3. J. Wislicenus, Annalen, 192, 106 (1878).
4. S. V. Amosova, A. N. Nikol'skaya, N. K. Gusarova, N. A. Belogorlova, E. V. Shevchenko, and N. A. Chernysheva, Summaries of Papers Presented at the All-Union Conference on the Chemistry of Unsaturated Compounds [in Russian], Part 1, Kazan (1986).
5. B. A. Trofimov, N. K. Gusarova, S. V. Amosova, and G. G. Efremova, USSR Author's Certificate No. 541,354, Byull. Izobret., No. 32, 236 (1979).
6. B. A. Trofimov and S. V. Amosova, Divinyl Sulfide and Its Derivatives [in Russian], Nauka, Novosibirsk (1983).
7. E. Breitmaier and W. Voelter, ^{13}C NMR Spectroscopy, Verlag Chemie, Weinheim—New York (1978), pp. 80, 182, 198.
8. B. A. Trofimov, N. K. Gusarova, G. G. Efremova, A. N. Nikol'skaya, and S. V. Amosova, Zh. Org. Khim., 17, 1984 (1981).
9. D. D. Lebedev, T. V. Korobkina, and I. V. Vereshchinskii, Zavod. Lab., 32, 530 (1966).
10. V. I. Skorobogatova, Yu. M. Faershtein, and G. A. Kravchenko, Zh. Anal. Khim., 23, 1876 (1968).
11. Dictionary of Organic Compounds [Russian translation], Vol. 3, Izd. Inostr. Lit., Moscow (1949).

CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

15.* DYES BASED ON THIAZOLO[3,4-b][1,2,4]TRIAZINE

Yu. P. Kovtun, N. N. Romanov,
and A. D. Kachkovskii

UDC 547.789'832.1.07:541.
27'651:543.422.6

Unsymmetrical tri- and pentamethinecyanine dyes with a thiazolo[3,4-b][1,2,4]triazine ring were synthesized. The electron-density distribution on the atoms of the dyes in the ground, first, and second excited states was calculated by a quantum-chemical method. It was established that the first two electron transitions are localized on the same atoms of the dyes and that charge transfer to the triazine fragment of the molecule is realized upon 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 an increase in the length of the polymethine chain.

It was recently shown [1] in an investigation of the absorption spectra of a series of symmetrical dyes — thiazolo[3,4-b][1,2,4]triazine derivatives — that significant interaction of the first two π-electron transitions localized on the atoms of the polymethine chain and the terminal heteroresidues is observed in their molecules. However, in this case the symmetrical dyes of this type must be strictly regarded as cyanines that contain a system of three interacting chromophones. The analysis of the spectra of such dyes is not always unequivocal [2].

For a detailed and more accurate elucidation of the nature of the absorption bands of cyanines that contain a thiazolotriazine ring it seemed of interest to synthesize the corresponding unsymmetrical dyes with different chain lengths and to investigate the absorption spectra of solutions of them.

For this, tri- and pentamethinecyanines Vb, c were obtained by the reaction of acetanilidovinyl derivative I [1] with 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate (II) and ethoxybutadienyl derivative III with 6-methyl-2,3,8-triphenylthiazolo[3,4-b][1,2,4]triazinium perchlorate (IV). (See first scheme on following page.)

In Table 1 the spectral characteristics of the synthesized compounds are compared with the analogous data for monomethinecyanine Va [3]. It is apparent from Fig. 1 that two bands

---

*See [1] for Communication 14.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 985-991, July, 1988. Original article submitted January 12, 1987; revision submitted June 22, 1987.

