

Spectroscopic and structural study of novel interaction product of pyrrolidine-2-thione with molecular iodine. Presumable mechanisms of oxidation



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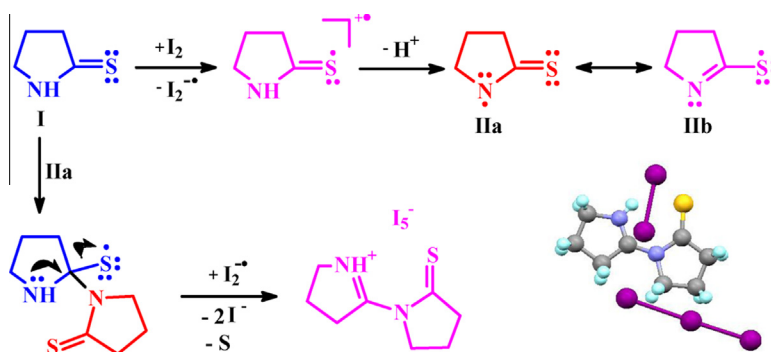
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HIGHLIGHTS

- The stability of molecular adduct of pyrrolidine-2-thione with iodine were evaluated.
- The iodine-mediated oxidative desulfurization of pyrrolidine-2-thione was presented.
- The ring fusion due to the formation of a new C–N bond was observed.
- The structure of reaction product was characterized by RSA.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis, spectroscopic and structural characterization of novel interaction product of pyrrolidine-2-thione with molecular iodine is reported. The ability of pyrrolidine-2-thione to form the outer-sphere charge-transfer complex $C_4H_7NS \cdot I_2$ with iodine molecule in dilute chloroform solution has been studied by UV/vis spectroscopy. Oxidative desulfurization promotes ring fusion of two pyrrolidine-2-thione molecules. The product of iodine induced oxidative desulfurization has been studied by X-ray diffraction method. The crystal structure of the reaction product is formed by 5-(2-thioxopyrrolidine-1-yl)-3,4-dihydro-2H-pyrrolium ($C_8H_{13}N_2S^+$) cations and pentaiodide anions I_5^- , which are linked by the intermolecular $I \cdots H-C$ and $I \cdots C$ close contacts. The angular pentaiodide anions can be considered as structures formed by coordination of two iodine molecules to the iodide ion (type 1) or by the coordination of iodine molecule to the triiodide ion (type 2).

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1. Introduction

Diverse and unusual structures, thermodynamic stability of complexes of heterocyclic thioamides with iodine stimulate steady interest to investigate them [1–3]. Studies of the $n - \sigma^*$ complexes

of heterocyclic thiones with molecular iodine are motivated by interest in understanding of the mechanism of antithyroid drugs action [4–6]. The facility of heterocyclic thiones reduction and the ability of the iodine molecule to undergo heterolysis results in the formation of a wide spectrum of iodine-containing compounds. Heteroaromatic thiones are readily oxidized with formation of radical cations or thiyl radicals as a result of the electron or hydrogen atom transfer [7–9].

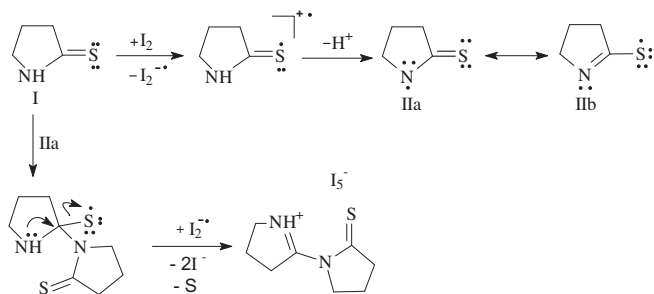
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Table 1

Crystal data and structure refinement for 5-(2-thioxopyrrolidine-1-yl)-3,4-dihydro-2H-pyrrolium pentaiodide.

