2-Methyl-4,4-diphenyl-4H-3,1-benzoxazine (XVI). A mixture of 1.57 g (5 mmole) compound XV in 10 ml acetic acid was refluxed until the precipitate had disappeared. The reaction mixture was then cooled, diluted with water, and the resulting precipitate was recrystallized from alcohol. Yield 1.2 g (76%). The physical chemical properties of benzoxazine XVI corresponded to those reported in [13].

LITERATURE CITED

1. C. Paal and E. Landenheimer, Chem. Ber., 25, 2967 (1892).
2. W. Holly and C. J. Cope, J. Am. Chem. Soc., 66, 1875 (1944).
3. F. Eiden, K. Schnadel, and H. Wiedemann, Arch. Pharm., 307, 204 (1974).
4. F. Eiden, K. Schnadel, and H. Wiedemann, ibid., 308, 622 (1975).
5. F. Kienzle, Tetrahedron Lett., 24, 2213 (1983).
6. R. Rihard Schmidt and B. Reitzke, Chem. Ber., 116, 2115 (1983).
7. W. Stewart Mayers and Homerk Spencer, U.S. Patent No. 4164407; RzhKh, 50437P (1980).
8. U.S. Patent No. 3678046; C07 d 87/14/Huber-Emden, Basel, Switzerland; Priority 29.04.69. Filed 27.04.70.
9. A. Montrup, K. Sehromm, E. Renth, W. Holfke, W. Gaida, I. Streller, and A. Fugner, British Patent No. 3026534; RzhKh 10147P.
10. E. V. Gromachevskaya, I. S. Arustamova, R. B. Valeev, B. A. Bazhenov, A. G. Sakhabutdinov, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 12, 1687 (1985).
11. A. H. Saeed and E. K. Fbraheem, Can. J. Spectr., 28, 169 (1983).
12. V. M. Potapov (ed.), Laboratory Course in Organic Chemistry, Moscow (1979), Vol. 2, p. 193.
13. A. Bayer and V. Williger, Chem. Ber., 37, 3191 (1904).

MESOIONIC COMPOUNDS WITH BRIDGING NITROGEN ATOMS.

14.* POLYMETHINE DYES CONTAINING A THIOZOLO[3,4-b][1,2,4]TRIAZINIUM OXIDE NUCLEUS

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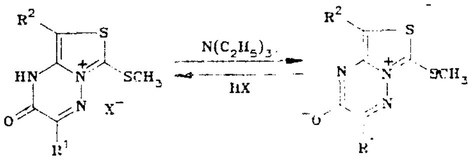
UDC 547.874'789.6:668.819.45

Monomethinecyanine and zeromethinemerocyanine dyes have been synthesized on the basis of mesoionic 6-methylthiothiazolo[3,4-b][1,2,4]triazinium-2-oxides. It was found that these newly synthesized compounds can exist both in mesoionic form and in salt form.

We have previously prepared 6-methylthiosubstituted thiazolo[3,4-b][1,2,4]triazines Ia-d and have investigated their conversion to mesoionic compounds IIa-d [2].



Ia-d IIa-d

I, IIa,c $R^1=CH_3$, b,d $R^1=C_6H_5$; a,b $R^2=H$, c,d $R^2=C_6H_5$

In order to be able to prepare polymethine dyes based on these derivatives of a novel heterocyclic system, it was of interest to us to examine the reaction of these compounds with nucleophilic intermediates, which are generally used for the synthesis of cyanines [3, p. 210, 269].

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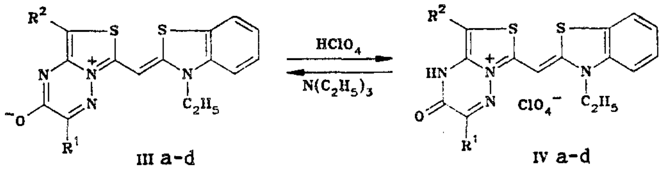
*For Communication No. 13, see Ref. [1].

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 848-851, June, 1988. Original article submitted December 17, 1986.

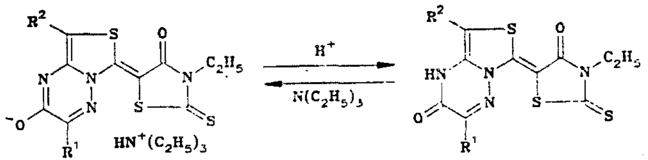
0009-3127/88/2406-0697$12.50

It was found that compounds I and II react readily both with quaternary salts formed from nitrogen heterocycles, which may contain an active methyl group, as well as with ketomethylene bases. Thus, for instance, reaction of thiazolotriazines Ic, d with 2-methyl-3-ethyl-benzothiazolium tosylate leads to the formation of the mesoionic monomethinecyanines IIIc, d.