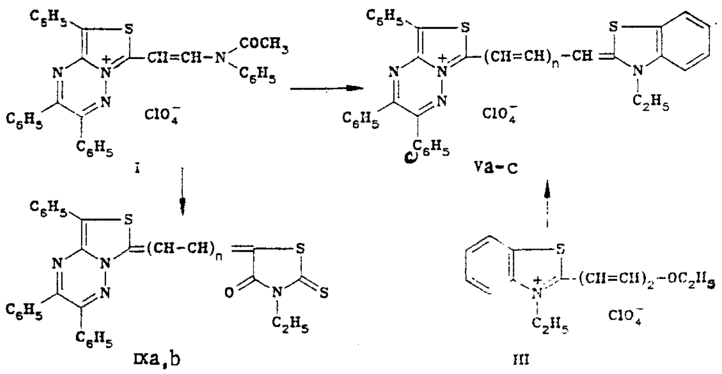
0009-3122/88/2407-0812$12.50

TABLE 1. Spectral Characteristics of Unsymmetrical Dyes of the Thiazolo[3,4-b][1,2,4]triazine Series

Compound	λ_{max}, nm (log ε)	$\varepsilon_1/\varepsilon_2$*	Vinylene shift, nm		$\lambda_1-\lambda_2$
			$\Delta\lambda_1$	$\Delta\lambda_2$	
Va	454 (4,68), 555 (3,84)	0,14	—	—	101
Vb	566 (4,76), 650 (4,37)	0,42	95	112	84
Vc	645 (4,69), 750 (4,33)	0,43	100	79	105
VIIa	478 (4,47), 545 (4,34)	0,74	—	—	67
VIIb	560 (4,27), 678 (4,71)	2,75	113	82	118
VIIc	~600†, 790 (4,91)	~4	112	~40	~190
IXa	458 (4,54), 645 (3,60)	0,11	—	—	187
IXb	539 (4,67), 675 (3,82)	0,14	30	81	136
Xa	470 (4,00), 556 (4,34)	2,19	—	—	86
Xb	514 (4,02), 668 (4,62)	3,98	112	44	154

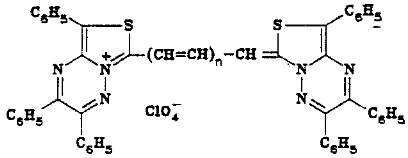
*Ratio of the intensities of the long-wave and short-wave bands.

†The band appears in the form of an inflection.



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

are observed in the visible part of the absorption spectra of solutions of the synthesized compounds. The short-wave band is more intense and narrower for all of the dyes, and the maximum of the long-wave band is characterized less distinctly, while for ordinary cyanine dyes, on the other hand, the long-wave band is narrow and falls precipitously to the long-wave side, while the short-wave band lies in the UV part of the spectrum. When the polymethine chain is lengthened by one vinylene group (carbocyanine Vb), the ratio of the intensities of the bands remains virtually constant. However, in the series of symmetrical dyes VIa-c [1] similar structural changes lead to a regular increase in the intensity of primarily the long-wave band, which becomes more intense than the short-wave band for dicarbocyanine VIc.



VIa-c

The data obtained undoubtedly constitute evidence, on the one hand, that this unusual form of the absorption bands of the investigated dyes is due to the specific characteristics of precisely the thiazolotriazine ring and, on the other, for the considerably greater degree of participation of the atoms of the latter in the electron transition responsible for the long-wave absorption bands as compared with the analogous contribution in the series of symmetrical dyes VIa-c. The second conclusion also follows from the theory of the chromaticity of organic compounds for dyes that contain a system of three interacting chromophores [4].

The fact that not only the long-wave band but also the short-wave band is shifted bathochromically with an increase in the length of the polymethine chain is extremely specific for the absorption spectra of solutions of the synthesized compounds Va-c; the vinylene shift

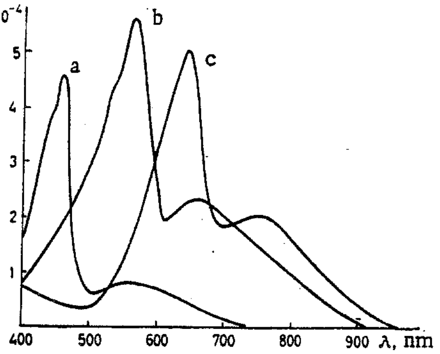
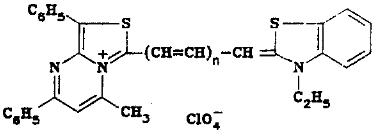


Fig. 1. Absorption spectra of dyes Va-c.

of both bands is approximately equal in magnitude to the vinylene shift of the first absorption band of typical polymethine dyes [5].

