The iodides of IX-XI and XIII were isolated by dilution of the cooled reaction mixtures with ether, dissolving of the precipitate or resinous mass in ethanol by heating, and by addition of an equal volume of 10% potassium iodide solution to the resulting solution.

The dyes were purified by recrystallization from ethanol. Dimethylidynemerocyanine XII was synthesized by condensation of 0.001 mole of the iodide of I with 0.001 mole of 5-acetanilidomethylene-3-ethylrhodanine in 2 ml of anhydrous ethanol in the presence of 0.002 mole of triethylamine by heating on a boiling-water bath for 60 min.

The dye that precipitated after cooling was removed by filtration and recrystallized from ethanol.

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SYNTHESIS OF 2-MERCAPTOTHIENO[3,2-d]- AND 2-MERCAPTOBENZO[4,5]THIENO[2,3-d]THIAZOLES

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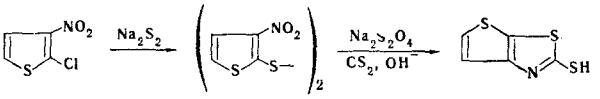
2-Mercaptothieno[3,2-d]- and 2-mercaptobenzo[4,5]thieno[2,3-d]thiazoles were synthesized by reduction of bis(3,3'-nitro-2,2'-thienyl) and bis(2,2'-nitrobenzo[b]thien-3,3'-yl) disulfides, respectively, with sodium hydrosulfite or sodium sulfide in the presence of carbon disulfide.

Mercaptobenzothiazole (Captax) is widely used as an accelerator for the vulcanization of rubber mixtures [1], as the starting compound for the synthesis of cyanine dyes [2], and as a stabilizer for photographic materials [3]. In this connection, it seemed of interest to synthesize its isosteres – 2-mercaptothieno- and 2-mercaptobenzothienothiazole – and investigate their physical and chemical properties.

2-Mercaptothieno[3,2-b]thiazole (I) was obtained by a multistep synthesis from 2-chlorothiophene through 2-chloro-3-nitrothiophene. The latter on heating with sodium disulfide is converted to bis-3,3'-nitro-2,2'-thienyl) disulfide (III), the reduction of which with sodium hydrosulfite in the presence of carbon disulfide gives thiazole I:



III I

2-Mercaptobenzo[4,5]thieno[2,3-d]thiazole (II) was synthesized via a similar scheme from benzo[b]thiophene through 2-nitro-3-bromobenzo[b]thiophene:

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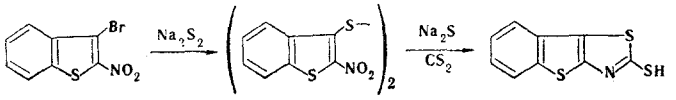

II

The IR spectra of I and II do not contain the absorption band at 2550-2600 cm^{-1} that is characteristic for the stretching vibrations of the SH group, and this indicates that the synthesized compounds, like 2-mercaptobenzothiazole [4], under normal conditions exist primarily in the thione form. The intense bands at 1500 cm^{-1} in the spectrum of thiazole I and at 1483 cm^{-1} in the spectrum of II (at 1495 cm^{-1} in the spectrum of 2-mercaptobenzothiazole [4]) can be assigned to the absorption of the $-NH-C=S$ grouping.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

2-Chlorothiophene-5-sulfonyl Chloride. This compound, with mp 26-28°, was obtained in 58.5% yield by the method in [5].

2-Chloro-3-nitrothiophene-5-sulfonyl Chloride. This compound, with mp 50-52°, was synthesized in 85% yield by nitration of 2-chlorothiophene-5-sulfonyl chloride with nitric acid (sp. gr. 1.5) [6].

2-Chloro-3-nitrothiophene. This compound was synthesized by the method in [6] by distillation with superheated steam in the presence of sulfuric acid of 2-chloro-3-nitrothiophene-5-sulfonic acid, obtained by hydrolysis of the sulfonyl chloride. The yield of product with mp 49-50° was 89%.

Bis(3,3'-nitro-2,2'-thienyl) Disulfide (III). Sodium disulfide, obtained by fusing 24.0 g (0.1 mole) of crystalline sodium sulfide and 3.2 g (0.1 g-atom) of sulfur, was added with stirring at 45-50° to a solution of 32.6 g (0.2 mole) of 2-chloro-3-nitrothiophene [4] in 100 ml of 90% ethanol, after which the mixture was refluxed for 2 h. It was then cooled, and the resulting precipitate was removed by filtration and washed with hot alcohol and water. The yield of III was 25.3 g (79%). Crystallization from ethanol gave yellow prisms with mp 172-173°. IR spectrum: 1525 and 1320 cm^{-1} (NO_2). Found %: C 30.0; H 1.1; N 8.8; S 39.7. $C_8H_4N_2O_4S_4$. Calculated %: C 30.0; H 1.2; N 8.75; S 40.0.

