B. The compound was obtained in 97% yield as described above from 0.8 g of sulfide II and 5 ml of 28% H_2O_2. The product was identical with respect to its IR and PMR spectra and melting point to the sample of sulfone IX.

C. The compound was obtained in 94% yield as described above for isoxazoline VII from equivalent amounts of oxide X and styrene in solution in CH_2Cl_2. The product had mp 85-87°C; no melting-point depression was observed for a mixture of this product with the product obtained in experiment A.

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SPECTRAL INVESTIGATIONS OF THE TAUTOMERIC EQUILIBRIA OF THIOACYL DERIVATIVES OF 2-AMINOTHIAZOLE AND 2-AMINOBENZOTHIAZOLE

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The positions of the tautomeric equilibria for a number of thioacyl derivatives of 2-aminothiazole and 2-aminobenzothiazole were determined by UV and IR spectroscopy with the use of model compounds. Quantum-chemical calculations by the CNDO/2 method were made for some of the acyl and thioacyl derivatives of 2-aminothiazole and 2-iminothiazole.

It is known that the existence of amino derivatives of heterocyclic compounds in the amino or imino form depends to a substantial extent on the basicity of the exocyclic nitrogen atom [1, 2]. A decrease in the basicity of this nitrogen atom gives rise to a shift of the tautomeric equilibrium to favor the imino form [3, 4]. The available literature data from spectral investigations of amine-imine tautomeric equilibria in series of 2-aminothiazoles and 2-aminobenzothiazoles pertain to NH, N-alkyl, and N-acyl derivatives [5, 6]. The present paper is devoted to an investigation by means of UV and IR spectroscopy of such equilibria for thioacyl derivatives of 2-aminothiazole and its benzo analog, which can also exist in two tautomeric forms: amino (A) and imino (B).

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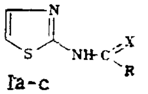
TABLE 1. Characteristics of the Thioacyl Derivatives

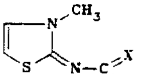
Compound	mp, °C*	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	S		C	H	S	
VIIa	229—230	38,1	4,0	40,4	$C_5H_6N_2S_2$	37,9	3,8	40,5	34
VIIb	152—154	28,6	1,8	30,3	$C_5H_3F_3N_2S_2$	28,3	1,4	30,2	58
VIIc	176—177	54,7	4,1	29,3	$C_{10}H_8N_2S_2$	54,5	3,7	29,1	41
VIIIa	202—204	52,3	4,3	31,0	$C_9H_8N_2S_2$	51,9	3,9	30,8	42
VIIIb	211—213	41,4	2,3	24,5	$C_9H_5F_3N_2S_2$	41,2	1,9	24,4	62
VIIIc	184—185	62,5	3,9	23,6	$C_{14}H_{10}N_2S_2$	62,2	3,7	23,7	74
IXa	138—139	42,1	5,2	37,6	$C_6H_8N_2S_2$	41,8	4,8	37,2	47
IXb	133—134	40,1	2,5	28,6	$C_6H_5F_3N_2S_2$	31,9	2,2	28,5	46
IXc	129—131	56,8	4,5	27,5	$C_{11}H_{10}N_2S_2$	56,4	4,3	27,4	52
Xa	138—139	54,5	4,8	29,1	$C_{10}H_{10}N_2S_2$	54,0	4,5	28,8	57
Xb	137—138	43,7	3,0	23,4	$C_{10}H_7F_3N_2S_2$	43,5	2,6	23,2	53
Xc	193—194	63,6	4,7	22,8	$C_{15}H_{12}N_2S_2$	63,3	4,3	22,5	63
XIa	118—119	54,3	4,7	28,8	$C_{10}H_{10}N_2S_2$	54,0	4,5	28,8	5
XIc	97—98,5	63,7	4,5	22,6	$C_{15}H_{12}N_2S_2$	63,3	4,3	22,5	7

*The compounds were crystallized: VIIa-c—IXa-c from CCl_4, Xa,b and XIa,c from heptane, and Xc from benzene—heptane.