A comparison of the absorption maxima of Va-c with the analogous characteristics of their structural analogs – the corresponding dyes VIIa-c, which are thiazolo[3,4-a]pyrimidine derivatives [6] – shows that isovalent replacement of the carbon atom of the heterocyclic residue by a nitrogen atom leads to additional intensification of the interaction of the electron transitions localized in the polymethine chains and the terminal heterocyclic residues of the thiazoloazinium ion, particularly in the case of dyes with a short chain.



VII a-c

In fact, it is apparent that the magnitude of the vinylene shift for the long-wave band decreases somewhat (maximally for the first vinylene shift) on passing from thiazolopyrimidine derivatives to the corresponding dyes based on thiazolotriazine, while for the short-wave band (which is considerably more intense) its magnitude increases substantially. Let us note that the maximum of the long-wave band is shifted bathochromically (10 nm) only for monomethinecyanine Va, whereas the maximum of the short-wave band is shifted hypsochromically (24 nm) as compared with the maxima of the corresponding thiazolopyrimidine analog VIIa. Here we most likely observe significant separation of the bands as a consequence of the high degree of interaction of the chromophores.

The deep color of monomethinecyanine Va, disregarding the possibility of interaction and interference of the electron transitions in its molecule, seems particularly unusual, since, according to the results of quantum-chemical analysis, the transition from thiazolo[3,4-a]-pyrimidine to thiazolo[3,4-b]triazines is accompanied by a decrease only in the effective length of the ring in the dyes (L_{TP} = 6.89 and L_{TT} = 5.69, respectively); however, it does not lead to a change in the electron-donor character (Φ_0 = 65°) – a parameter that characterizes the basic properties of the terminal groups in the dyes [7, 8]. Thus it follows from the theoretical evaluation of the heteroresidues that monotypic dyes Va-c and VIIa-c in pairs should be similar in electronic asymmetry; the latter are more deeply colored.

With an increase in the length of the polymethine chain the location of the bands becomes the opposite: in carbocyanine Vb and dicarbocyanine Vc the long-wave bands (in agreement with the results of calculations of the effective length of the thiazolotriazine ring in the dyes) are shifted hypsochromically (28 and 40 nm), while the short-wave bands are shifted bathochromically (6 and 45 nm, respectively).

In a quantum-chemical investigation of the nature of the first absorption bands in series of symmetrical dyes based on thiazolotriazine it was established [1] that distinct localization of the electron transitions with respect to the individual fragments of the molecule cannot be accomplished. However, in the case of unsymmetrical dyes of the thiazolopyrimidine series VII it was shown [6] that the first π–π^* electron transition, which is responsible for the long-wave absorption band, is, as in the case of ordinary polymethine dyes, localized on the carbon atoms of the polymethine chain, while the second is due to transfer of electron

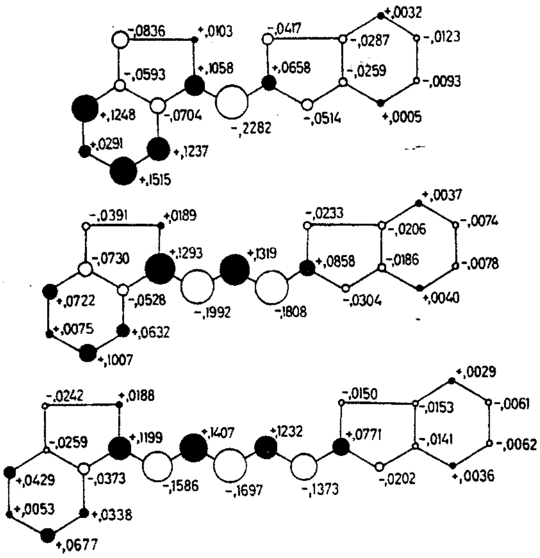
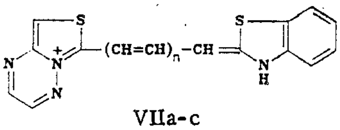


