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# THIAZANE-2, 4-DITHIONE AND ITS 3-ARYL DERIVATIVES

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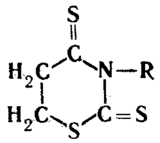
Reaction of 2-thiothiazane-4-one and its 3-aryl derivatives with phosphorus pentasulfide in toluene or dichloroethane gives thiazane-2, 4-dithione, or the corresponding 3-aryl derivatives. The compounds are characterized by absorption maxima (or bends) at three bands, 244–262, 315–321, and 339–350 mμ. The IR spectra exhibit bands at 14.93 μ (C–S–C), 6.64, and 6.84 μ (N–C–S), and 7.34, 8.43, 7.14 μ ($CH_2$).

The literature does not disclose any reactions of 2-thiothiazane-4-one or its derivatives, except hydrolytic scission of the thiazane ring by alkalies, phenylhydrazine, and hydrazine hydrate [1], ammonia, and amines [2, 3], and the methylation of a 3-ethyl derivative [1]. In contrast to the 5-membered ring homolog, i.e., rhodanine, 2-thiothiazane-4-one cannot condense with oxo compounds to give arylidene derivatives.

Since 2-thiothiazane-4-one is related to amides of cyclic acids, we attempted to react it with phosphorus pentasulfide, to convert the amide group to a thioamide one. Experiments showed that when the reaction is run in dichloroethane or toluene, 2-thiothiazane-4-one and its 3-aryl derivatives give good yields of the corresponding thiazane-2, 4-dithiones.

The table gives the compounds synthesized: they have not hitherto been described in the literature. Tisler attempted unsuccessfully to prepare them in 1961 [4].

Thiazane-2, 4-dithione and its 3-Aryl Derivatives

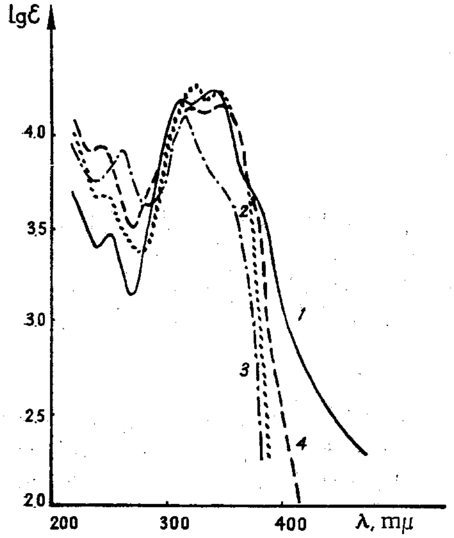


| R | Yield, % | Mp, °C | Formula | Found, % | | | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | C | H | N |
| H | 91.8 | 109 | $C_4H_5NS_3$ | 28.97 | 3.26 | 8.35 | 28.95 | 3.08 | 8.58 |
| $o$-$CH_3$—$C_6H_4$ | 75.0 | 98 | $C_{11}H_{11}NS_3$ | 52.02 | 4.41 | 5.90 | 52.14 | 4.37 | 5.52 |
| $p$-$CH_3$—$C_6H_4$ | 60.7 | 110 | $C_{11}H_{11}NS_3$ | 52.20 | 4.29 | 5.59 | 52.14 | 4.37 | 5.52 |
| $p$-$C_2H_5O$—$C_6H_4$ | 91.7 | 127 | $C_{12}H_{13}ONS_3$ | 50.86 | 4.87 | 4.91 | 50.85 | 4.62 | 4.94 |

Thiazane-2, 4-dithione is a yellow crystalline compound which, when stored in moist air, or on treatment with water, is slowly decomposed, as shown by the smell of hydrogen sulfide. The compound dissolves in NaOH, $Na_2CO_3$, and $NH_4OH$, when there is gradual hydrolysis, a reddish violet color being obtained with freshly-prepared sodium nitroprusside solution.

