

## SYNTHESIS AND PROPERTIES OF DERIVATIVES OF 4-IMINO-1,3-THIAZANE

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The reaction of thiazane-2,4-dithiones with thiosemicarbazide and *p*-nitrophenylhydrazine has given the corresponding derivatives of 4-imino-1,3-thiazane. The 4-thiosemicarbazones obtained have one absorption maximum at 247-255 nm and a characteristic inflection at about 300 nm; the 4-*p*-nitrophenylhydrazones are characterized by three maxima in the 238-265, 303-316, and 400-405 nm regions.

As is well known, the sulfur atom in position 4 of the molecule of thiazane-2,4-dithione has a typical thioketone nature [1,2]. This fact has enabled us to obtain, starting from thiazane-2,4-dithiones, a number of previously undescribed 3-substituted derivatives of 4-iminothiazane-2-thione.

In order to obtain derivatives of 4-imino-1,3-thiazane, we condensed 3-ethylthiazane-2,4-dithione, 3,3'-ethylenebis(thiazane-2,4-dithione), 3,3'-hexamethylenebis(thiazane-2,4-dithione), and 3-(4'-oxo-2'-thioxothiazan-3'-ylethylene)thiazane-2,4-dithione with thiosemicarbazone in propanol [in the case of 3,3'-ethylenebis(thiazane-2,4-dithione), in dioxane] and with *p*-nitrophenylhydrazine in butanol [in the case of 3,3'-hexamethylenebis(thiazane-2,4-dithione), in propanol].

Under these conditions 3-(4'-oxo-2'-thioxothiazan-3'-ylethylene)thiazane-2,4-dithione formed a mono-

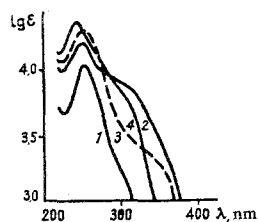
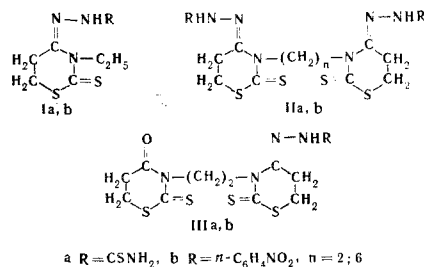


Fig. 1. UV spectra of the thiosemicarbazones: 1) 3-ethyl-1,3-thiazane-2,4-dithione 4-thiosemicarbazone (Ia); 2) 3,3'-dimethylenebis(thiazane-2,4-dithione 4-thiosemicarbazone) (IIa,  $n = 2$ ); 3) 3,3'-hexamethylenebis(thiazane-2,4-dithione 4-thiosemicarbazone) (IIa,  $n = 6$ ); 4) 3-(4'-oxo-2'-thioxothiazan-3'-dimethylene)thiazane-2,4-dithione 4-thiosemicarbazone (IIIa).

thiosemicarbazone and, correspondingly, a mono-*p*-nitrophenylhydrazone, since the oxygen atom in position 4' of the starting material is unreactive.



The thiosemicarbazones obtained consist of light yellow crystalline substances soluble on heating in

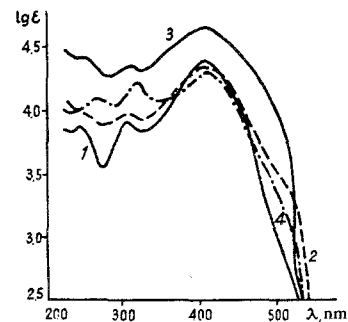


Fig. 2. UV spectra of the nitrophenylhydrazones: 1) 3-ethylthiazane-2,4-dithione 4-*p*-nitrophenylhydrazone (Ib); 2) 3,3'-dimethylenebis(thiazane-2,4-dithione 4-*p*-nitrophenylhydrazone) (IIb,  $n = 2$ ); 3) 3,3'-hexamethylenebis(thiazane-2,4-dithione 4-*p*-nitrophenylhydrazone) (IIb,  $n = 6$ ); 4) 3-(4'-oxo-2'-thio-3'-dimethylene)thiazane-2,4-dithione 4-*p*-nitrophenylhydrazone (IIIb).

dilute solutions of hydrochloric acid and in concentrated  $\text{CH}_3\text{COOH}$ , sparingly soluble in solutions of alkalis even on heating, and insoluble in the majority of organic solvents. The *p*-nitrophenylhydrazones are dark red or "bordeaux" crystalline substances readily soluble in acetone and sparingly soluble in the majority of organic solvents and in solutions of alkalis even on heating.

The UV absorption spectra of the 4-thiosemicarbazono-2-thio-1,3-thiazane derivatives are characterized by a single absorption maximum in the 247-255 nm region (Fig. 1). This maximum is undoubtedly connected with the presence of the thioamide chromo-