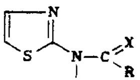
For a comparison of the behavior of thioamides and their oxygen analogs we also synthesized and investigated a large series of amides of the indicated heterocyclic amines, since the published data on the tautomerism of these compounds are not sufficiently complete. In the research we used fixed models of the tautomeric forms. All of the thioamides were obtained by sulfuration of the corresponding acyl derivatives with P_2S_5 in dioxane (Table 1).



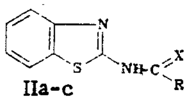
Ia-c
VIIa-c



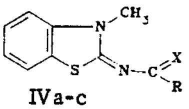
IIIa-c
IXa-c



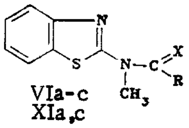
Va-c



IIa-c
VIIIa-c



IVa-c
Xa-c



VIa-c
XIa,c

I—XI a $R=CH_3$, b $R=CF_3$, c $R=C_6H_5$; I—VI, IX $X=O$; VII, VIII, X, XI $X=S$

UV Spectra. According to our data, in complete conformity with [3, 4], acetyl derivatives Ia and IIa ($X = O$, $R = CH_3$) exist primarily in the amino form, regardless of the polarity of the medium. In the case of benzoyl derivatives Ic and IIc ($X = O$, $R = C_6H_5$) in solvents with any kind of polarity the tautomeric equilibria are shifted to favor amino form A, although traces of the imino tautomers can be observed (Table 2). In the case of trifluoroacetyl derivatives Ib and IIb ($X = O$, $R = CF_3$) a completely different pattern is observed: in a polar solvent (methanol) they exist in the imino form, while in a nonpolar solvent (cyclohexane) the tautomeric equilibrium is shifted to favor the amino form (Table 2).

The transition to the thio analogs results in a bathochromic shift of the absorption maxima in the UV spectra. A low-intensity band of an $n-\pi^*$ transition, which is shifted hypsochromically with an increase in the polarity of the solvent, is observed in the spectra for all of the thioamides (Table 3).

Like their oxygen analogs, thioacetyl derivatives VIIa and VIIIa ($X = S$, $R = CH_3$) exist in the amino form, regardless of the polarity of the medium. This possible percentage of the imino tautomer should not exceed the accuracy of the spectrophotometric method (3-5%).

The spectra of thiobenzoyl derivatives VIIc and VIIIc ($X = S$, $R = C_6H_5$) are more complex, and the maxima at 339 and 345-385 nm, respectively, can evidently be regarded as diagnostic maxima for determination of the position of the tautomeric equilibrium (Table 3). It follows from a comparison of the spectra of thiobenzoylaminobenzothiazole VIIIc with the spectra of fixed forms Xc and XIc that in cyclohexane it exists primarily in the amino form, whereas in methanol it exists primarily in the imino form (Table 3). In contrast to this, the thioben-

TABLE 2. UV and IR Spectra of Acyl Derivatives of 2-Amino(imino)thiazole(thiazoline) and 2-Amino(imino)-benzothiazole(thiazoline)

