# SPECTROPHOTOMETRIC STUDY OF 5-ARYLIDENE- AND 5-(5-ARYLFURFURYLIDENE)RHODANINES

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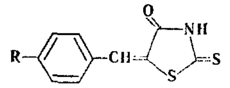
5-Arylidenerhodanines and the previously undescribed 5-[5-(4-R-phenyl)furfurylidene]rhodanines were synthesized by the Andreasch method. It is assumed that Fermi resonance appears in the IR spectra of some of these compounds in the region of carbonyl absorption; bands of associated N—H bonds were identified. It is shown that in the case of 4-N$(CH_3)_2$-benzylidenerhodanine the long-wave band in the electronic spectra is a bathochromically shifted band of the same nature as the band in the spectra of 5-arylidenerhodanine derivatives with weak donor groups. The introduction of an arylfurfurylidene grouping gives rise to a substantial bathochromic shift of the absorption band of their molecules.

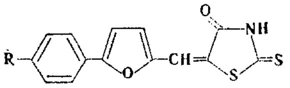
Arylidenerhodanines (5-arylidene-2-thionothiazolidin-4-ones) are extremely important, in a practical respect, class of substances, since some of them are known as reagents for silver, gold, and copper ions [1], photosensitizers [2], and physiologically active compounds [3-5].

In addition, there are a number of unexplained problems with respect to their UV and IR spectra. In carrying out our search for new physiologically active compounds, we synthesized a number of 5-(5-arylfurfurylidene)rhodanines by the Andreasch method [6].

We subjected rhodanine and 5-arylfurfurals to condensation in acetic acid in the presence of fused sodium acetate; we chose 5-arylfurfurals because, according to the data in [7], they themselves have antibacterial action. Some 5-arylidenerhodanines were obtained under the same conditions in order to compare their properties.



Ia-e



IIa-g

I-II a R = H; I b R = $CH_3O$; c R = $N(CH_3)_2$; I-II d R = Br; e R = $NO_2$; II b R = $CH_3$;
c R = Cl; f R = CN; g R = $CH_3CO$

The electronic absorption spectra of rhodanine derivatives Ia, b, d are characterized by low-intensity long-wave bands at 480-490 nm. The low intensity ($\varepsilon \simeq 20-25$) and the solvent effect (a hypsochromic shift of the absorption band as compared with isooctane is observed in methanol) undoubtedly attest to the $n-\pi^*$ nature of this band. The remaining observed bands have rather high intensities and are affiliated with bands of the $\pi-\pi^*$ type.

In a discussion of the nature of the long-wave bands in the spectra of arylidenerhodanines, N. M. Turkevich [8] noted the participation of benzylidene groupings in these transitions. At the same time, these bands, which are shifted regularly when substituents are introduced into the aromatic ring, were characterized as new bands. In our opinion, the introduction of a benzylidene group actually has a substantial effect on the spectrum of rhodanine, but the interpretation of the effects of substitution should be different.

The presence of a band analogous to the long-wave band of benzalacetone can be assumed in the spectrum of benzylidenerhodanine. The assumption of the "benzalacetone" character of this band can be based on the assumption of weak participation of the unshared pairs of electrons of the imine nitrogen atom in this band due to cross-conjugation with the CO and C = S groups. However, the magnitude of the bathochromic shift on passing from benzalacetone (278 nm) to 5-benzylidenerhodanine (375 nm) does not, in our opinion, find a logical explanation for a number of reasons.

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TABLE 1. Characteristics of the Rhodanine Derivatives