2-Mercaptothieno[3,2-d]thiazole (I). A total of 122 g (0.7 mole) of sodium hydrosulfite, 10 ml (0.17 mole) of carbon disulfide, 200 ml of ethanol, and 16.0 g (0.05 mole) of III were added with stirring to a solution of 4.8 g (0.2 mole) of sodium sulfide in 400 ml of water, after which the mixture was stirred at 50° for 2 h. Sodium hydrosulfite [61.0 g (0.35 mole)] and 5 ml (0.08 mole) of carbon disulfide were then added. After a few minutes, the color of the reaction mixture changed from orange-red to slightly yellow. The reaction was continued at 50-55° for 4 h, after which the mixture was cooled to room temperature and acidified with 15% hydrochloric acid. The resulting precipitate was removed by filtration and treated several times with 5% sodium hydroxide solution. The combined alkaline solutions were acidified with hydrochloric acid, and the resulting precipitate was removed by filtration, reprecipitated from 5% sodium hydroxide solution by the addition of hydrochloric acid, washed with water, and air dried to give 3.7 g (28%) of product. Recrystallization from ethanol gave light-yellow prisms with mp 194-195°. IR spectrum: 1500 (NHC=S) and 1280 cm^{-1} (Ar—NH). Found %: C 34.8; H 1.6; N 8.2. $C_5H_3NS_3$. Calculated %: C 34.65; H 1.7; N 8.1.

3-Bromobenzo[b]thiophene. This compound, with bp 140-144° (12 mm), was obtained in 87% yield by the action of bromine on benzo[b]thiophene in chloroform [7].

2-Nitro-3-bromobenzo[b]thiophene. This compound was obtained by a somewhat modified method [8] by the action of a solution of 90 ml (1.67 mole) of nitric acid (sp. gr. 1.5) in 90 ml of glacial acetic acid on a solution of 64 g (0.8 mole) of 3-bromobenzo[b]thiophene in 125 ml of glacial acetic acid at 15-20°. The yield was 46.5 g (60%). Crystallization from alcohol gave light-yellow needles with mp 159-160°.

Bis(2,2'-nitrobenzo[b]thien-3,3'-yl) Disulfide (IV). This compound was obtained by the method in [8] by the action of sodium disulfide on 2-nitro-3-bromobenzo[b]thiophene in 90% ethanol by refluxing for 12 h. The yield of product with mp 238-239° was 50%.

2-Mercaptobenzo[4,5]thieno[2,3-d]thiazole (II). Carbon disulfide (5 ml) and 8.4 g (0.02 mole) of IV were added with stirring at 40° to a solution of 26.0 g (0.108 mole) of crystalline sodium sulfide in 16 ml of water, after which the mixture was heated at 105-110° for 2 h. It was then cooled and acidified with 15% hydrochloric acid, and the resulting precipitate was removed by filtration, washed with water, and worked up as in the preparation of I to give 3.85 g (45%) of II. Recrystallization from ethanol gave light-yellow prisms with

mp 233-234°. IR spectrum: 1483 (NHC=S) and 1290 cm^{-1} (Ar–NH). Found %: C 48.6; H 2.2; N 6.0. $C_9H_5NS_3$. Calculated %: C 48.5; H 2.3; N 6.25.

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THIAZOLOCYANINES

XVIII.* N-HETARYLTHIAZOLIUM SALTS AND CYANINE DYES BASED ON THEM

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Some results of an investigation of thiazolocyanines containing α-hetaryl residues attached to the nitrogen atoms of the thiazole ring are summed up. The effect of the nature of these residues, their basicities, and mainly the steric hindrance generated by them on the absorption of the dyes was investigated. The angles of rotation of the hetaryl residues about their bond with the nitrogen atom of the thiazole ring in the dyes both in the presence and absence of substituents in the thiazole ring were calculated, and the associated disruption of the planarity of the thiazolotrimethylidynecyanine molecules is examined.

One of our earlier papers [2] was the first publication dealing with systematic investigations of N-hetarylthiazolocyanines and intermediates for their synthesis – quaternary thiazolium salts in which residues of heterocyclic nitrogen bases were substituents attached to the nitrogen atom of the thiazole rings. In the present paper some of the preliminary results, with the inclusion of additional data, are summed up.

A peculiarity of the structure of the investigated N-α-hetarylthiazolium salts is the fact that the hetaryl residues are bonded to the nitrogen atom of the thiazole ring in the α position and thus are to a certain degree analogs of the electronegative CN group. It has long been known that attachment of electronegative groups (for example, CN, dinitrophenyl, etc.) to the pyridinium nitrogen atoms promotes facile cleavage of the pyridine ring. Cleavage of a pyridinium salt in which a 2-benzoxazolyl residue is attached to the nitrogen atom is also known [3]. It is very possible that this is the reason that quaternary salts of the thiazole series and dyes with electronegative residues, particularly those with N-α-hetaryl rings, were not obtained prior to our studies, although individual communications regarding dyes of the pyridine [4] and benzimidazole [5] series of this type have appeared in the literature.

We have developed several variants of the synthesis of N-α-hetarylthiazolium salts with active methyl (IA) [2] and methylthio (IB) [6] groups and have synthesized dyes from them – nullimethylidynemerocyanines

*See [1] for communication XVII.

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