Compound	UV spectrum, λ_{max}, nm (log ε)		IR spectrum, cm^{-1}
	methanol	cyclohexane	
Ia	265 (3,96)	264 (3,83)	1700 s (C=O), 157s (11H)
IIIa	295 (4,16)	294 (4,13)	1590 s (C=O), 1570 m, 1495 s
Va	268 (3,96)	267 (3,41)	1670 s(C=O), 1512 ms, 1470 sh
Ib	294 (3,99)	273 (4,12)	1640 s (C=O), 1580 s (11H), 1520 s
IIIb	227 (3,30), 303 (4,17)	240 (3,30), 302 (4,12)	1620 s (C=O), 1565 m, 1500 s
Vb	218 (3,20), 257 (3,88)	227 sh (3,60), 257 (4,12)	1665 br.s (C=O)
Ic	227 (4,01), 283 (4,09)	226 (4,04), 280 (4,01)	1685 s (C=O), 1610 m, 1560 s (11H)
IIIc	242 (4,08), 278 (3,96) sh, 284 (3,97), 324 (4,26)	240 (4,09), 248 (3,96) 284 (3,64), 321 (4,26)	1599 ms (C=O), 1555 s, 1505 s 1485 s
Vc	215 (4,06) sh, 278 (4,09)	217 (4,06) sh, 278 (4,00)	1638 s (C=O), 1510 m, 1485 w
IIa	246 (3,92), 275 (4,18) 287 (4,08), 298 (4,00)	244 (3,97), 270 (4,13) 286 (4,01), 297 (3,94)	1708 s (C=O), 1615 m, 1575 s(11H)
IVa	259 (3,98), 271 (4,09)sh. 276 (4,10) sh, 312 (4,39)	278 (3,83), 303 (4,33) 312 (4,43)	1621 s (C=O), 1612 s. 1505 br.s 1470 s
VIa	245 (3,93), 274 (4,24), 286 (4,15), 297 (4,10)	245 (3,92), 275 (4,16) 287 (4,06), 298 (4,08)	1675 s (C=O), 1500 s
IIb	251 (3,82) sh, 259 (3,90) 287 (4,09) sh, 298 (4,14) sh, 312 (4,17)	241 (3,76), 250 (3,81) 279 (4,02), 294 (3,94) sh 322 (3,26) sh	1635 s (C=O), 1610 m, 1595 w, 1560 m (11H) 1505 m, 1475 s
IVb	260 (3,92), 278 (3,95) sh 315 (4,32)	260 (3,68), 271 (3,70) 280 (3,72), 313 (4,33) 320 (4,30) sh	1650 s (C=O), 1610 sh, 1585 w, 1550 sh, 1505 s 1470 s
VIb	266 (4,18), 296 (3,50)sh	243 (3,75), 252 (3,81) 282 (4,07), 294 (4,04) sh	1695 s (C=O), 1595 w, 1505s
IIc	229 (4,34) sh, 294 (4,22) sh, 303 (4,25)	227 (4,34), 285 (4,10) sh 294 (4,13) sh 302 (4,15)	1678 s (C=O), 1600 m, 1560 s (11H)
IVc	238 (3,94), 331 (4,18)	240 (4,35), 326 (4,52), 335 (4,43) sh	1610 s (C=O), 1575 ms, 1510 s, 1490 sh., 1470 s
VIc	247 (3,90) sh, 282 (4,19) 290 (4,18), 302 (4,16)	247 (3,84) sh, 282 (4,15) 290 (4,13), 302 (4,13)	1660 s (C=O), 1600 vw, 1505 m

zoyl derivative (VIIc) of 2-aminothiazole exists in the amino form in solutions, regardless of the polarity of the medium (Table 3).

The transition to trifluoroacetyl derivatives VIIb and VIIIb (X = S, R = CF_3) results in a significant shift of the equilibrium to favor the imino tautomer; in contrast to oxygen analogs Ib and IIb, the state of the equilibrium depends little on the polarity of the solvent.

IR Spectra. To investigate the effect of the aggregate state and association on the tautomerism of acyl and thioacyl derivatives of 2-aminothiazole and 2-aminobenzothiazole we turned to the IR spectra, once again using the method of comparison with the spectra of fixed structures. The tautomerism of acetyl, chloroacetyl, and trifluoroacetyl derivatives of these heterocycles was previously investigated by this method [4, 7]. It was established that in the solid state acetyl derivatives Ia and IIa exist primarily in amino form A, while trifluoroacetyl derivatives Ib and IIb exist primarily in the imino form [4]. Since Sheinker and coworkers [4] did not have certain model fixed structures (for example, Vb and VIb) at their disposal and did not investigate the benzoyl derivatives, we undertook a more systematic investigation of the tautomerism of acyl derivatives of 2-aminothiazole and 2-aminobenzothiazole.

