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TAUTOMERISM OF 2-ARYLAMINO- AND 2-BENZYLAMINOTHIAZOLINE

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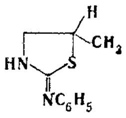
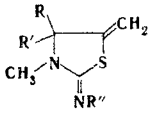
It was established by means of the IR, UV, and PMR spectra that 2-arylamino-4,4-dialkyl-5-methylenethiazolines have the 2-aryliminothiazolidine structure in the crystalline state and in solutions, whereas the 2-benzylamino derivatives can exist in both the amino and imino forms.

The problem of the structure of 2-aminothiazolines has been discussed repeatedly [1, 2]. It has been shown that 2-alkylaminothiazolines exist in the amino form, while 2-acylamino derivatives exist in the iminothiazolidine form. The data on the tautomerism of 2-arylaminothiazolines are contradictory. Thus Ramsh and co-authors have proved the existence of 2-phenylamino-4-thiazolidone in the form of a mixture of two tautomeric species [3], whereas an imino structure is assigned to this compound in [4].

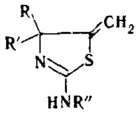
The possibility of obtaining thiazolidines with a fixed imino structure (IIa-IXa) enabled us to investigate the effect of an N-aryl substituent on the amine—imine equilibrium. We investigated IIb-IXb (Table 1), which were obtained by the method in [5].



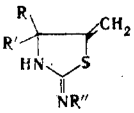
I



IIa–IXa



IIb-IXb
A



IIb-IXb
B

The structures of IIb-IXb were determined by spectral methods.

IR Spectra

We investigated only the intense absorption bands in the 1500-1700 cm^{-1} region (Table 2). As a rule, the spectra of the investigated compounds in the crystalline state (in KBr) in this region contain three intense bands at 1590, 1610-1620, and 1640-1670 cm^{-1} due to the stretching vibrations of the methylene group, the phenyl ring, and the C=N bond [6]. To assign the absorption of the methylene bond and the phenyl ring we made an analysis of the spectra of I and II. Compounds IIa, b (R = R' = CH_3, R" = C_2H_5) [5] do not contain a phenyl ring, and we assigned the absorption at 1610 cm^{-1} to the absorption of the methylene bond. Compound I [7] does not contain a methylene bond, and its spectrum does not contain a band at 1610 cm^{-1}; we therefore assigned the band at 1590 cm^{-1} to the absorption of the phenyl ring. The intensity of the absorption band at 1610 cm^{-1} is lower than the intensities of

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*Deceased.

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TABLE 1. 2-Aminothiazoline Derivatives

Compound	R'	R"	mp, °G;* bp, °C (mm)	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
IIIa	CH_3	$CH_2C_6H_5$	140 (2)	68,1	7,6	10,4	$C_{14}H_{18}N_2S$	68,3	7,3	11,3	83
IIIb-B	CH_3	$CH_2C_6H_5$	70	67,3	6,7	12,1	$C_{13}H_{16}N_2S$	67,2	6,9	12,1	91
IIIb-A	CH_3	$CH_2C_6H_5$	82	66,8	6,7	—	$C_{13}H_{16}N_2S$	67,2	6,9	12,1	60
IVa	C_2H_5	$CH_2C_6H_5$	145 (2)	69,1	7,7	10,1	$C_{15}H_{20}N_2S$	69,2	7,6	10,7	79
IVb-A	C_2H_5	$CH_2C_6H_5$	93	67,7	6,8	11,1	$C_{14}H_{18}N_2S$	68,3	7,3	11,4	78
IVb-B	C_2H_5	$CH_2C_6H_5$	83	—	—	11,0	$C_{14}H_{18}N_2S$	68,3	7,3	11,4	80
Vb-A	$(CH_2)_5$†	$CH_2C_6H_5$	102—103	70,9	8,1	10,9	$C_{16}H_{20}N_2S$	70,6	7,4	10,3	97
VIa	CH_3	C_6H_5	70	67,1	6,8	12,1	$C_{13}H_{16}N_2S$	67,2	6,9	12,1	73
VIIa	C_2H_5	C_6H_5	55	69,0	7,7	11,9	$C_{14}H_{18}N_2S$	68,3	7,3	11,4	81
VIIIa	C_2H_5	$p\text{-}CH_3C_6H_4$	Oil	69,1	7,8	10,4	$C_{15}H_{20}N_2S$	69,2	7,7	10,8	85
VIIIb-B	C_2H_5	$p\text{-}CH_3C_6H_4$	100	68,3	7,4	11,6	$C_{14}H_{18}N_2S$	68,3	7,3	11,4	98
IXa	C_2H_5	$p\text{-}ClC_6H_4$	60	59,7	6,1	10,6	$C_{14}H_{17}ClN_2S$	59,7	7,7	9,9	96
IXb-B	C_2H_5	$p\text{-}ClC_6H_4$	100	58,7	5,7	10,4	$C_{13}H_{15}ClN_2S$	58,8	5,6	10,5	95