Fig. 2. Change in the electron density on the atoms of model dyes VIIIa-c on passing from the ground to the first excited state.

density from the atoms of the polymethine chain in the odd-numbered positions and the carbon atom in the 8 position of the heteroring to the pyrimidine fragment of the molecule.

Since this approach proved to be informative for ascertaining the nature and localization of the electron transitions responsible for the color of dyes of this type, we made a similar calculation [within the Pariser—Parr—Pople (PPP) approximation] of the distribution of the electron density on the atoms of the cations of model compounds VIIIa-c in the ground, first, and second excited states.



VIIa-c

The results of the calculation are presented in Table 2. Diagrams of the change in the π-electron density on the atoms when the molecules of the cations of dyes VIII pass from the ground singlet (S_0) to the first (S_1) (Fig. 2) and second (S_2) (Fig. 3) excited singlet states are also presented.

It is apparent from the data presented on the change in the charge upon excitation that the molecules of the cations of unsymmetrical dyes VIII differ substantially from symmetrical VI [1] and especially from thiazolopyrimidine derivatives VII [6]. In fact, in the series of thiacyanines VIIIa-c the first transition involves not only the atoms of the polymethine chromophore, in which the greatest redistribution of electron density occurs, but also — to a significant degree — the atoms of the triazine fragment of the heterocyclic residue. Let us note that the participation of these atoms in the transition is maximal in the case of monomethinecyanine VIIIa and even exceeds the analogous change in the second excitation, which in this case is localized on the atoms of the polymethine chain.

It must be noted that redistribution of the electron density on the same atoms of the polymethine chain is observed not only in the first transition but also in the second transition. In this case only for the nodal nitrogen atom of the thiazolotriazine ring does its overcharging in the first and second excitation occur.

In the transition of the monomethinecyanine molecule VIIIa to the first excited state the greatest increase in the negative charge occurs on the doubly coordinated nitrogen atoms and the carbon atom in the 3 position. The electron density is transferred primarily from the α-carbon atom of the polymethine chain and, to a lesser extent, from the carbon atom in the 8 position of the thiazolotriazine ring. Charge transfer to the carbon atoms of the chain increases regularly with an increase in the length of the polymethine chain, while charge transfer to the atoms of the triazine fragment decreases. Secondary excitation for the same

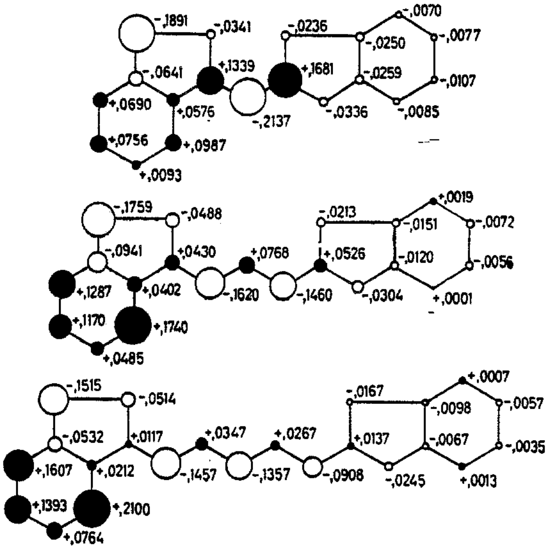
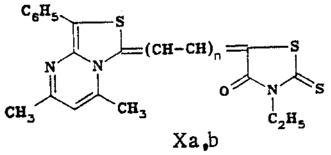


Fig. 3. Change in the electron density on the atoms of model dyes VIIIa-c on passing from the ground state to the second excited state.

monomethinecyanine leads to significant transfer of negative charge from the α-carbon atom and, to a greater extent, from the carbon atom in the 8 position to the carbon atoms of the Kuhn chain and, to a lesser extent, to the thiazolotriazine atoms. The magnitude of this transfer with an increase in the length of the polymethine chain changes in reverse order as compared with the first transition: The participation of the atoms of the triazine fragment increases, while the participation of the polymethine chain decreases.