TABLE 3. UV and IR Spectra of Thioacyl Derivatives of 2-Amino-(imino)thiazole(thiazoline) and 2-Amino(imino)benzothiazole(thiazoline)

Compound	UV spectrum, λ_{max}, nm (log ε)		IR spectrum, cm^{-1}
	methanol	cyclohexane	
VIIa	250 (3,64), 317 (3,98)	312 (4,01) sh, 317 (4,04) 328 (3,92), 333 (3,81) sh 405 (1,60)	1590 s 1495 m 1420 ms, 1365 s 1331 s, 1180 ms
IXa	360 (4,28), 417 (2,16) sh	360 (4,18), 454 (1,65)	1560 m, 1465 br. s, 1405 sh, 1370 br. s 1355 sh
VIIb	269 (3,78), 348 (4,07) 429 (1,98) sh	360 (3,97)	1570 s (11H), 1550 sh, 1498 s 1430 s 1379 s
IXb	370 (4,24), 435 (2,00)	375 (4,21), 465 (1,70)	1565 m, 1485 br. s 1435 s 1408 ms, 1370 m
VIIc	227 (4,12), 286 (4,11) 339 (3,78)	244 (4,15), 282 (4,05) 339 (3,92), 435 (2,43)	1560 ms, 1449 ms, 1350 m
IXc	258 (4,17), 294 (4,20) 385 (4,12), 454 (2,33)	256 (3,94) sh, 308 (4,17) 385 (4,05), 500 (2,18)	1560 m, 1498 s, 1470 s 1450 sh, 1420 s, 1390 s 1370 sh
VIIIa	294 (3,75) sh, 332 (4,26)	294 (3,76) sh, 308 (3,98) sh, 330 (4,21)	1570 s, 1460 m, 1439 ms 1370 sh, 1350 vs 1330 s, 1160 m
Xa	370 (4,39), 429 (2,00) sh	370 (4,37), 476 (1,65)	1505 sh, 1498 ms, 1465 ms, 1450 sh, 1405 sh, 1390 m, 1350 m
XIa	294 (3,90) sh, 330 (4,15)	297 (3,94) sh, 309 (4,02) sh, 323 (4,12), 402 (1,09)	1490 m, 1450 m, 1420 ms, 1380 m, 1360 m, 1160 m,
VIIIb	367 (4,26), 455 (1,93) sh	377 (4,03), 385 (4,00)	1520 s (11H), 1470 s, 1455 s, 1420 s, 1405 sh 1369 sh
Xb	385 (4,36), 391 (4,33) sh, 455 (1,94) sh	385 (4,36) sh, 390 (4,37), 488 (1,70)	1500 ms. 1460 ms 1424 ms, 1400 sh 1352 m
VIIIc	250 (4,14) sh, 288 (4,16), 345 (3,90) sh, 385 (3,86) sh	252 (4,15), 286 (4,14), 351 (4,00), 444 (2,32)	1560 sh, 1450 m, 1435 m, 1330 s
Xc	250 (4,10) sh, 282 (3,91) sh, 318 (4,19), 395 (4,31), 488 (2,32)	286 (4,00) sh, 320 (4,26), 394 (4,29), 517 (2,20)	1505 sh 1498 s 1460 s, 1450 sh, 1406 s, 1388 m, 1354 m
XIc	340 (4,18), 417 (2,58) sh.	340 (4,19), 455 (2,51)	1490 s, 1460 w., 1450 m, 1435 s, 1378 s, 1360 sh, 1339 s

