of methylamine were added to 1.8 g (0.01 mole) of 2-imino-5-benzylidenethiazolidin-4-one (Ic) in 30 ml of ethanol, and the mixture was stirred at 60-70°C for 10-15 min until starting Ic dissolved completely. The IIk that precipitated after the reaction mixture was cooled was removed by filtration. Compounds II*l*-o were similarly obtained.

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MESOIONIC COMPOUNDS WITH A BRIDGED NITROGEN ATOM.

6.* POLYMETHINE DYES OF THE THIAZOLO[3,2-*a*]QUINOLINIUM 1-OXIDE SERIES

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Mesoionic compounds formed from (2-quinolylthio)acetic acids readily give polymethine dyes. The structures of the synthesized compounds were confirmed by data from the PMR spectra and the results of elementary analysis.

It has been assumed [2, 3] that the reaction of acetic anhydride with (4-methyl-2-quinolylthio)acetic acid (Ib) gives 5-methylthiazolo[3,2-*a*]quinolinium 1-oxide (IIb), which reacts with the intermediates used for the synthesis of cyanine dyes [for example, with 3-ethyl-2-(2-acetanilidovinyl)benzothiazolium iodide] to give compounds of the III type [4]. Products of the latter condensation with precisely this structure have been patented [5] as spectral sensitizers of silver halide emulsions. However, spectral characteristics of such dyes have not been presented in the literature, analytical data are not available for a number of compounds, and half a molecule of methanol has been assigned to the empirical formulas in some cases to obtain satisfactory analytical data [5].

We have established that the primary product obtained from acid Ib under the conditions indicated in the literature is not oxide IIb, as was previously assumed, but rather its acetyl derivative (IV); the latter itself also gives dyes, which up until now have been assumed to be derivatives of 2-unsubstituted thiazoloquinolinium 1-oxide. For example, a dye with the V structure is formed with 3-methyl-2-methylthiobenzothiazolium salts [7].

Further studies showed that the reaction of (2-quinolylthio)acetic acids Ia, b with a mixture of acetic anhydride and pyridine at room temperature gives the previously unknown thiazolo[3,2-*a*]quinolinium 1-oxides (IIa, b) [6]. The latter readily undergo reaction in

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*See [1] for Communication 5.

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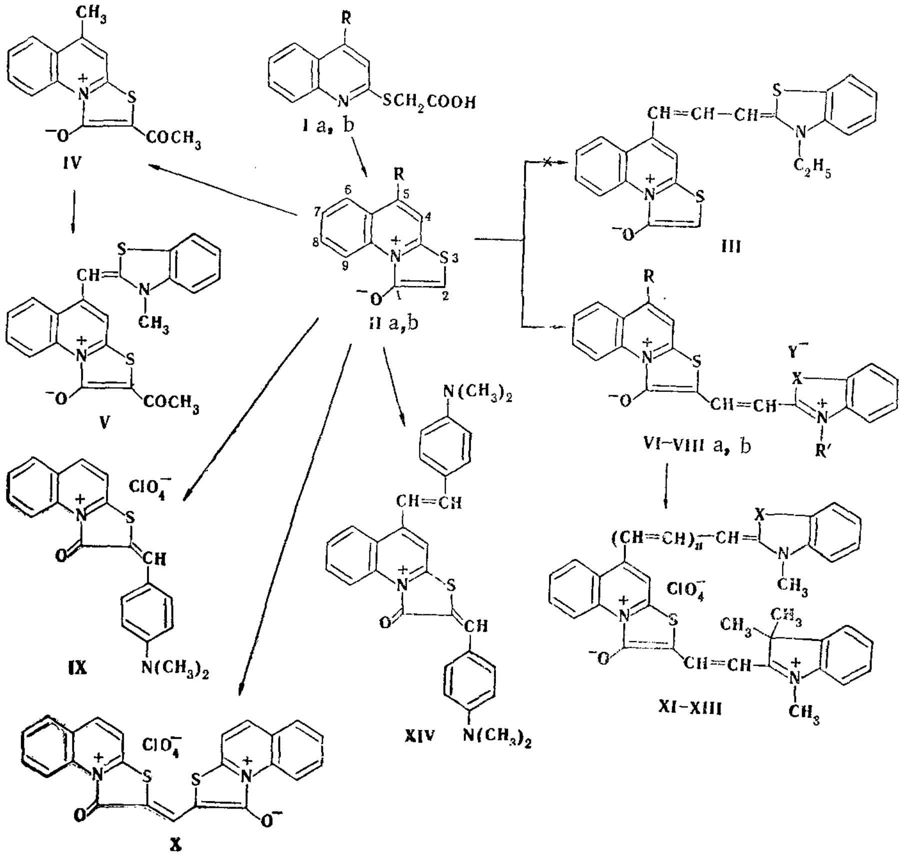
the 2 position with acetanilidovinyl derivatives of quaternary salts of nitrogen heterocycles to give dyes with VIa, b-VIIIa, b structures (Table 1). Benzylidene derivative IX was similarly obtained from oxide IIa and p-dimethylaminobenzaldehyde, while symmetrical dye X was obtained with ethyl orthoformate. The fact that the methyl group in the 5 position of thiazolo[3,2-*a*]quinolinium 1-oxide remains unaffected in these reactions is confirmed by the PMR spectra. In fact, the spectrum of a solution of dimethylidynemerocyanine VIIIb in trifluoroacetic acid contains singlets of protons of methyl groups with chemical shifts of 1.43 (6H), 2.51 (3H), and 3.53 ppm (3H), two doublets centered at 6.37 and 8.30 ppm (J = 15 Hz) related to the protons of the methylidyne groups of the polymethine chain, a multiplet of aromatic protons at 7.00-8.00 ppm (8H), and a multiplet centered at 9.73 ppm (1H), which can probably be assigned to the proton in the 9 position of the mesoionic fragment. The spin–spin coupling constant (15 Hz) indicates a trans orientation of the corresponding protons.