From a comparison of the data obtained with similar calculations for the cations of model dyes – thiazolopyrimidine derivatives VII – it may be concluded that the introduction into the molecule of the terminal heteroring of an additional electron-acceptor nitrogen atom leads to appreciable participation of the atoms of this ring in the first and not only in the second π–π* electron transition; the indicated effect is even greater than in series of corresponding symmetrical dyes based on thiazolotriazine. This explains the large shifts of the maximum of the short-wave band with an increase in the length of the polymethine chain, as well as the significant interaction of the transitions (particularly in the case of dyes with a short chain, for which the two transitions are close in energy). It may evidently be asserted that, with respect to its nature, the π–π* electron transition in the monomethinecyanine molecules based on thiazolo[3,4-b][1,2,4]triazine that is responsible for the long-wave band most closely resembles the transitions in the starting heterocycles rather than those in the cyanine dyes.

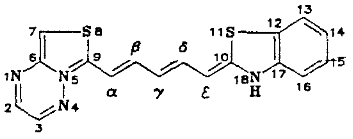
It might have been assumed that when the benzothiazole ring in the dyes is replaced by a 3-ethylrhodanine residue, which has high Brucker basicity [9], transfer of the electron density from the polymethine chain to the triazine fragment of the molecule and, consequently, participation of the atoms of the latter in the first electron transition would be considerably more pronounced, as a consequence of which the effect of the interaction of the chromophores is manifested more distinctly.



Xa,b

In fact, when one compares the spectral characteristics of nullomethinemerocyanine IXa [3] and its analog Xa [10] it is apparent that, as in the case of the corresponding monomethinecyanines, aza substitution leads to separation of the absorption bands; the degree of this interaction in the case of merocyanines is substantially greater. For the same reason, lengthening of the polymethine chain (transition to dimethinemerocyanine IXb) leads to a slight shift (30 nm) of the long-wave band and to the normal shift (81 nm) of the short-wave band.

TABLE 2. Distribution of the Electron Density on the Atoms of Model Dyes VIIIa-c in the Ground (P^0) and First (P^*) and Second (P^{**}) Excited States