A comparison of the IR spectra of fixed amino forms Va and VIa (X = O, R = CH_3) with the spectra of fixed imino forms IIIa and IVa (X = O, R = CH_3) revealed differences over a wide range of frequencies, particularly at 1400-1700 cm^{-1}. The spectra of amino forms Va and VIa (X = O, R = CH_3) are the spectra of typical amides [8, 9]. The bands of stretching vibrations of the carbonyl groups in them lie at 1638-1695 cm^{-1}, depending on the electronic effects of substituent R of the acyl residue. The vibrations of the endocyclic C=N bond interact significantly with the vibrations of the rings and may participate in several bands at 1400-1500 cm^{-1}. In the N-methyl derivatives (IIIa-c and IVa-c) of iminothiazolines and iminobenzothiazolines the frequencies of the stretching vibrations of the CO and C=N groups are decreased as a result of the mutual conjugation of these groups. We assign the bands of medium intensity at 1590-1650 cm^{-1} to CO groups and the band at 1550-1580 cm^{-1}, as well as the relatively intense band at 1470-1500 cm^{-1}, to C=N groups. In the investigated region of the spectrum the amino and imino forms also differ with respect to the frequencies of the deformation vibrations of methyl groups (1380-1470 cm^{-1}), as well as with respect to ring vibrations (1300-1600 cm^{-1}) [2] (Table 2).

It should be noted that the identification of tautomers on the basis of a comparison of their IR spectra with the spectra of fixed forms requires great caution, since replacement of the hydrogen atoms of the NH group by methyl substituents may lead to a significant change in the spectra and masking of the 1550-1590 cm^{-1} region by deformation vibrations of the NH group. Thus the regions of stretching vibrations of carbonyl groups and the 1470-1500 cm^{-1} range can be regarded as diagnostic (Table 2).

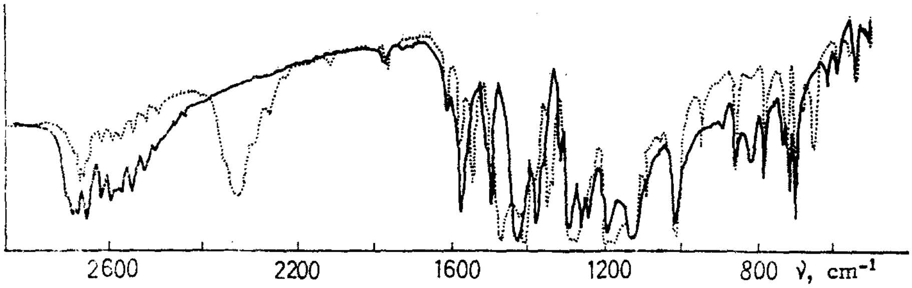


Fig. 1. IR spectra of 2-(trifluoroacetylimino)thiazoline (continuous line) and 3-deutero-2-(trifluoroacetylimino)-thiazoline (dotted line).

TABLE 4. Quantum-Chemical Calculations of the Amino Tautomers of 2-Acyl(thioacyl)aminothiazoles and the Imino Tautomers of 2-Acyl(thioacyl)thiazoles

R	X	E_{tot}, kcal/mole	E_{bond}, kcal/mole	μ, D	E_{tot}, kcal/mole	E_{bond}, kcal/mole	μ, D
		Amino tautomers			Imino tautomers		
CH_3	O	−58109,06	4340,25	3,725	−58091,75	4322,95	4,253
CH_3	S	−53409,97	4233,58	3,731	−53399,98	4223,57	5,084
CF_8	O	−108915,19	4470,99	3,724	−108909,00	4464,77	6,353
CF_3	S	−104217,50	4365,55	4,389	−104211,63	4359,69	7,328

In the IR spectra of acetyl derivatives Ia and IIa we observe ν_{CO} bands at 1700 and 1708 cm^{-1}, respectively (Table 2), and the absence of intense absorption at 1470-1500 cm^{-1}. In addition, the spectrum of IIa in the low-frequency region coincides significantly with the spectrum of fixed amino form VIa. The combination of these data once again confirms the previously expressed opinion that acetyl derivatives Ia and IIa exist in the amino form.

On the other hand, in the case of trifluoroacetyl derivatives Ib and IIb a comparison with the spectra of fixed forms IIIb and IVb provides evidence in favor of their existence in the imino form. Thus bands at 1640 and 1520 cm^{-1}, which correspond to the bands at 1620 and 1500 cm^{-1} for fixed imino form IIIb, are observed in the spectrum of Ib (Table 2). Similarly, the spectrum of IIb is similar to the spectrum of fixed imino model IVb in both the low-frequency region and at 1635 (1650 for IVb) and 1475 cm^{-1} (1470 cm^{-1} for IVb).

