

# Color and Structure of Molecules of Some Derivatives of Thiazolidone and 1,3 - Thiazane

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## Abstract

The possibility of linking of color of some thiazolidones and 1,3-thiazane, their bicyclic derivatives-alkilen /arylen/-bis(thiazolidones-4) and alkilen/arylen/-bis (thiazanones-4), initial and intermediate products of their synthesis with structure of some chromophores and size of formed macro-cycles is described at this paper.

## Introduction

Mechanism of color appearance in chemistry of thiazolidynes and their six-membered analogues-1,3-thiazanes practically has not been investigated. It also concerns to their bicyclic non-condensed derivatives-alkilen/arylen/ - bis(thiazolidones-4) and alkilen/arylen/-bis(thiazanones-4). Some monocyclic thiazolidones and 1,3-thiazanes, intermediate products of their synthesis and transformation are considered as possible analytic reagents for metal ions with forming of colored products<sup>1</sup>. Their bicyclic non-condensed derivatives are investigated at the present time as analytic reagents<sup>2,3</sup>.

## Results and Discussion

We have established that intermediate products of synthesis of monocyclic 2-thioxo-thiazolidones-4 and 2-thioxo-1,3-thiazanones-4 - dithiocarbaminates  $[H_4NSC(S)NH]R$ , that are synthesized on the base of corresponding monoamines<sup>4,5,8-12</sup>, form colored products with  $Pd^{2+}$  ions. Dithiocarbaminates, that are synthesized on the base of aliphatic and aromatic diamines and that are intermediate products in synthesis of bicyclic non-condensed 2-thioxo-derivatives of thiazolidones-4 (7) and 1,3-thiazanone-4, form colored products with  $Ag^+$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Pd^{2+}$ ,  $Se^{2+}$  ions<sup>3,6,7</sup>.

Dithiocarbaminates with cyclic structure (1), synthesized on the base of similar diamines in anhydrous mediums, form similar colored products. It is necessary to note that elongation of alkilen bridges in diamines and, correspondingly, increase of macrocycle size decreases color intensity<sup>3</sup>. It is caused by forming of metal binds inside the cycle.

Incorporation of fragments of thioacetic<sup>3</sup> (3,6) or  $\beta$ -thiopropionic (2) acids into the structure of cyclic dithiocarbaminates leads to specific reaction for the metal ions. The colored products form only with  $Ag^+$  and  $Pd^{2+}$ .

$N,N'$  - Alkilen/arylen/ - bis(S - thiocarbamoyl -

thioacetic) acids (3,6) and  $N,N'$  - Alkilen /arylen/ - bis(S - thiocarbamoyl -  $\beta$  - thiopropionic) acids (2) are cyclized to 2-thioxo-derivatives of thiazolidones-4 (3,7) and 1,3-thiazanones-4<sup>6,7</sup>. Desulfation of 2-thioxo-derivatives leads to 2,4-dioxo-derivatives<sup>5</sup> (8) and their thionizing by phosphorus pentasulfide leads to 4-thioxo-derivatives<sup>7</sup> (9). During the synthesis and transformation of corresponding substances the color varies. It generally depends on presence of conjugation systems. Elongation of the conjugation system  $-S-C(S)-N-$ , that is typically for

intermediate S - thiocarbamoyl - thioacetic and S - thiocarbamoyl -  $\beta$  - thiopropionic acids, to the  $-S-C(S)-N-C(O)-$  system, that is typically for 2-

thioxo derivatives of thiazolidones and 1,3-thiazane, leads to appearance of yellow-green and red-orange color in these substances. Transition from conjugation system  $-S-C(S)-N-C(O)-$  (in 2-thioxo-derivatives) to  $-S-C(O)-N-C(O)-$  system (in 2,4-dioxo-derivatives)