Atom No.	VIIIa			VIIIb			VIIIc		
	P^0	P^*	P^{**}	P^0	P^*	P^{**}	P^0	P^*	P^{**}
N-1	1,1288	1,2536	1,1976	1,1309	1,2031	1,2596	1,1320	1,1749	1,2927
C-2	0,8659	0,8950	0,9415	0,8672	0,8747	0,9842	0,8684	0,8677	1,0017
C-3	0,8497	1,0012	0,8590	0,8553	0,9560	0,9038	0,8590	0,9267	0,9354
N-4	1,2030	1,3267	1,3019	1,1969	1,2601	1,3709	1,1943	1,2281	1,4043
N-5	1,5063	1,4359	1,5639	1,5031	1,4503	1,5433	1,5039	1,4666	1,5251
C-6	1,0362	0,9769	0,9721	1,0357	0,9984	0,9773	1,0358	1,0099	0,9826
C-7	1,0463	0,9627	0,8572	1,0485	1,0094	0,8726	1,0519	1,0277	0,9004
S-8	1,7372	1,7455	1,7031	1,7333	1,7522	1,6845	1,7348	1,7536	1,6834
C-9	0,9704	1,0762	1,1043	0,9723	1,1016	1,0153	0,9751	1,0950	0,9868
C-α	1,2147	0,8865	1,0010	1,1495	0,9503	0,9875	1,1381	0,9795	0,9924
C-β	—	—	—	0,9067	1,0386	0,9835	0,9072	1,0479	0,9419
C-γ	—	—	—	1,1661	0,9853	1,0201	1,0979	0,9282	0,9692
C-δ	—	—	—	—	—	—	0,9000	1,0232	0,9268
C-ε	—	—	—	—	—	—	1,1576	1,0203	1,0668
C-10	0,9228	0,9886	1,0909	0,9176	1,0034	0,9702	0,9198	0,9969	0,9337
S-11	1,8038	1,7621	1,7802	1,7995	1,7762	1,7782	1,8001	1,7851	1,7834
C-12	1,0448	1,0144	1,0198	1,0426	1,0020	1,0275	1,0420	1,0267	1,0322
C-13	1,0006	1,0038	1,0075	1,0020	1,0057	1,0039	1,0028	1,0057	1,0035
C-14	0,9784	0,9661	0,9707	0,9817	0,9743	0,9741	0,9842	0,9781	0,9785
C-15	0,9762	0,9669	0,9655	0,9790	0,9712	0,9734	0,9808	0,9746	0,9773
C-16	1,0272	1,0277	1,0357	1,0285	1,0325	1,0286	1,0298	1,0334	1,0285
C-17	1,0604	1,0345	1,0579	1,0393	1,0459	1,0345	1,0563	1,0422	1,0496
N-18	1,6271	1,5757	1,5935	1,6258	1,5954	1,5954	1,6280	1,6080	1,6037

TABLE 3. Characteristics of the Synthesized Compounds

Compound	mp, ℃	Found, %		Empirical formula	Calc., %		Yield, %
		Cl (N)	S		Cl (N)	S	
IVb	187—188	5,1	9,6	$C_{35}H_{27}ClN_4O_4S_2$	5,3	9,6	47
IVc	190—192	4,9	9,6	$C_{37}H_{29}ClN_4O_4S_2$	5,1	9,3	55
IXb	248—249	(10,0)	17,3	$C_{30}H_{22}ClN_4OS_3$	(10,2)	17,5	36

Let us note that the first vinylene shifts for the corresponding thiazolopyrimidine derivatives Xa, b [10, 11] or benzothiazole derivatives [5] are somewhat greater (112 and 96 nm, respectively).

EXPERIMENTAL

The electronic spectra of solutions of the compounds in acetonitrile were obtained with an SF-8 spectrophotometer. The quantum-chemical calculations were made within the Pariser—Parr—Pople (PPP) approximation as in [12] with the same set of parameters. Only the singly excited configurations were taken into account for the calculation of the excited states. The properties of the synthesized compounds are presented in Table 3.

2,3,8-Triphenyl-6-[3-(3-ethyl-2(3H)-benzothiazolylidene)-1-propenyl]thiazolo[3,4-b][1,2,4]triazine Perchlorate (Vb). A solution of 0.62 g (1 mmole) of acetanilidovinyl derivative I and 0.35 g (1 mmole) of salt II in 10 ml of pyridine was refluxed for 3 min, after which the mixture was cooled to room temperature and treated with 50 ml of water. The dye was removed by filtration and crystallized from acetic acid. The yield was 0.31 g.

2,3,8-Triphenyl-6-[5-(3-ethyl-2(3H)-benzothiazolylidene)-1,3-pentadienyl]thiazolo[3,4-b][1,2,4]triazinium Perchlorate (Vc). A 0.1-g (1 mmole) sample of triethylamine was added to a heated (to the boiling point) solution of 0.48 g (1 mmole) of perchlorate IV and 0.37 g (1 mmole) of ethoxybutadienyl derivative III in 5 ml of acetic anhydride, and the mixture was cooled rapidly to room temperature. The dye was precipitated with 25 ml of isopropyl alcohol and washed with ethanol. The yield was 0.38 g.