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*The compounds were recrystallized: IIIb-B and VIIIb from heptane, VIIa from hexane, IVb-B and Vb-A from hexane—benzene, and IXa and IXb from heptane—benzene. Compound VIIIa was purified by chromatography on Al_2O_3 (elution with benzene).

†In the case of Vb-A, R + R' = $(CH_2)_5$, whereas R = CH_3 in the remaining compounds.

TABLE 2. IR and UV Spectra of Thiazolines

Compound	IR spectra, ν, cm^{-1}			UV spectra, λ_{max}, nm (log ε)		
	phenyl ring C=C	$C{=}CH_2$	C=N			
I	1590	—	1640			
IIa	—	1610 m	1650 vs			
IIb-A	—	1610 m	1565 vs			
IIIa	1620 vs		1650 vs	225 (3,30)		
IIIb-B	1600—1620 vs br			208 (3,29)		
IIIb-A	1590 s	1630 m	1560	204 (3,27)*	228 (2,98)	269 (2,44)
IVa	1615 vs		1645 s	227 (3,42)	—	—
IVb-A	1605 vs		1575 m	204 (3,40)	228 (3,20)	269 (3,10)
IVb-B	1600—1620 vs br			205 (3,29)	—	—
VIa	1590	1610 m	1640 vs	204 (3,27)	238 (3,11)	
VIb-B	1590	1620 m	1670 vs	203 (3,07)	256 (3,00)	
VIIa	1590 s	1610 m	1640 vs	206 (3,60)	240 (3,20)	
VIIb-B	1590 s	1620 m	1670 vs	206 (3,26)	236 (3,08)	
VIIIa	1590 s	1620 m	1640 vs	202 (3,54)	236 (3,36)	
VIIIb-B	1605 s		1650 vs	205 (3,38)	235 (3,28)	
IXa	1585 m	1615 m	1640 m	202 (3,51)	236 (3,34)	
IXb-B	1590 m	1620 s	1650	203 (3,46)	263 (3,42)	

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*This is the UV spectrum of a solution of IIIb-A in cyclohexane.