a R=H, b R=CH_3; VI X=O; VII, XI X=S; VIII, XII, XIII X=$C(CH_3)_2$; XI, XII n=0; XIII n=1; VI, VII R′=C_2H_5, Y=I; VIII R′=CH_3, Y=ClO_4

Symmetrical dye X, like its analog in the thiazolopyridinium oxide series, contains the chromophore system that is characteristic for oxanines, while VI-VIII contains the chromophore system that is characteristic for merocyanines. It is apparent from the spectral data presented in Table 1 that the introduction of a methyl group in the 5 position of the thiazoloquinolinium ring leads to a small increase in the intensity of the color of the corresponding dyes (VIb, VIIb, VIIIb). In contrast to dimethylidynemerocyanines that are thiazolopyridinium oxide derivatives, in the long-wave absorption bands of which two distinctly expressed maxima were observed [8], the long-wave bands of acetonitrile solutions of VI-VIII do not have a fine structure. The bands in the 400-nm region in the spectra of the dyes obtained are evidently due to the absorption of the thiazoloquinolinium fragments themselves. Dyes that contain thiazoloquinolinium oxide residues are somewhat more deeply colored than the analogous derivatives of the thiazolopyridinium oxide series (Table 1). This fact is in agreement with the greater effective length [9]* in dyes of the examined

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*The value characterizes the number of vinylene groups to which a given heteroresidue is equivalent in the sense of the effect on the absorption of light.

TABLE 1. Cyanine Dyes of the Thiazolo[3,2-*a*]quinolinium 1-Oxide Series

Compound	mp, °C*	λ_{max}, nm (log ε) in CH_3CN	Δλ†	Found, %		Empirical formula	Calc., %		Yield, %
				N	S		N	S	
VIa	230—232	390 (4,35), 563 (4,70)	18	5,8	6,4	$C_{22}H_{17}IN_2O_2S$	5,6	6,4	61
VIb	228—229	390 (4,37), 558 (4,75)	13	5,5	6,1	$C_{23}H_{19}IN_2O_2S$	5,4	6,2	95
VIIa	256—257	411 (4,17), 589 (4,81)	15	5,3	12,4	$C_{22}H_{17}IN_2OS_2$	5,4	12,4	62
VIIb	223—224	412 (4,12), 587 (4,77)	13	5,2	12,0	$C_{23}H_{19}IN_2OS_2$	5,3	12,1	70
VIIIa	255—256	400 (4,13), 592 (4,72)	16	5,9	6,8	$C_{24}H_{21}ClN_2O_5S$	5,8	6,6	93
VIIIb	253—254	403 (4,15), 588 (4,67)	12	5,7	6,4	$C_{25}H_{23}ClN_2O_5S$	5,6	6,4	80
IX	250—252	393 (4,13), 618 (4,67)	33	6,6	7,4	$C_{20}H_{17}ClN_2O_5S$	6,5	7,4	42
X	274—275	605 (4,65), 644 (4,82)	36	5,4	12,4	$C_{23}H_{13}ClN_2O_6S_2$	5,5	12,5	43
XI	273—274	430 (4,53), 477 (4,42), 660 (5,03)	—	6,4	9,7	$C_{33}H_{28}ClN_3O_5S_2$	6,5	9,9	83
XII	262—264	430 (4,40), 483 (4,42), 673 (4,83)	—	6,4	5,0	$C_{36}H_{34}ClN_3O_5S$	6,4	4,9	55
XIII	215—216	455 (4,55), 550 (4,48), 765 (5,22)	—	6,2	4,7	$C_{38}H_{36}ClN_3O_5S$	6,2	4,7	73
XIV	320—322	400 (4,38), 582 (4,87), 740 (5,01)	—	7,3	5,5	$C_{30}H_{28}ClN_3O_5S$	7,3	5,5	52