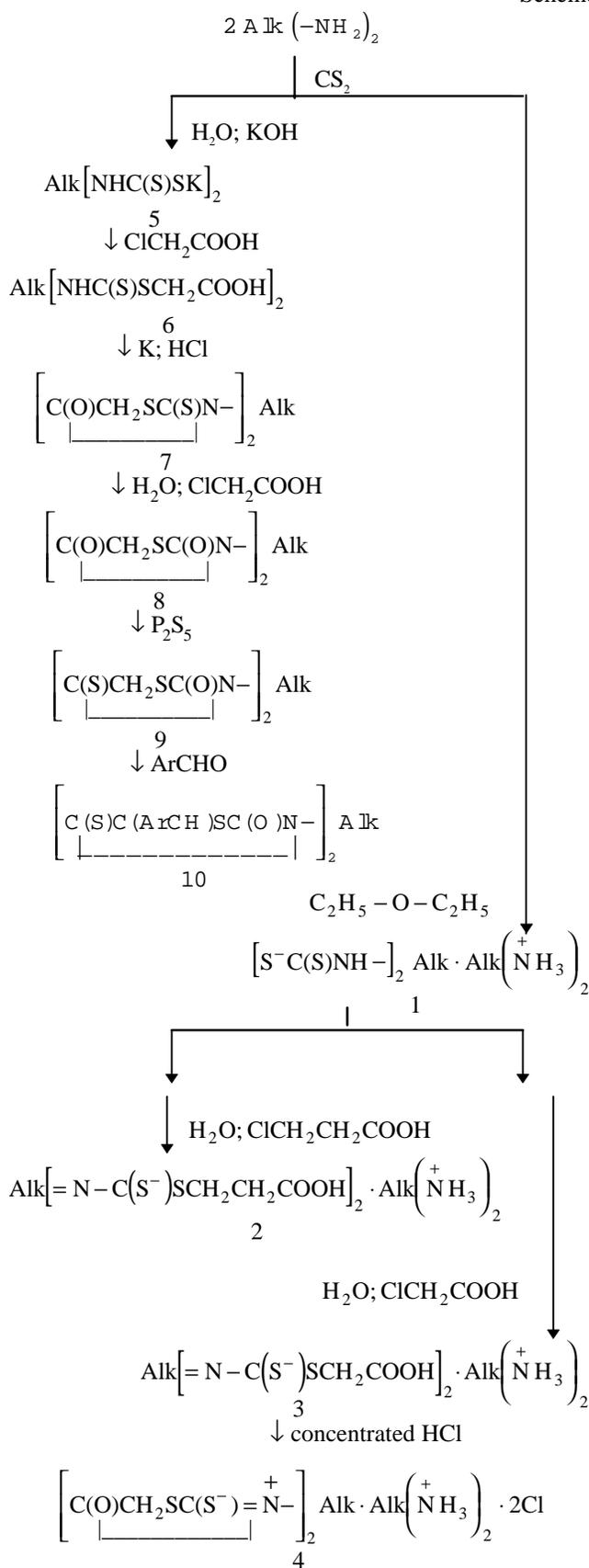
and, correspondingly, to  $-S-C(O)-N-C(S)-$  system (in 4-thioxo-derivatives) passes through loses of color and after it color appears again.

Incorporation of alkiliden traces into 2,4-dioxo-derivatives and 4-thioxo-derivatives in position 5 by the way of aldolic condensation with hydrocompounds of aliphatic series does not lead to color improving. Incorporation of aryliden traces leads to elongation of conjugation chain and, correspondingly, color deepening or color variation of the output compounds<sup>15,16</sup> (10). Especially it concerns to  $-N(Alk)_2$  and  $-NO_2$  groups in aryliden traces. Color deepening can be achieved by incorporation of azogroups into position 5 in reaction of azocoupling with primary aromatic amines<sup>17</sup>.

## Experimental Section

Synthesis of the most sensitive reagents is described below. Elemental analysis of all new compounds and calculated values (C, H, N, S  $\pm$  0.3) have satisfactory agreements. Synthesized compounds structures are confirmed by IR-spectroscopy (UR-20 spectrometer, Carl Ceiss, Iena, Germany).