III a-d IV a-d

In analogy with the behavior of the heterocyclic precursors IIc, d, dyes IIIc, d react readily with acids to give salt forms of the cyanines, IVc, d. Reaction with 3-ethylrhodanine gives merocyanine dyes, which separate from solution in the form of their triethylammonium salts, structures, Vc, d; acidification of their solutions yields the thiazolotriazinone derivatives VIc, d.



V a-d VI a-d

Further studies revealed that attempts to synthesize dyes IIIa, b and Va,b on the basis of thiazolotriazines Ia, b, which do not contain substituents in the 8-position, rather than compounds IIa, b, led to the isolation from the reaction mixtures of a product with an absorption maximum in the 700 nm region. As the reaction mixture was allowed to stand the amount of this precipitated product, which we were not able to characterize, increased rapidly. The corresponding dyes IVa, b, and VIa, b were precipitated upon acidification of the filtrates (from these reaction mixtures). We assume that the low stability of the mesoionic dyes IIIa, b and of the merocyanine anions Va, b is due to the occurrence of side reaction at the free nucleophilic site in these molecules, namely, the carbon atom in the 8-position, which leads predominantly to trinuclear dyes.

As can be seen from the spectral characteristics of these synthetic dyes, which are summarized in Table 1, the visible absorption spectra of solutions of these dyes contain two bands, whose positions and intensity ratios are determined to a large extent by the nature of the substituents in the thiazolotriazinium nucleus: replacement of a methyl group in the 3-position by a phenyl group, either in the mesoionic or salt form of the dyes, leads to a bathochromic shift of the long wavelength band (by 20-40 nm), and also to enhanced intensity of the short-wavelength band; introduction of a phenyl group in the 8-position produces a bathochromic shift in both the long- and short-wavelength bands, and also affects their intensities, but to a lesser degree. It should be noted that similar spectral patterns due to substituent effects are observed in the series of heterocyclic precursors I, II [2], which suggests an apparent similarity in the nature of the chromophoric effect (color) in the corresponding thiazolotriazines, thiazolotriazinium oxides, and dyes derived from them.

It is significant that in the transition from the dyes, to the thiazolotriazinone derivatives, to the corresponding oxides the color intensity of their solutions increase. These spectral effects are characteristic of dyes prepared on the basis of other mesoionic condensed heterocycles containing a thiazole ring, for example, imidazo[1,2-c]thiazolium-2-oxide [4]; also, in contrast to cations of conventional monomethinecyanine dyes, dyes IIIc, d exhibit negative solvatochromism. Thus, for example, in the case of solutions of compound IIId, a reduction in solvent polarity (in the transition from acetic acid solution to methanol, and further to acetonitrile and benzene) leads to a bathochromic shift of the long-wavelength absorption maximum [512, 544, 555, and 568 nm, respectively), while the short-wavelength band becomes broader and more structured. This type of solvatochromic behavior is characteristic of thiazoloazinium oxides [5, 6], as well as of dyes derived from them [7], and indicates that

TABLE 1. Spectral Characteristics of Synthetic Dyes

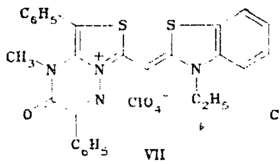
Compound	λ_{max}, nm (log ε)*	$\varepsilon_1/\varepsilon_2$*	λ_{max}, nm (log ε)**	$\varepsilon_1/\varepsilon_2$**
IIIc	422 (3,64), 531 (4,35)	1,20		
IIId	421 (4,17), 555 (4,38)	1,05	413 (4,33), 512 (4,30)	0,99
IVa			391 (4,15), 460 (4,38)	1,06
IVb			398 (4,15), 499 (4,24)	0,99
IVc			410 (4,10), 488 (4,42)	1,08
IVd			414 (4,32), 514 (4,31)	1,00
Vc	418 (3,89), 530 (4,39)	1,13		
Vd	430 (4,21), 570 (4,13)	0,98		
VIa	402, 490			
VIb	402, 528			
VIc	413 (4,01), 524 (4,24)	1,06	419 (4,36), 502 (4,13)	0,95
VId	420 (4,30), 555 (4,14)	0,96	425 (4,42), 550 (3,95)	0,87
VII	400 (4,31), 504 (4,40)	1,02	400 (4,27), 504 (4,36)	1,02
VIII	434 (4,45), 534 (4,19)	0,94	436, 532	
IX	440 (4,39), 570 (3,85)	0,88	437, 534	

*In CH_3CN.
**In CH_3COOH.

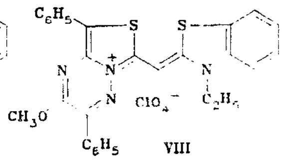
the long-wavelength absorption bands in these cyanines are associated with π-π^* electronic transitions, which are localized not on the atoms in the polymethine chain, but rather on the atoms in the mesoionic heterocyclic residue.