the other two bands, and this also confirms the legitimacy of the assignment made. In the case of the N-benzyl and N-tolyl derivatives the frequency of the absorption of the phenyl ring is increased to 1605-1620 cm^{-1} (IIIa, b, IVa, b, and VIIIb) and is superimposed on the frequency of the methylene bond. Only two bands — 1605-1620 and 1640-1670 cm^{-1} — are observed in the investigated region for these compounds (Table 2). We assigned the intense absorption band at 1640-1670 cm^{-1} to the vibrations of the C=N bond, since it is present in the spectra of compounds that do not contain a $C{=}CH_2$ group (I) or phenyl rings (IIa, b). The assignment of the tautomeric forms was made from the change in the position of this band on passing from the investigated compounds to model compounds. Thus the C=N frequency increases from 1565 to 1650 cm^{-1} on passing from 2-ethylaminothiazoline (IIb), for which an amino structure (IIb-A) was previously proved [1], to the fixed imino form (IIa); in this case the intensity of the band increases considerably. A similar change in the absorption of the C=N bond is also observed for N-benzyl derivatives. In the case of a model compound with an imino structure (IVa) the stretching vibrations of the exocyclic C=N group are observed at 1645 cm^{-1}. Isomers with higher melting points (IIIb, with mp 82°C, and IVb, with mp 93°C) and decreased frequencies of absorption of the C=N bond (1560 and 1575 cm^{-1}, respectively) and low-melting isomers (IIIb, with mp 70°C, and IVb, with mp 83°C) with higher

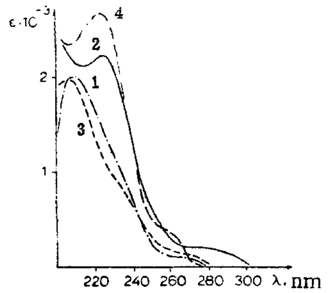

Fig. 1

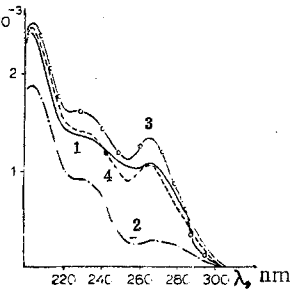

Fig. 2

Fig. 1. UV spectra of iminothiazolidines in alcohol: 1) 2-benzylimino-4,4-dimethyl-5-methylenethiazolidine (IIIb-B); 2) 2-benzylimino-3,4,4-trimethyl-5-methylenethiazolidine (IIIa); 3) 2-benzylimino-4-methyl-4-ethyl-5-methylenethiazolidine (IVb-B); 4) 2-benzylimino-3,4-dimethyl-4-ethyl-5-methylenethiazolidine (IVa).

Fig. 2. UV spectra of aminothiazolines in alcohol: 1) 2-benzylamino-4,4-dimethyl-5-methylenethiazoline (IIIb-A); 2) IIIb-A in cyclohexane, 3) 2-benzylamino-4-methyl-4-ethyl-5-methylenethiazoline (IVb-A); 4) 2-benzylamino-4,4-pentamethylene-5-methylenethiazoline (Vb-A).

$\nu_{C=N}$ frequencies (Tables 1 and 2) were isolated for IIIb and IVb with unfixed tautomeric forms. These changes in the frequencies of the C=N bond can be explained by the amino structure of the former (IIIb-A and IVb-A) and the imino structure of the latter (IIIb-B and IVb-B). A similar increase in the frequency of the absorption of the C=N bond on passing from the amino to the imino compounds is also observed in the case of N-ethylaminothiazoline (IIa, b).

Vibrations of an exocyclic C=N bond are observed at 1640 cm^{-1} in the IR spectra of N-aryliminothiazolidines (VIa-IXa). In the case of VIb-IXb the frequency of the absorption of the C=N bond is not only not decreased as in the case of benzyl derivatives but is even shifted 10-30 cm^{-1} to the high-frequency region with retention of the absorption intensity. This sort of behavior in the absorption of the C=N bond can be explained by the imino structure of VIb-IXb (VIb-B-IXb-B).

UV Spectra

To determine the tautomeric forms we also made a comparative analysis of the absorption curves of the investigated compounds (Table 2). The absorption spectra of VIb-IXb are similar to the spectra of the model aryliminothiazolidines (VIa-IXa) — in both cases the curves have two absorption maxima: 235-263 and 202-206 nm (Table 2). The similarity in the spectra of the model and investigated compounds confirms the imino structure of the N-aryl derivatives (VIb—B-IXb—B). A different picture is observed for the benzyl derivatives of 2-aminothiazoline (III and IV). Iminothiazolidines IIIa and IVa, as well as IIIb-B (mp 70°C) and IVb-B (mp 83°C), have one absorption maximum, while the absorption curves of IIIb-A (mp 82°C) and IVb-A (mp 93°C) have three maxima — 204, 228, and 269 nm. These data confirm the imino structure of the former and the amino structure of the latter (Figs. 1 and 2).