Scheme



2a: (CH<sub>2</sub>)<sub>2</sub>  
 b: (CH<sub>2</sub>)<sub>4</sub>  
 c: (CH<sub>2</sub>)<sub>6</sub>

10a: Alk = (CH<sub>2</sub>)<sub>2</sub>, Ar = C<sub>6</sub>H<sub>5</sub>  
 b: Alk = (CH<sub>2</sub>)<sub>2</sub>, Ar = m - NO<sub>2</sub>  
 c: Alk = (CH<sub>2</sub>)<sub>2</sub>, Ar = n - N(CH<sub>3</sub>)<sub>2</sub>  
 d: Alk = (CH<sub>2</sub>)<sub>4</sub>, Ar = C<sub>6</sub>H<sub>5</sub>  
 e: Alk = (CH<sub>2</sub>)<sub>4</sub>, Ar = m - NO<sub>2</sub>  
 f: Alk = (CH<sub>2</sub>)<sub>4</sub>, Ar = n - N(CH<sub>3</sub>)<sub>2</sub>  
 g: Alk = (CH<sub>2</sub>)<sub>6</sub>, Ar = C<sub>6</sub>H<sub>5</sub>  
 h: Alk = (CH<sub>2</sub>)<sub>6</sub>, Ar = m - NO<sub>2</sub>  
 i: Alk = (CH<sub>2</sub>)<sub>6</sub>, Ar = n - N(CH<sub>3</sub>)<sub>2</sub>

### N,N'-Ethylene-bis(S-thiocarbamoyl-β-thio-propionic acid's ethylenediamine (2a).

2.72g (0.01 mole) of 1,2-Ethylene-bis (dithiocarbamate) of ethylenediamine<sup>3</sup> was added to 10ml of aqueous solution of β-chloropropionic acid (3.25g, 0.03 mole) and is mixed 30 min. 50 ml of dioxane was added to mixture. Oily substance that precipitated was separated and rinsed by acetone and dioxane to crystallization. Yield - 46%. Melting point - 69-71°C (from water/acetone).

3360-3330 cm<sup>-1</sup> (ν<sub>NH</sub>), 2975-2945 cm<sup>-1</sup> (ν<sub>NH</sub><sup>+</sup>), 3215-3005 cm<sup>-1</sup> (ν<sub>OH</sub>), 3010-2820 cm<sup>-1</sup> (ν<sub>CH</sub>), 2970-2945 cm<sup>-1</sup> (ν<sub>asCH<sub>2</sub></sub>), 2880-2865 cm<sup>-1</sup> (ν<sub>sCH<sub>2</sub></sub>), 1630-1615 cm<sup>-1</sup> (ν<sub>C=N</sub>), 1525-1500 cm<sup>-1</sup> (δ<sub>NH</sub><sup>+</sup>), 1390-1345 cm<sup>-1</sup> (ν<sub>C-N</sub>), etc.

### N,N'-Tetramethylene-bis(S-thiocarbamoyl-β-thiopropionic acid's tetramethylenediamine (2b)

By analogous way it was received N,N'-tetramethylene-bis(S-thiocarbamoyl-β-thiopropionic acid's hexamethylene-diamine. Yield - 41%. Melting point - 60-62°C (from water/ dioxane). The substance is characterized by similar absorption frequency in IR spectrum range.

### N,N'-Hexamethylene-bis(S-thiocarbamoyl-β-thiopropionic acid's hexamethylenediamine (2c).

By analogous way it was received N,N'-hexamethylene-bis(S-thiocarbamoyl-β-thiopropionic acid hexamethylene-diamine. Yield - 40%. Melting point - 56-58°C (from water/dioxane). The substance is characterized by similar absorption frequency in IR spectrum range.

### 1,2-Bis(5-benzyliden-thiazolidyn-2-oxo-4-thioxo-3-yl) ethane (10a) 1,4-bis(5-benzyliden-thiazolidyn-2-oxo-4-thioxo-3-yl) butane (10d) and 1,6-bis(5-benzyliden-thiazolidyn-2-oxo-4-thioxo-3-yl) hexane (10g).