The overlap observed in the positions of the absorption maxima for solutions of the monomethinecyanines IVd and IIId in acetic acid solution demonstrates the ease of protonation of the latter even by a weak acid. On the other hand, in the case of molecules of the salt forms of monomethinecyanines IV and zeromethinecyanines VI, keto-enol tautomerism is possible, i.e., the existence of these forms and their mixtures is possible.

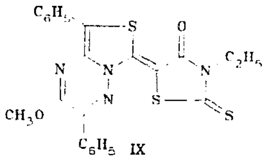
In order to clarify the effect of structure of the thiazolotriazine nucleus on the spectral properties of dyes prepared on the basis of isomeric methylation products of oxide IId, which were reported previously [2], we have synthesized the corresponding monomethinecyanines VII and VIII and merocyanine IX, in which one of the forms is fixed in the thiazolotriazine nucleus.



VII



VIII



IX

Based on their spectral data (Table 1), in analogy with conventional cyanine cations, and in contrast to mesoionic cyanines, the monomethine cyanines VII and VIII are not solvatochromic. In addition, in these dyes, which are derivatives of methoxy-substituted thiazolotriazine, the absorption bands have been displaced bathochromically relative to the analogous bands for O-unsubstituted monomethinecyanines VII and IVd (by 30 and 20 nm, respectively). On the basis of these results we conclude that in terms of their chemical structure type IV dyes are similar to monomethinecyanine VII, i.e., they exist in solution predominantly in the form of thiazolotriazinone derivatives; we also assume that since the spectral characteristics of the zeromethinecyanines VId and IX are significantly different, the thiazolotriazinone structure is also characteristic of this class of dyes as well.

EXPERIMENTAL

Electronic spectra were measured on an SF-8 spectrophotometer. The physical characteristics of the newly synthesized compounds are summarized in Table 2.

8-Phenyl-6-[(3-ethyl-2(3H)-benzothiazolylidene)methyl]thiazolo[3,4-b][1,2,4]triazinium-2-oxides (IIIc, d). A mixture of 1 mmole of the required benzenesulfonate Ic, d and 0.35 g (1 mmole) 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate in 50 ml alcohol was heated to boiling and 0.2 g (2 mmole) triethylamine was added. The dye was removed by filtration and recrystallized.

TABLE 2. Physical Characteristics of Newly Synthesized Compounds

Compound	mp, °C*	Found, %		Molecular formula	Calculated, %		Yield, %
		N (Cl)	S		N (Cl)	S	
IIIc	304—305	13,1	15,1	$C_{22}H_{18}N_4OS_2$	13,4	15,4	67
IIId	288—289	11,5	13,6	$C_{27}H_{20}N_4OS_2$	11,6	13,3	73
IVa	275—276	(8,2)	14,3	$C_{16}H_{15}ClN_4O_5S_2$	(8,0)	14,5	56
IVb	237—238	(7,2)	12,8	$C_{21}H_{17}ClN_4O_5S_2$	(7,0)	12,7	64
IVc	286—287	(6,9)	12,3	$C_{22}H_{19}ClN_4O_5S_2$	(6,8)	12,4	76
IVd	279—280	(6,2)	11,0	$C_{27}H_{21}ClN_4O_5S_2$	(6,3)	11,0	87
Vc	258—259	13,7	19,2	$C_{23}H_{29}N_5O_2S_3$	13,9	19,1	60
Vd	261—262	12,3	17,1	$C_{28}H_{31}N_5O_2S_3$	12,4	17,0	75
VIa	244—245	16,9	29,7	$C_{11}H_{10}N_4O_2S_3$	17,2	29,6	27
VIb	179—180	14,2	25,0	$C_{16}H_{12}N_4O_2S_3$	14,4	24,8	29
VIc	256—257	13,5	23,5	$C_{17}H_{14}N_4O_2S_3$	13,8	23,7	95
VId	270—271	12,1	20,7	$C_{22}H_{16}N_4O_2S_3$	12,1	20,7	88
VII	256—257	(5,8)	10,9	$C_{28}H_{23}ClN_4O_5S_2$	(6,0)	10,8	59
VIII	261—262	(6,0)	10,8	$C_{28}H_{23}ClN_4O_5S_2$	(6,0)	10,8	70
IX	273—274	11,8	20,3	$C_{23}H_{18}N_4O_2S_3$	11,7	20,1	63

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*Compounds IVa-c, VII, and VIII were recrystallized from a mixture of CH_3COOH—HCOOH (5:1); compounds IIIc, d from a mixture of alcohol—DMF (4:1); Vc, d from isopropyl alcohol.