On the basis of the positions of the bands of stretching vibrations of carbonyl groups in the spectra of benzoyl derivatives Ic and IIc and the absence of intense absorption at 1470-1500 cm^{-1} it may be concluded that they exist in the solid state in the amino form. However, the spectra of these compounds (particularly 2-aminobenzothiazole derivative IIc) are appreciably complicated because of superimposition of the ring vibrations at ~1600 cm^{-1}.

The analysis of the tautomerism in the series of thioacyl derivatives VII-XI is complicated significantly by the difficulty in identification of the band of stretching vibrations of the C=S group. The smaller (than for the carbonyl function) force constant of the C=S bond, its facile polarizability, and conjugation with other bonds are the reason that the C=S band can be found over a wide range of frequencies (600-1200 cm^{-1}) [10]. In the indicated "fingerprint" region this band may undergo additional deformation or be overlapped by bands of vibrations of other types. The liability of the electronic structure and interaction of the vibrations lead to significant complication of the IR spectra of the thioamides. The indicated strong interaction of vibrations can be demonstrated graphically by the substantial change in the frequencies of vibrations in the spectrum of 2-trifluoroacetylaminothiazole VIIb as compared with the spectrum of its N-deuterated analog (Fig. 1).

A comparison of the IR spectra of fixed amino forms XIa,c with the spectra of fixed imino forms Xa,c makes it possible to reveal a number of differences; however, it does not give such expressive and distinctive criteria as in the case of the oxygen analogs. The imino forms are characterized by more intense absorption at 1460-1500 cm^{-1} and ~1400 cm^{-1}. However, the deformation vibrations of methyl groups and ring vibrations also lie in this region. Also characteristic for thioacyl derivatives of 2-aminothiazole is the band at 1560 cm^{-1}, which, in analogy with the oxygen analogs, can be assigned to vibrations of the C=N bond. For the analysis of the tautomerism of the thioamides we used the 1370-1600 cm^{-1} range, taking into account the fact that bands of vibrations of NH and SCN fragments also lie in it.

The absorption that is characteristic for fixed forms IXa and Xa is absent in the spectra of thioacetyl derivatives VIIa and VIIIa (X = S, R = CH_3), i.e., they exist in the amino form and are typical secondary thioamides; this is confirmed by the existence of a group of thioamide bands at 1590, 1331, and 1180 cm^{-1} for VIIa [10] and at 1570, 1330, and 1160 cm^{-1} for benzo analog VIIIa (Table 3).

As in the case of the oxygen compounds, trifluoroacetamides VIIb and VIIIb (X = S, R = CF_3), according to the IR spectra, exist in imino form B. Thus the spectrum of VIIb is characterized by the presence of bands at 1570, 1498, 1430, and 1379 cm^{-1} that are sensitive to deuteration (Fig. 1) (Table 3). The band at 1570 cm^{-1} is ascribed to deformation vibrations of an NH group, while the remaining bands are characteristic for fixed imino form IXb. Also typical are the presence of a band at 1560 cm^{-1} and the similarity in the spectra of the investigated VIIb and model IXb samples in the low-frequency region. A similar pattern is observed when one compares the spectra of benzo analogs VIIIb and Xb (Table 3).

An analysis of the IR spectra of the thiobenzoyl derivatives (VIIc and VIIIc) of 2-aminothiazole and 2-aminobenzothiazole indicates that they exist in amino form A. In the case of VIIc the thioamide I and II bands lie at 1560 and 1350 cm^{-1}, respectively, as compared with 1560 and 1330 cm^{-1} for benzo analog VIIIc (Table 3).

Thus the spectral investigations show that electronic factors are the deciding factors in the existence of the investigated compounds in amino or imino forms both in solutions and in the solid state.