| Compound | mp, °C | Literature mp, °C | Empirical formula | N, % |  | IR spectra (KBr) |  |  |  |  | UV spectra (methanol), $\lambda_{max}$, nm ($\varepsilon \cdot 10^{-3}$)* |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | found | calc. | $\nu_{C=O}$ | $\nu'_{C=S}$ | $\nu''_{C=S}$ | $\nu_{C=C}$ | $\nu_{C-H}$ |  |
| Rhodanine | — | — | — | — | — | 1715 | 1079 | 1239 | — | — | 252 (12,6); 294 (15,4) |
| Ia | 204 | 204[6] | $C_{10}H_7NOS_2$ | — | — | 1701; 1708 | 1081 | 1244 | 1591 | 928 | 237 (11,0); 272 (10,2); 375 (37,6) |
| Ib | 252 | 250 | $C_{11}H_9NO_2S_2$ | — | — | 1687 | 1081 | 1247 | 1589 | 954 | 238 (12,7); 289 (11,7); 394 (46,7) |
| Ic | 275—280 | 275—280[1] | $C_{12}H_{12}N_2OS_2$ | — | — | 1678 | 1066 | 1215 | 1568 | 945 | 298 (14,9); 320 (31,2); 465 (61,5) |
| Id | 238 | 237—238[14] | $C_{10}H_6Br_2NOS_2$ | — | — | 1718; 1726 | 1081 | 1244 | 1596 | 926 | 239 (14,9); 272 (13,8); 375 (47,5) |
| Ie | 259 | 250—252[4] | $C_{10}H_6N_2O_3S_2$ | — | — | 1716; 1727 | 1071 | 1245 | 1591 | — | 230 (7,35); 270 (8,25); 392 (33,6) |
| IIa | 255—256 | — | $C_{14}H_9NO_2S_2$ | 4,87 | 4,90 | 1692 | 1043 | 1216 | 1610 | 921 | 235 (12,9); 243 (13,3); 306 (23,8); 436 (40,8) |
| IIb | 268—269 | — | $C_{15}H_{11}NO_2S_2$ | 4.65 | 4,64 | 1687 | 1046 | 1213 | 1602 | 922 | 233; 244; 309; 446 |
| IIc | 288 | — | $C_{14}H_8ClNO_2S_2$ | 4,35 | 4,33 | 1690 | 1043 | 1218 | 1611 | 926 | 243 сл; 308; 439 |
| IId | 293—294 | — | $C_{14}H_8BrNO_2S_2$ | 3,82 | 3,79 | 1680 | 1033 | 1213 | 1612 | 927 | 243; 309; 439 |
| IIe | 348 | — | $C_{14}H_8N_2O_4S_2$ | 8,43 | 8,44 | 1690 | 1046 | 1219 | 1608 | 927 | 247; 310; 438 |
| IIf | 337 | — | $C_{15}H_8N_2O_2S_2$ | 8,97 | 8,99 | 1684 | 1047 | 1218 | 1608 | 923 | 240; 250; 333; 445 |
| IIg | 254—256 | — | $C_{16}H_{11}NO_3S_2$ | 4,25 | 4,21 | 1674; 1707 | 1036 | 1208 | 1608 | 925 | 236; 249; 319; 438 |

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*Because of their insufficient solubility, the ε values of IIb-g were not measured.

Replacement of the acetyl group by an imide group should lead to a hypsochromic shift of the benzalacetone band. However, the bathochromic shift due to fixation of the compressed s-cis structure does not exceed 10 nm, as can be indirectly estimated in the case of 2-(2-thienylidene)cyclopentanone [9].

In the case of benzylidenerhodanine Ia the electron transition localized on the benzalacetone fragment most likely characterizes the band with λ 278 nm (see Table 1). The introduction of substituents (Ia-IIe) and replacement of the phenyl group by an arylfuran group (IIa-g) cause regular shifts of this band, which correspond to the electronic character of the substituting groups. As compared with the absorption of benzalacetone itself, this band in the spectrum of Ia is shifted 6 nm hypsochromically; this is undoubtedly due to weakening of the interaction of the styryl group with the C = O group because of the cross-conjugation effect of the imide nitrogen atom.

The intense long-wave band with $\lambda_{max}$ 375 in the spectrum of Ia is also characterized by the participation of a benzylidene grouping, but in addition to this, an ArCH=CSC=S group is included in the chromophore system.

A similar conclusion regarding the role of the sulfide bridge was drawn by S. N. Baranov [10] during a comparison of related compounds. The determining role in the long-wave absorption band of the π-electron system of the thiono group also follows from a comparison of the spectra of rhodanine [$\lambda_{max}$ 294 nm ($\varepsilon$ $15.4 \cdot 10^{-3}$)] and thiazolidinedione [$\lambda_{max}$ 225 nm ($\varepsilon$ $20.0 \cdot 10^{-2}$)] [11]. The effect of a substituent on this band follows the trend observed for the benzalacetone band, and the long-wave band for Ic is therefore a band of the same nature, which for Ia, b, d is shifted regularly to the red region of the spectrum because of the strong electron-donor effect of the $N(CH_3)_2$ group, rather than a new band, as asserted by N. M. Turkevich [8].