2,3,8-Triphenyl-6-[2-(4-oxo-2-thioxo-3-ethylthiazolidin-5-ylidene)ethylidene]thiazolo-[3,4-b][1,2,4]triazine (IXb). A solution of 0.16 g (1 mmole) of 3-ethylrhodanine and 0.62 g (1 mmole) of acetanilidovinyl derivative I in 5 ml of pyridine was refluxed for 5 min, after which the dye was precipitated with 25 ml of water and crystallized from acetic acid–DMF (5:1). The yield was 0.20 g.

LITERATURE CITED

1. Yu. P. Kovtun, A. D. Kachkovskii, and N. N. Romanov, Khim. Geterotsikl. Soedin., No. 3, 418 (1988).
2. A. I. Kiprianov, Usp. Khim., 40, 1283 (1971).
3. A. D. Kachkovskii, Yu. P. Kovtun, and N. N. Romanov; Khim. Geterotsikl. Soedin., No. 12, 1693 (1986).
4. A. I. Kiprianov, Introduction to the Electronic Theory of Organic Compounds [in Russian], Naukova Dumka, Kiev (1975), p. 142.
5. T. H. James, Theory of the Photographic Process [Russian translation], Khimiya, Leningrad (1980).
6. G. G. Dyadyusha (Dyaduasha), A. I. Tolmachev, N. N. Romanov, E. K. Mikitenko, and A. D. Kachkovskii (Kachkovski), Dyes Pigments, No. 4, 179 (1983).
7. G. G. Dyadyusha and A. D. Kachkovskii, Ukr. Khim. Zh., 43, 948 (1978).
8. G. G. Dyadyusha and A. D. Kachkovskii, Teor. Éksp. Khim., 17, 393 (1981).
9. G. Platt, J. Chem. Phys., 25, 80 (1956).
10. E. K. Mikitenko, A. D. Kachkovskii, and N. N. Romanov, Khim. Geterotsikl. Soedin., No. 5, 634 (1982).
11. E. K. Mikitenko and N. N. Romanov, Ukr. Khim. Zh., 48, 1071 (1983).
12. G. G. Dyadyusha, N. N. Romanov, A. D. Kachkovskii, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 12, 1618 (1980).

RING-CHAIN TRANSFORMATIONS OF SUBSTITUTED 2-IMINO-1,3-THIAZINOAZOLES

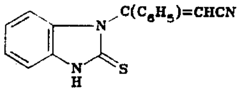
N. D. Abramova, L. V. Andriyankova,
T. V. Kashik, S. M. Ponomareva,
N. N. Chipanina, A. V. Afonin,
and E. S. Domnina

UDC 547.783.9'785.5'869.
07'792:543.257.1

The ring-chain transformations of substituted 2-imino-1,3-thiazinoazoles in DMSO under the influence of tetraalkylammonium or alkali metal hydroxides were studied by acid–base potentiometric titration and PMR, IR, and UV spectroscopy.

The alkaline opening of the ring of imino-1,3-benzothiazines is known [1, 2]. Irreversible opening of the thiazine ring also occurs in 2-imino-4-phenyl-1,3-thiazino[2,3-b]benzimidazole (I) and leads to the formation of 1-(1-phenyl-2-cyanovinyl)benzimidazole-2-thione (II) [3]. At the same time, the reversible opening of the thiazine ring has been described: When 2,3-dihydro-2-imino-4H-1,3-benzothiazine-4-one is heated in 10% NaOH, the heteroring is opened to give the disodium salt of o-mercaptobenzoylcyanamide [1], while neutralization of a solution of this salt is accompanied by reversible intramolecular cyclization.

In this connection we studied the ring–chain transformations of 2-imino-1,3-thiazinoazoles I and III-V. Thione II was used as a model compound with an open structure [3].



II

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 992-994, July, 1988. Original article submitted February 5, 1987; revision submitted September 23, 1987.