Empirical formula	C ₁₂ H _{19.50} I _{7.50} N ₃ S _{1.50}	
Formula weight	1205.65	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	<i>a</i> = 30.720(3) Å	$\alpha = 90^\circ$
	<i>b</i> = 9.4034(7) Å	$\beta = 92.880(2)^\circ$
	<i>c</i> = 36.847(3) Å	$\gamma = 90^\circ$
Volume	10630.5(14) Å ³	
Z	16	
Density (calculated)	3.013 Mg/m ³	
Absorption coefficient	8.877 mm ⁻¹	
F(000)	8544	
Crystal size	0.44 × 0.35 × 0.17 mm ³	
Theta range for data collection	1.11–26.00°	
Index ranges	−37 ≤ <i>h</i> ≤ 37, −11 ≤ <i>k</i> ≤ 11, −45 ≤ <i>l</i> ≤ 45	
Reflections collected	46,164	
Independent reflections	10394 [R(int) = 0.0410]	
Completeness to theta = 26.00°	99.4%	
Max. and min. transmission	0.3137 and 0.1116	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	10394/0/443	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R ₁ = 0.0362, wR ₂ = 0.0697	
R indices (all data)	R ₁ = 0.0422, wR ₂ = 0.0723	
Largest diff. peak and hole	1.425 and −1.820 e Å ⁻³	

**Scheme 1.**

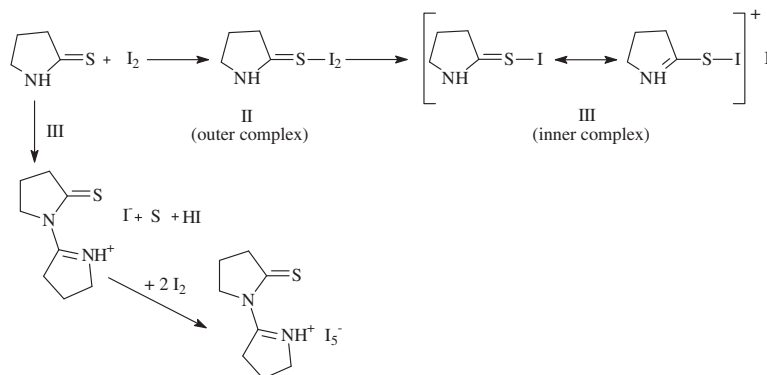
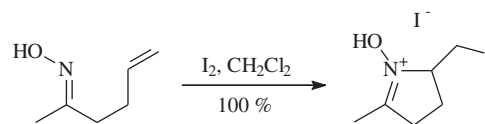
There are few examples of iodonium salts which are formed by S-coordination of two thioamide molecules by I⁺ resulting from heterolysis of the diiodine. The structures and the reactivity of the iodonium salts Ar(R)I⁺X⁻ (R is the alkynyl, alkenyl, or fluoroalkyl group) were discussed in the review of Zhdankin and Stang [10]. Diiodine in combination with ionic iodide species (as I⁻ or I₃⁻) forms a large variety of oligomeric anionic polyiodides [11–13].

Reaction of imidazolidine-2-thione with copper(II) salt yields Cu(II) complex with 1-(1'-imidazolidine-2'-yl)-imidazolidine-2-thi-

one which is formed due to ring condensation of two imidazolidine-2-thione molecules by formation of new C–N bond and simultaneous H₂S elimination [14]. The same product was obtained when I₂ was used in the reaction instead of the Cu(II) salt [15]. Similar process was registered for thiazolidine-2-thione [16].

The authors [17] describe a new synthesis pathway to 2-azaindolizones that is based on iodine-mediated oxidative desulfurization that promotes cyclizations of N-2-pyridylmethyl thioamides. The reaction of N-2-pyridylmethyl-2-pyridinecarbothioamide with molecular iodine generates 2-azaindolizine (89% yield) along with a rare compound, the sulfur-bridged 2-azaindolizine dimer (7% yield). N-arylpyrrolidine-2-thiones have been used as precursors for a flexible synthesis of tricyclic analogues of quinolone antibacterial agents [18].

Cyclization of γ - and δ -alkenyloximes with I₂ or ICl yields the cyclic nitrones or their dimeric salts [19].

**Scheme 2.**

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