Quantum-chemical calculations that we performed by the CNDO/2 method with the original parametrization [11] for 2-acetyl(thioacetyl)- and 2-trifluoroacetyl(trifluorothioacetyl)-aminothiazoles constitute a confirmation of the peculiarities of amine-imine tautomerism in acyl and thioacyl derivatives of 2-aminothiazole. In the calculations we used the standard geometrical parameters for the thiazole ring [12] and the amido and thioamido groups [13]. The total energies of the bonds and the dipole moments of the isolated molecules were calculated.

The total energy is the sum of the electronic energy and the energy of interaction of the nuclei of the atoms that enter into the composition of a given system:

$$E_{\text{tot}} = E_{\text{elect}} + \sum_{A<B}\sum \frac{z_A z_B}{R_{AB}}$$

The bond energy is the difference between the total energy of the system and the electronic energy of the atoms:

$$E_{\text{bond}} = -E_{\text{tot}} + \sum E_{e,A}$$

The results of the calculations are presented in Table 4.

The difference between the total energies of the imino and amino forms was taken as the stabilization energy.

$$\Delta E = (E_{\text{tot}})_{\text{imine}} - (E_{\text{tot}})_{\text{amine}}$$

The stabilization energies obtained indicate the dominant role of the amino tautomers; the stability of this form depends to a great extent on the substituents. For acetyl derivatives of 2-aminothiazole ΔE = 17.31 kcal/mole, as compared with 6.2 kcal/mole for trifluoroacetyl derivatives. In the case of thioacetyl derivatives of 2-aminothiazole ΔE = 10.0 kcal/mole, as compared with 5.9 kcal/mole for the trifluoroacetyl derivatives.

In these theoretical calculations we did not take into account the effect of the solvent, which may completely change the state of the tautomeric equilibrium. It is known that the stabilization energy of tautomers depends on their dipole moments. It is apparent from the results obtained that the imino forms will be more polar and, consequently, stabilized to a greater extent by the solvent. Taking the effect of the solvent and the E value for 2-acetylaminothiazole it may be asserted that the amino form should be dominant for it; this is in agreement with the spectral data.

EXPERIMENTAL

Compounds Ia-c—IVa-c and Va were obtained by the methods in [4, 14]. The UV spectra of solutions in methanol and cyclohexane were recorded with Specord UV-vis and Specord M-40 spectrophotometers. The IR spectra of suspensions in mineral oil and hexachlorobutadiene were recorded with a Pye-Unicam 1100S spectrometer. The quantum-chemical calculations were made with an RIAD-42 computer.

2-Methyltrifluoroacetylaminothiazole (Vb) and 2-Methyltrifluoroacetylaminobenzothiazole (VIb). A 12.6 g (0.6 mole) sample of trifluoroacetic acid anhydride was added dropwise to a stirred and water-cooled mixture of 0.6 mole of 2-methylaminothiazole or 2-methylaminobenzothiazole, 0.6 mole of pyridine, and 30 ml of dry THF, after which the mixture was heated on a water bath for 30 min. It was then poured into a mixture of water and ice, and the precipitated crystals were removed by filtration. An oil that began to solidify was liberated in the case of Vb. Compound Vb was obtained in 34% yield and had mp 71-72°C (from petroleum ether). Found, %: C 34.7, H 2.9. $C_6H_5F_3N_2OS$. Calculated, %: C 34.3, H 2.4. Compound VIb was obtained in 77% yield and had mp 163-164°C (from heptane). Found, %: C 46.5, H 2.9 $C_{10}H_7F_3N_2OS$. Calculated, %: C 46.1, H 2.7.