1,2-Dihydro-2-oxo-6-[(3-ethyl-2(3H)-benzothiazolylidene)methyl]thiazolo[3,4-b][1,2,4]triazinium Perchlorates (IVa, b). A mixture of 1 mmole of the appropriate bromide Ia, b and 0.35 g (1 mmole) 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate in 50 ml alcohol was heated with stirring to 50°C and 0.1 g (1 mmole) triethylamine was added; the mixture was cooled rapidly to room temperature and filtered into a flask containing 1 ml of perchloric acid. The product was removed by filtration and recrystallized.

1,2-Dihydro-2-oxo-8-phenyl-6-[(3-ethyl-2(3H)-benzothiazolylidene)methyl]thiazolo[3,4-b]-[1,2,4]triazinium Perchlorates (IVc, d). The appropriate monomethinecyanine IIIc, d (1 mmole) was dissolved in 50 ml acetic acid and 1 ml of 57% perchloric acid was added. The product was filtered and recrystallized.

Triethylammonium-6-(2-thioxo-4-oxo-3-ethylthiazolidine-5-ylidene)-8-phenyl-6H-thiazolo[3,4-b][1,2,4]triazine-2-oxides (Vc, d). A mixture of 1 mmole of the appropriate benzenesulfonate Ic, d and 0.16 g 3-ethylrhodanine in 50 ml alcohol was heated to boiling and 0.2 g (2 mmole) triethylamine was added. The resulting dye which precipitated was filtered and recrystallized.

1,2-Dihydro-6-(2-thioxo-4-oxo-3-ethyl-thiazolidene-5-ylidene)-6H-thiazolo[3,4-b][1,2,4]-triazin-2-one (VIa, b). A mixture of 1 mmole of the required bromide Ia, b and 0.16 g 3-ethylrhodanine in 50 ml alcohol was heated at 50°C and 0.1 g (1 mmole) triethylamine was added; the mixture gas quickly cooled to room temperature and the solution was filtered into a flask containing 1 ml of hydrochloric acid. The dye was filtered and washed with hot alcohol.

Zeromethinecyanines VIc, d. Prepared by action of hydrochloric acid on alcohol solutions of dyes Vc, d.

1,2-Dihydro-1-methyl-2-oxo-3,8-diphenyl-6-[(3-ethyl-2(3H)-benzothiazolylidene)methyl]-thiazolo[3,4-b][1,2,4]triazinium Perchlorate (VII). A mixture of 0.35 g (1 mmole) 1,2-dihydro-1-methyl-2-oxo-6-methylthio-3,8-diphenylthiazolo[3,4-b][1,2,4]triazinium perchlorate and 0.35 g (1 mmole) 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate in 50 ml alcohol was heated to boiling and 0.1 g (1 mmole) triethylamine was added. The dye was filtered and recrystallized. Yield 0.35 g.

2-Methoxy-3,8-diphenyl-6-[(3-ethyl-2(3H)-benzothiazolylidene)methyl]-thiazolo[3,4-b][1,2,4]triazinium Perchlorate (VIII). A mixture of 0.35 g (1 mmole) 2-methoxy-3,8-diphenyl-6-methylthiothiazolo[3,4-b][1,2,4]triazinium perchlorate and 0.35 g (1 mmole) 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate in 50 ml alcohol was heated to boiling and 0.1 g (1 mmole) triethylamine was added. The dye was filtered and recyrstallized. Yield 0.42 g.

2-Methoxy-3,8-diphenyl-6-(2-thioxo-4-oxo-3-ethylthiazolidine-5-ylidene)-6H-thiazolo[3,4-b][1,2,4]triazine (IX). A mixture of 0.35 g (1 mmole) 2-methoxy-3,8-diphenyl-6-methylthiothiazolo[3,4-b][1,2,4]triazinium perchlorate and 0.16 g 3-ethylrhodanine in 50 ml alcohol was heated to boiling and 0.1 g (1 mmole) triethylamine was added. The dye was filtered and washed with hot alcohol. Yield 0.30 g.

LITERATURE CITED

1. E. K. Mikitenko and N. N. Romanov, Khim. Geterotsikl. Soedin., No. 4, 502 (1985).
2. Yu. P. Kovtun and N. N. Romanov, ibid., No. 11, 1497 (1985).
3. G. E. Fiken, Chemistry of Synthetic Dyes (K. Venkataraman, editor) [in Russian], Khimiya, Leningrad (1975), Vol. 1.
4. E. K. Mikitenko and N. N. Romanov, Khim. Geterotsikl. Soedin., No. 1, 36 (1984).
5. N. N. Romanov, K. V. Fedotov, A. A. Ishchenko, and A. I. Tolmachev, Ukr. Khim. Zh., 49, 857 (1983).
6. A. A. Ishchenko, A. D. Kachkovskii, N. N. Romanov, and N. N. Fedotov, ibid., 51, 987 (1985).
7. K. V. Fedotov and N. N. Romanov, Ukr. Khim. Zh., 52, 76 (1986).