PMR Spectra

Because of the different positions of the C=N bond in the amino and imino forms one can expect differences in the anisotropic effect of this bond on the chemical shifts of the protons of the α-carbon atoms of the alkyl groups attached to the exocyclic nitrogen atom. However, the introduction of alkyl substituents at N_3 in the iminothiazolidines in all cases shifts the signals of the geminal 4-CH_3 groups to strong field, although this shift is not accompanied by a change in the tautomeric forms (e.g., VIa,b-IXa,b). For this reason, the assignment of the amino and imino forms from the change in the chemical shifts of the 4-CH_3 protons is not always reliable [8].

TABLE 3. PMR Spectra of Thiazoline Derivatives [δ, ppm (J, Hz)]*

Compound	Solvent	R′	R	NH or $3-CH_3$	R″		$=\mathrm{C}\langle^{\mathrm{H}}_{\mathrm{H}}$
					C_2H_5, CH_3, $-CH_2-$	C_6H_5	
IIa	CCl_4	1,27	1,27	2,67	1,09 t 3,01 q	—	5,05 d (2), 4,92 d (2)
IIb-A	CCl_4	1,25	1,25	5,50	1,12 t 3,18 q		4,97
IIIa	CCl_4	1,23	1,23	2,80	4,24	7,15 m	4,90 d (2), 5,02 d (2)
IIIb-B	CCl_4	1,28	1,28	5,57	4,27	7,16; 7,24	4,95
IIIb-B	CS_2	1,20	1,20	6,35	4,18	7,20	4,90
IIIb-A	CS_2	1,24	1,24	5,50	4,72 d (4)	7,15; 7,22	4,95
IVa	CCl_4	1,34	0,78 t 1,66 q	2,80	4,22	7,15	5,00
IVb-A	CCl_4	1,32	0,72 t 1,50 q	5,73	4,87 d (4)	7,35; 7,40	5,00 d (2), 5,15 d (2)
IVb-A	CS_2	1,23	0,65 t 1,48 q	5,52	4,73 d (4)	7,12; 7,20	4,93 d (2), 5,05 d (2)
IVb-B	CS_2	1,17	0,70 t 1,54 q	5,78	4,24	7,13; 7,22	4,95 m
Vb-A	$CDCl_3$	1,57 m	2,10 m	6,48	4,82	7,27 m	4,93
VIa	CCl_4	1,35	1,35	2,87	—	7,00 m	4,85 d (2), 5,00 d (2)
VIb-B	CCl_4	1,30	1,30	9,00	—	6,93 m	4,86 m
VIIa	CCl_4	1,36	0,84 t 1,67 q	2,91	—	7,07 m	5,02
VIIb-B	CS_2	1,24	0,82 t 1,48 q	8,9	—	7,10 m	4,95
VIIIa	CCl_4	1,35	0,80 t 1,68 q	—	2,24	6,58 d (9); 6,88 d (9)	4,94
VIIIb-B	CCl_4	1,24	0,87 t 1,57 q	9,08	2,32	6,7 d (9); 7,13 d (9)	5,07 d (2), 5,32 d (2)
IXa	CCl_4	1,33	0,80 t 1,65 q	2,88	—	6,67 d (9); 7,15 d (9)	4,95
IXb-B	DMSO	1,33	0,78 t 1,64 q	9,25	—	7,18 d (9); 7,55 d (9)	5,12; 5,2

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*The positions of the centers are indicated for the split signals (d is doublet, t is triplet, q is quartet, and m is multiplet). When $J/\Delta\delta \leqslant 0.27$, the δ values were determined from the rules for AX systems, whereas when $J/\Delta\delta \geqslant 0.34$, the spectral parameters were determined from the rules for an AB system [9].