The appearance of a bridge grouping in the form of a 2,5-disubstituted furan ring (IIa-g) led to a substantial red shift of the entire absorption spectrum, the reason for which is, in our opinion, the simultaneous effect of two factors: lengthening of the π system and the greater, as compared with the phenyl group, electron-donor influence of the 2,5-furylene group. A particularly large shift of $\lambda_{max}$ is observed for the long-wave absorption band; this attests to the great polarizability of the corresponding chromophore system. Since electron-acceptor substituents, which are characterized by a counterpolarization effect with respect to the C = O and C = S groups, were primarily introduced into the aromatic ring, their effect, as might have been expected, is small.

The nitro group, the introduction of which probably changes the direction of polarization in the molecule, constitutes an exception.

The IR spectra play an important role in the understanding of the chemical nature of rhodanine derivatives of the I and II type; the frequencies of the most characteristic bands are presented in Table 1.

The vibrations of the carbonyl group appear in peculiar (for cyclic imides) regions of the spectrum; the strain of the five-membered ring to a considerable extent determines the $\nu_{CO}$ values. The introduction of a benzylidene group in the rhodanine molecule lowers $\nu_{CO}$; this constitutes evidence for the existence of conjugation between these groups in the ground state of the molecule. This is also confirmed by the regular changes in this frequency that are observed when substituents are introduced.

It is interesting to note that the phenylfurfurylidene group gives rise to an appreciable decrease in $\nu_{CO}$ (12 $cm^{-1}$) as compared with the benzylidene group. The effect of the same two factors that were discussed above in the analysis of the UV spectra also are manifested here.

Two bands are observed for Ia, d, e and IIg, c in the region of carbonyl absorption. For the first three arylidenerhodanines this is most likely due to Fermi resonance, which is quite characteristic for cyclic ketones (for example, compare this with the data for cyclopentanone [12]). This conclusion is, in our opinion, valid, since the effect is observed only for compounds the carbonyl absorption of which lies at 1701-1727 $cm^{-1}$.

In addition, this splitting vanishes in the case of $CCl_4$ solutions, in the spectra of which the band under discussion is shifted strongly.

The presence of two bands in the spectrum of IIg corresponds to the functional composition of the molecule, but the $\nu_{CO}$ values that we found for both bands were unexpected. The exocyclic C = O groups in the IR spectra of the related compounds IIa-f absorbs at 1680-1692 $cm^{-1}$. The acetyl group in acetophenone is characterized by a band at 1686 $cm^{-1}$ (see [12]). We spoke above of the absence of a substantial interaction between the substituents and the five-membered ring above. Consequently, it remains to assume that Fermi resonance due to coincidence of the absorption frequencies of two carbonyl groups is also reflected in this spectrum. In this case the characteristic absorption of both C = O groups should have been observed at 1690 $cm^{-1}$, i.e., in complete conformity with the general principles. Unfortunately, it is difficult to verify this assumption by variation of the conditions of measurement primarily because of the low solubility of this compound.

Frequencies of out-of-plane deformation vibrations of the C—H group, which, according to [13], attest to a transoid orientation of aryl and carbonyl groups relative to the double bond conjugated with them, are observed at 920-950 $cm^{-1}$.

To assign the frequencies of the C = S stretching vibrations of the thiono group (see Table 1) we used the ratio $\nu_{CO}/\nu_{CS} = 1.59$-$1.65$ found in [11] for related compounds. One's attention is directed to the appreciable decrease in this frequency in the case of IIa-g; this is probably due to the electron-conducting character of the sulfide bridge.

A similar regularity is also observed for the "thioamide II" band at 1212-1247 $cm^{-1}$.

By analyzing the frequencies of the N—H stretching vibrations we arrived at the conclusion that there is strong hydrogen bonding in the indicated substances, as evidenced by the intense absorption bands at 3050-3150 $cm^{-1}$ that are characteristic for associated amides. However, there is no unambiguous information in the literature regarding the nature of these bands. According to the data in [11, 14], similar bands were observed in the spectra of phthalimide, thiophthalimide, hydantoin, and related compounds; the high-frequency band was then assigned to the stretching vibrations of N—H groups linked by a hydrogen bond with the carbonyl group, and the low-frequency bond was assigned to complex vibrations associated with molecular hydrogen bonds of various types.