2-Methylbenzoylaminothiazole (Vc) and 2-Methylbenzoylaminobenzothiazole (VIc). A thoroughly sealed flask containing a mixture of 0.02 mole of 2-methylaminothiazole or 2-methylaminobenzothiazole, 0.1 mole of NaOH, 40 ml of water, and 0.03 mole of benzoyl chloride was shaken until the odor of the latter had vanished, after which the mixture was allowed to stand overnight. The precipitated crystals were removed by filtration, washed with water, and air dried. Compound Vc was obtained in 90% yield and had mp 65-66.5°C (from petroleum ether). Found, %: C 60.9, H 5.0. $C_{11}H_{10}N_2OS$. Calculated, %: C 60.5, H 4.6. Compound VIc was obtained in 94% yield and had mp 115-116°C (from petroleum ether). Found, %: C 67.5, H 4.7, S 12.1. $C_{15}H_{12}N_2OS$. Calculated, %: C 67.1, H 4.5, S 11.9.

Thioacyl Derivatives VIIa-c—Xa-c and XIa,c. General Method. A mixture of 0.01 mole of the corresponding acyl derivative, 0.011 mole of P_2S_5, and 100 ml of dioxane was heated on a boiling-water bath with monitoring of the course of the reaction by TLC on Silufol. At the end of the reaction the mixture was poured into water, and the aqueous mixture was extracted with chloroform or ethyl acetate. The organic layer was washed several times with water and dried with Na_2SO_4. The solvent was removed by distillation in vacuo, and the residue was chromatographed with a column packed with silica gel by elution with benzene—ethyl acetate (4:1) (elution with benzene was used in the case of Xa,c). The yields, constants, and results of elementary analysis for the thioamides are presented in Table 1.

Attention! All operations must be carried out in a fume hood because of the very unpleasant odor of the sulfur derivatives.

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CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

14* NATURE OF THE ELECTRONIC SPECTRA OF SYMMETRICAL POLYMETHINE DYES OF THE THIAZOLO[3,4-b][1,2,4]TRIAZINE SERIES

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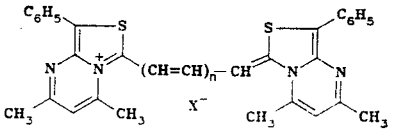
Symmetrical mono-, tri-, and pentamethinecyanine dyes with a thiazolo[3,4-b][1,2,4]triazine ring were synthesized. The electron-density distributions in the dye molecules in the ground and first and second excited states were obtained by quantum-chemical calculations. It was established that the first two electron transitions are localized on the same atoms and that charge transfer to the triazine fragment of the molecule is realized in the case of excitation. The degree of participation of the heterocyclic ring in the first electron transition, which is responsible for the color of the dye, decreases with lengthening of the polymethine chain.

Narrow high-intensity bands due to the first $\pi-\pi^*$ electron transition are observed in the visible part of the absorption spectra of most polymethine dyes [2]. This transition is localized primarily on the atoms of the polymethine chain, where the maximum change in the electron density occurs during primary excitation. A second shorter-wave band is most often due to $\pi-\pi^*$ transitions in the terminal heterocyclic residues and is observed in the UV part of the spectrum. A bathochromic shift (~100 nm) of the long-wave absorption band is observed with lengthening of the polymethine chain of symmetrical cyanines by one vinylene group [3], while the position of the short-wave band is virtually unchanged. However, in an investigation of the spectral characteristics of polymethine dyes – thiazolo[3,4-*a*]pyrimidine derivatives Ia-c – it was established [4] that both absorption bands of solutions of such compounds are observed in the visible part of the spectrum; with an increase in the length of the chain both bands are shifted to the red part of the spectrum: the long-wave band to a greater extent, and the short-wave band to a smaller extent (Table 1). In this connection it seemed of interest to study the interrelationship between the chemical structure and spectral characteristics of similar dyes with other terminal heteroresidues.



Ia-c
a n=0, b n=1, c n=2

The previously synthesized 6-methylthio-substituted thiazolotriazines of the II type [6] can be used in the synthesis of merocyanines or unsymmetrical monomethinecyanines. The corresponding 6-methylthiazolotriazines are necessary for the synthesis of symmetrical dyes; the former can be obtained by conversion of the active alkylthio group of quaternary salts

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*See [1] for communication 13.

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