The use of PMR spectroscopy was successful during an examination of the N-benzyl derivatives of thiazolines (III-V). The presence of N-methylene groups makes it possible to not only observe the presence of amino or imino compounds but also makes it possible to give a quantitative estimate of the ratios of the isomers in the mixtures. In the case of model N-ethyl- and N-benzyliminothiazolidines (IIa-IVa) the $-CH_2N-$ group resonates at stronger field than the same group does in the compounds with an amino structure (IIb-IVb, Table 3). The different structures of the benzyl derivatives (IIIb-A, IIIb-B, IVb-A, and IVb-B) that were detected from the UV spectra were confirmed by a study of the PMR spectra. In the case of IIIb-B and IVb-B the chemical shifts of the N-methylene group (4.24-4.27 ppm) coincide with the δ value of the analogous group of the model iminothiazolidine (4.2 ppm for IIIa and IVa), whereas in the case of IIIb-A and IVb-A, which, according to the UV spectra, have an amino structure, a 0.65 ppm shift of the methylene signal to weak field as compared with the same signal of the imino compounds (IIIa, IIIb-B, and IVb-B) is observed. Such a distinct difference in the chemical shifts of the NCH_2 groups of the amino and imino forms made it possible to detect the existence of benzyl derivatives in the form of mixtures of isomers in the crude reaction products. The percentages of the isomers differed depending on the reaction conditions. The highest percentages of amino isomers (IIIb-A and IVb-A up to 75%) were obtained when the reaction was carried out in benzene at 0°C with subsequent standing at room temperature. When the reaction was carried out without a solvent and cooling of the reagents, IIIb was isolated only in the imino form (IIIb-B, 100%), and IVb-B was isolated containing up to 60% of the imino form. The isolated isomers are stable, and this made it possible to obtain their physical and physicochemical characteristics (Tables 1-3).

A difference in the chemical shifts of not only the N-methylene groups was observed during a study of the PMR spectra of mixtures of the isomers. Despite the fluctuation of the shifts of the protons of the NH groups in the endocyclic and exocyclic positions (their

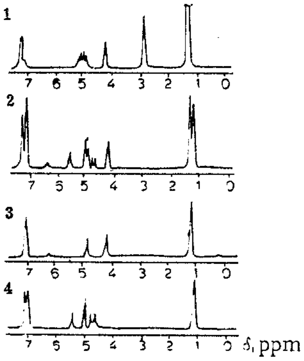

Fig. 3. PMR spectra in carbon disulfide: 1) IIIa; 2) IIIb-A + IIIb-B; 3) IIIb-B; 4) IIIb-A.

dependence on the concentration and the solvent), the protons of the imino groups resonate, as a rule, at weaker field as compared with the protons of the amino groups. The signals of the geminal CH_3 groups of a mixture of isomers (IIIb-A, IIIb-B) in CCl_4 solution are recorded in the form of one singlet, while splitting of the 4-$(CH_3)_2$ singlet into two signals is observed in CS_2 solution; in this case the chemical shift of the amino form (IIIb-A) is shifted to weak field as compared with the singlet of the imino form (IIIb-B, Fig. 3).

It may be concluded from the above discussion that the aminothiazoline form (A) is stable in the case of the N-alkyl derivatives, whereas the iminothiazolidine form (B) is stable in the case of N-aryl derivatives. The N-benzyl compounds are stable both in the amino form (A) and in the imino form (B).

