparable with the van der Waals interactions.[37]

It was shown[27,28] that the mechanism of the reaction (the formation of disulfide or the iodonium salt containing the hypervalently bonded iodine) depends on the electron-releasing properties of the thione molecule determined by the nature of the heteroaromatic moiety and the character of the oxidizing agent.

Table 1. Bond lengths (*d*) and bond angles (ω) in the structure of $[(C_3H_4N_2S_2)_2I^+]I_5^-$

Bond	*d*/Å	Angle	ω/deg
I(1)—I(4)	3.0069(6)	I(4)—I(1)—I(2)	98.593(15)
I(1)—I(2)	3.1499(6)	I(3)—I(2)—I(1)	179.307(18)
I(2)—I(3)	2.7662(6)	I(5)—I(4)—I(1)	174.627(18)
I(4)—I(5)	2.8402(6)	S(4)—I(6)—S(2)	178.93(4)
I(6)—S(4)	2.6242(14)	C(1)—S(1)—C(2)	89.2(3)
I(6)—S(2)	2.6445(14)	C(1)—S(2)—I(6)	99.60(19)
S(1)—C(1)	1.725(6)	C(4)—S(3)—C(5)	89.3(3)
S(1)—C(2)	1.746(6)	C(4)—S(4)—I(6)	100.28(19)
S(2)—C(1)	1.693(6)	C(1)—N(1)—N(2)	118.2(5)
S(3)—C(4)	1.726(6)	C(2)—N(2)—N(1)	110.0(5)
S(3)—C(5)	1.749(6)	C(4)—N(3)—N(4)	117.7(5)
S(4)—C(4)	1.693(6)	C(5)—N(4)—N(3)	110.6(5)
N(1)—C(1)	1.329(8)	N(1)—C(1)—S(2)	122.8(4)
N(1)—N(2)	1.367(7)	N(1)—C(1)—S(1)	108.7(4)
N(2)—C(2)	1.292(8)	S(2)—C(1)—S(1)	128.6(3)
N(3)—C(4)	1.334(7)	N(2)—C(2)—C(3)	124.3(6)
N(3)—N(4)	1.375(7)	N(2)—C(2)—S(1)	114.0(5)
N(4)—C(5)	1.273(8)	C(3)—C(2)—S(1)	114.1(5)
C(2)—C(3)	1.498(8)	N(3)—C(4)—S(4)	123.7(4)
C(5)—C(6)	1.491(8)	N(3)—C(4)—S(3)	108.3(4)
N(3)—H(3N)	0.8999	S(4)—C(4)—S(3)	128.0(3)
		N(4)—C(5)—C(6)	124.1(5)
		N(4)—C(5)—S(3)	114.1(4)
		C(6)—C(5)—S(3)	121.8(4)

The stability of the outer-sphere complex of 5-methyl-1,3,4-thiadiazoline-2-thione with molecular iodine of the composition $C_3H_4N_2S_2 \cdot I_2$ in dilute chloroform solutions was estimated by UV spectroscopy with the use of the average iodine number.

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