Introduction of an aryl group at position 3 stabilizes the thiazane ring, since 3-arylthiazane-2, 4-dithiones do not give a positive reaction with sodium nitroprusside.

From the UV absorption spectra graphs shown in the figure, it is seen that thiazane-2, 4-dithione and its 3-aryl derivatives, are characterized by maxima or bends in three bands, at 244–262, 315–321, and 339–350 mμ. The first band, provisionally called a thione one, and the second, called an amide one or dithiocarbonate one, are also characteristic of rhodanides [5] and 2-thiothiazan-4-ones [6]. For rhodanides and 2-thiothiazan-4-ones, the third band is low intensity and non-characteristic.



UV absorption spectra: 1) thiazane-2, 4-dithione; 2) 3-o-tolylthiazane-2, 4-dithione; 3) 3-p-tolylthiazane-2, 4-dithione; 4) 3-p-ethoxyphenylthiazane-2, 4-dithione.

In the IR absorption spectra of thiazane-2, 4-dithione, strong bands were observed at 734, 743, 8.14 μ (CH$_2$) and 14.93 mμ (C–S–C), and medium bands at 6.64 and 6.84 μ (N–C–S). At the same time, according to Randall's results [7], the bands most characteristic of rhodanine are strong ones at 5.68–5.95 μ (C=O) and 6.33–6.92 μ (N–C–S), while 2-thiothiazan-4-one is [4] characterized by bands at 3.21 μ (N–H), 5.86–5.89 μ (C=O), and 922–950 μ (C–S).

Substitution of an oxygen atom at position 4 in the 2-thiothiazan-4-one molecule by a sulfur atom, increases the lability of the hydrogen atoms at position 5, so that thiazane-2, 4-dithiones readily condense with aromatic aldehydes to give 5-arylidenethiazane-2, 4-dithiones [8], which will form the subject of a separate communication.

## Experimental

Thiazane-2, 4-dithione. A mixture of 19.8 g 2-thiothiazan-4-one, 18.1 g P$_2$S$_5$, and 150 ml toluene was refluxed for 6 hr in a flask, the boiling solution filtered, and the solid remaining in the flask twice extracted with 50 ml toluene each time. The toluene solution was concentrated to small volume, and the precipitate which formed on cooling filtered off, yield 20.2 g yellow crystals, mp 109° C (ex toluene).

3-Arylthiazane-2, 4-dithiones. A mixture of 2.67 g 3-p-ethoxyphenyl-2-thiothiazan-4-one, 1.33 g P$_2$S$_5$, and 25 ml dichloroethane was refluxed for 6 hr, and worked up as described above. 3-o-Tolylthiazane-2, 4-dithione and 3-p-tolylthiazane-2, 4-dione were prepared similarly.

The UV spectra of the compounds were observed with a SF-4 spectrophotometer, using EtOH as the solvent, and the IR spectra with a Zeiss UR-10 spectrophotometer, in KBr tablets.

## REFERENCES

1. J. Seyden-Penne, Ann. Chim., 3, 599, 1958.
2. J. E. Jansen, U.S. Patent no. 2 709 706, 1955; C. A., 50, 5746, 1956.
3. T. H. Shelley and N. J. Spottswood, U. S. Patent no. 2 614 095, 1952; C. A., 47, 2541, 1953.
4. M. Tisler, Arch. Pharm., 296/64, 348, 1961.
5. N. M. Turkevich, Ukr. khim. Zh., 25, 487, 1959.
6. F. C. Brown, C. K. Bradsher, B. F. Moser, and S. Forrester, J. Org. Chem., 24, 1056, 1959.
7. H. M. Randall, N. Fuson, R. G. Fowler, and J. R. Dangl, Infrared Determination of Organic Structures, Van Nostrand Prom. New York-London, 1949.
8. E. V. Vladzimirskaya, Author's Certificate 170993, 1964; Byull. izobr., no. 10, 1965.

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