In order to interpret the bands and ascertain the type of hydrogen bonding in the investigated compounds we measured the IR spectra of dilute solutions of several substances in $CCl_4$ at concentrations from $5 \cdot 10^{-3}$ (saturated solution) to $1 \cdot 10^{-4}$ mole/liter. In this case we observed a decrease in the intensity of the band at 3050 $cm^{-1}$, disappearance of the band at 3150 $cm^{-1}$, and the appearance of a new peak at 3400 $cm^{-1}$. The position of the latter did not change when the solutions were diluted. Hence it follows that arylidene- and arylfurfurylidenerhodanine molecules in the solid state and in concentrated solutions form both types of hydrogen bonds. We measured the spectrum of the partially N-deuterated derivative of Ia and observed a considerable decrease in the intensity of the band at 3400 $cm^{-1}$ and the appearance of a new band at 2550 $cm^{-1}$. All of this enables us to unambiguously assign the band at 3400 $cm^{-1}$ to free N—H stretching vibrations.

In a comparison of the spectra of benzylidenerhodanine Ia measured in the solid phase and in dilute $CCl_4$ solution one may note a considerable shift (33 $cm^{-1}$) in the $\nu_{CO}$ frequency to the higher-frequency region; this is associated with the absence of association in solution. In this case the $\nu_{C=S}$ frequency remains practically constant.

This enables us to assume primary localization of the intermolecular hydrogen bond on the C = O group.

## EXPERIMENTAL

For the spectral studies, compounds of the I and II type were recrystallized from appropriate solvents (chloroform and acetic acid). The individuality of the compounds was monitored by thin-layer chromatography [Silufol UV-254 in a benzene—methanol system (1 : 10)]; the characteristics of the compounds and the results of elementary analysis are presented in Table 1.

The deutero derivative was obtained by exchange of the protons by deuterium by the action of heavy water in $CCl_4$. The UV spectra were recorded with a Specord spectrophotometer, and the IR spectra were recorded with a UR-20 spectrometer.

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# SYNTHESIS OF METHYL-SUBSTITUTED THIAZOLE BASES WITH A CONDENSED FURAN, THIOPHENE, OR SELENOPHENE RING

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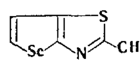
Methyl-substituted heterocyclic bases with a furan, thiophene, or selenophene ring condensed with a thiazole ring were synthesized by heating the appropriate o-bromo acetamido derivatives with phosphorus pentasulfide or by oxidation of thioacyl compounds with potassium ferricyanide in alkaline media.

Methyl-substituted thieno- and benzothienothiazoles have been previously synthesized [1-5]. Polymethine dyes of various types have been obtained from the quaternary salts of bases of this type, and their color has been studied [6-8]. It seemed of interest to obtain dyes based on derivatives of heterocyclic bases containing a selenophene or furan ring condensed with the thiazole ring and to study their spectral and photographic properties.

In the present communication we describe the synthesis of methyl-substituted selenopheno-, benzofuro-, and benzoselenopheno[2,3-d]thiazoles (I-III).



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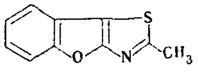

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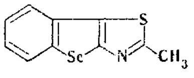

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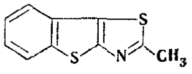
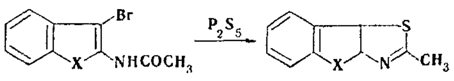


IV

2-Methylselenopheno[2,3-d]thiazole (I) was synthesized by acetylation of 2-aminoselenophene by the action of phosphorus pentasulfide on the acetamido derivative and subsequent oxidation of 2-thioacetamidoselenophene with potassium ferricyanide in alkaline media. 2-Methylbenzofuro[2,3-d]thiazole (II) and 2-methylbenzofuro[2,3-d]thiazole (IV), which was previously obtained by a different method [3], were synthesized similarly from the corresponding amino derivatives of benzofuran and benzothiophene. Base II was also synthesized by bromination of 2-acetamidobenzofuran and by heating phosphorus pentasulfide with 2-acetamido-3-bromobenzofuran (V, X = O).



V II, III

II X = O; III X = Se; V X = O, Se

2-Methylbenzoselenopheno[2,3-d]thiazole (III) was similarly obtained from 2-acetamido-3-bromoselenophene (V, X = Se).

It should be noted that II is not formed in the reduction of 2,2'-dinitro-3,3'-benzofuryl disulfide under various conditions because of facile opening of the furan ring in this case to give an intermediate amino deriva-

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