Heated solution of 0.27g (0.0025 mole) of benzaldehyde and 0.20g (0.0025 mole) of anhydrous sodium acetate in 10 ml of butanol was added to heated solution of 1,2-bis(thiazolidyn-2-oxo-4-thioxo-3-yl) ethane in 15 ml of butanol. The mixture was boiled for ≈ 60 min. The mixture was cooled and precipitate was filtered and washed by 5 ml of methanol and diethyl ether. Yield - 41%. Melting point - 217-218°C (from butanol).

1710-1690 cm<sup>-1</sup> (ν<sub>C=O</sub>), 1340-1335 cm<sup>-1</sup> (ν<sub>C-N</sub>), 1125-1115 cm<sup>-1</sup> (ν<sub>C=S</sub>), 690-685 cm<sup>-1</sup> (ν<sub>C-S</sub>), 1590-1585, 1375-1370, 1255-1250 cm<sup>-1</sup> (ν<sub>C<sub>6</sub>H<sub>5</sub></sub>), etc.

By analogous way it was received 1,4-bis(5-benzyliden-thiazolidyn-2-oxo-4-thioxo-3-yl) butane, yield -

53%, melting point - 130-132°C (from butanole) and 1,6 - bis(5-benzyliden-thiazolidyn-2-oxo-4-thioxo-3-yl) hexane, yield - 61%, melting point - 84-86°C (from butanole). The substance is characterized by similar absorption frequency in IR spectrum range.

**1,2-Bis(5-(m-nitrobenzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) ethane (10b), 1,4-bis(5-(m-nitrobenzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) butane (10e) and 1,6-bis(5-(m-nitrobenzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) hexane (10h).**

By analogous way it was received 1,2-bis(5-(m-nitrobenzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) ethane, yield - 72%, melting point - 256-258°C (from butanole) 1,4 - bis(5-(m-nitrobenzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) butane, yield - 70%, melting point - 309-311°C (from butanole) and 1,6 - bis(5-(m-nitrobenzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) hexane, yield - 84%, melting point - 186-187°C (from butanole).

1705-1690 cm<sup>-1</sup> (ν<sub>C=O</sub>), 1325-1320 cm<sup>-1</sup> (ν<sub>C-N</sub>), 1130-1120 cm<sup>-1</sup> (ν<sub>C-S</sub>), 1525-1520 cm<sup>-1</sup> (ν<sub>as NO<sub>2</sub></sub>), 1605-1595, 1370-1365, 1250-1245 cm<sup>-1</sup> (ν<sub>C-H<sub>s</sub></sub>), etc.

**1,2-Bis(5-(n-dimethylamino-benzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) ethane (10c), 1,4-bis(5-(n-dimethylamino-benzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) butane (10f) and 1,6-bis(5-(n-dimethylamino-benzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) hexane (10i).**

By analogous way it was received 1,2-bis(5-(n-dimethylamino-benzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) ethane, yield - 30%, melting point - 64-66°C (from water/ethanol), 1,4 - bis(5-(n-dimethylamino-benzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) butane, yield - 42%, melting point - 262-263°C (from water/retanol) and 1,6 - bis(5-(n-dimethylamino-benzyliden)-thiazolidyn-2-oxo-4-thioxo-3-yl) hexane, yield - 41%, melting point - 216-218°C (from water/ethanol).

1715-1695 cm<sup>-1</sup> (ν<sub>C=O</sub>), 1325-1320 cm<sup>-1</sup> (ν<sub>C-N</sub>), 1120-

1110 cm<sup>-1</sup> (ν<sub>C-S</sub>), 680-675 cm<sup>-1</sup> (ν<sub>C-S</sub>), 2735-2730 cm<sup>-1</sup> (ν<sub>N(CH<sub>3</sub>)<sub>2</sub></sub>), 1600-1595, 1375-1370 cm<sup>-1</sup> (ν<sub>C-H<sub>s</sub></sub>), etc.

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