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of alcohol solutions were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of 10% solutions of the compounds in CCl_4 and CS_2 were obtained at room temperature with a Carl Zeiss ZKR-60 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

2-Benzylamino-4,4-dimethyl-5-methylenethiazoline (IIIb-A). A 2.98-g (0.02 mole) sample of benzyl isothiocyanate was added dropwise with stirring at 0°C to a solution of 1.66 g (0.02 mole) of 3-amino-3-methyl-1-butyne in 10 ml of benzene, after which the mixture was allowed to stand at room temperature for 1 h. The solvent was then removed by distillation (at 40-50°C and 30-50 mm), and the reaction product was purified by two crystallizations from heptane. The yield of product with mp 82°C was 2.8 g (60%).

Compound IVb-A. This compound was obtained by a similar method (Table 1).

2-Benzylimino-4,4-dimethyl-5-methylenethiazolidine (IIIb-B). A 2.98-g (0.02 mole) sample of benzyl isothiocyanate was added without cooling to 1.66 g (0.02 mole) of 3-amino-3-methyl-1-butyne. The reaction was exothermic, and the temperature rose to 40°C. After 30 min, the product was purified by crystallization from heptane to give 4.25 g (91%) of a substance with mp 70°C.

Compound IVb-B. This compound was obtained by a similar method.

2-Benzylimino-3,4,4-trimethyl-5-methylenethiazolidine (IIIa). A 2.98-g (0.02 mole) sample of benzyl isothiocyanate was added with stirring and cooling (to 0°C) to a solution of 1.94 g (0.02 mole) of 3-methylamino-3-methyl-1-butyne in 10 ml of petroleum ether, and the mixture was maintained at 0°C for 30 min and at 22°C for 1 h. The solvent was removed by distillation, and the product was distilled at 140°C (2 mm). The yield was 4.09 g (83%).

Compounds Va,b-IXa,b (Table 1) were similarly obtained, and I was obtained by the method in [7]. Compounds IIa,b ($R = R' = CH_3$, $R'' = C_2H_5$), VIb ($R = R' = CH_3$, $R'' = C_6H_5$), and VIIb ($R = CH_3$, $R' = C_2H_5$, $R'' = C_6H_5$) were previously described [5].

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PRODUCTS OF THE REACTION OF THE BASES OF CYANINE DYES WITH SILVER IONS

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and G. P. Sennikov

UDC 668.819.45:547.789.6'829+543.253

The reaction of 2-[3'-(3"-alkyl-2"-benzothiazolylidene)propenyl]benzothiazole, -pyridine, and -quinoline with silver ions in various solvents was studied. In anhydrous methanol, chloroform, and acetonitrile the indicated bases of cyanine dyes reduce silver ions with the liberation of acid in an amount equivalent to the silver metal formed, and the bases are partially converted to the salts. Similar reaction products are obtained by electrolysis of solutions of them in methanol and acetonitrile at the potentials established for them. It was established that the unstable salts of their N-oxides are formed in the presence of water in the reaction of the bases with silver salts; the products of the transformations of the N-oxides were identified.

The dependence of the color of the bases of symmetrical cyanine on their structure was studied in [1]. In the case of bases of unsymmetrical monomethylidynecyanines [2] and in a number of bases of unsymmetrical carbocyanines [3] it has been established that of the two isomeric compounds, the more deeply colored compound is that in which the alkyl group is bonded to the nitrogen atom of the more basic heterocyclic residue. A relationship between the structures of the bases of the cyanines and their pK_a values and dipole moments was revealed in the latter study. It has been shown [4] that bases of carbocyanines with a dihydrobenzo-1,5-thiazepine residue form complexes with silver salts.

In the patent literature it is mentioned that the bases of cyanine dyes, particularly those that contain a nitrile group in the α position of the polymethylidyne chain, are sensitizers of silver halide emulsions (e.g., see [5, 6]). In this connection it seemed of interest to study the reaction of these compounds with silver ions, since it may occur in photographic layers.

In the present research we studied the reaction with silver ions in various solvents of bases of carbocyanines of the general structure

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