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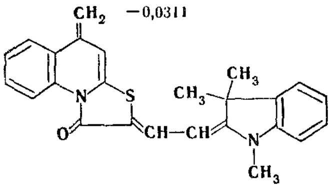
*The compounds were recrystallized: VIa, b, VIIa, VIIIa, and X-XII from $(CH_3CO)_2O$, VIIb, VIIIb, and XIII from CH_3COOH, and IX and XIV from CH_3CN.

†The shift of the absorption maximum on passing to the analogous derivatives of the thiazolo[3,2-*a*]pyridinium 3-oxide series.

heterocyclic system (5.60 and 5.40, respectively). Like their bicyclic analogs [8], the dimethylidynemerocyanines obtained display negative solvatochromism [10]. Thus the absorption maximum of dye VIIa is shifted from 602 to 580 nm on passing from a solution in dichloroethane to a solution in methanol. Under the same conditions the hypsochromic shift of the absorption maximum of a solution of the thiazolopyridinium analog of dye VI has a close value (19 nm), which is in agreement with a theoretical estimate [9] of the electron-donor character of the examined heterocyclic residues, which amounts to 29° for thiazoloquinolinium oxide and 27° for thiazolopyridinium oxide.

We found that, despite the relatively low value of the negative charge on the carbon atom (calculated as in [1]) of, for example, methylene base VIIIb', which is possibly formed from dye VIIIb by the action of triethylamine, the methyl group in the 5 position of the thiazoloquinolinium 1-oxide ring of dimethylidynemerocyanines VIb, VIIb, and VIIIb is quite active and reacts readily with the intermediates that are usually employed for the synthesis of cyanine dyes. For example, dyes XI-XIII were obtained from VIIIb. Similar products can also be synthesized directly from acid Ib by heating with suitable reagents under the conditions of the formation of a mesoionic ring. Styryl XIV was obtained with p-dimethylaminobenzaldehyde in acetic anhydride. The isolated dyes can be regarded as biscyanines constructed from fragments of mono- or trimethylidynecyanine dyes and dimethylidynemerocyanines. Three maxima are observed in the visible region of the absorption spectra of their solutions. As in the case of dyes VI-IX, the short-wave absorption band of these compounds is due to the substituted ring of thiazoloquinolinium 1-oxide; however, the other two, one of which is lower, and the other of which is higher than the corresponding "parent" dyes (for which V and VIII can be taken for dye XI) are due to interaction of the chromophores [11].



VIII b'

EXPERIMENTAL

The electronic spectra of solutions of the compounds in CH_3CN were measured with an SF-8 spectrophotometer. The PMR spectrum of a solution in CF_3COOH was recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the external standard.

2-(3-Ethylbenzoxazolio-2-vinyl)thiazolo[3,2-*a*]quinolinium 1-Oxide Iodide (VIa). A mixture of 0.22 g (1 mmole) of (2-quinolylthio)acetic acid, 0.42 g (1 mmole) of 3-ethyl-2-(2-acetanilidovinyl)benzoxazolium iodide, and 10 ml of acetic acid was heated to 75°C, 1 ml of acetic anhydride was added, and the mixture was heated to 40 min. The resulting precipitate was removed by filtration (Table 1).

Dimethylidynemerocyanines VI-VIII. These compounds were obtained as in the preceding experiment from (2-quinolylthio)acetic acids Ia, b and the corresponding intermediates.

1,2-Dihydro-2-(p-dimethylamino)benzylidene-1-oxothiazolo[3,2-*a*]quinolinium Perchlorate (IX). A 0.22-g (1 mmole) sample of (2-quinolylthio)acetic acid was dissolved in 5 ml of acetic acid, the solution was heated to 80°C, 0.15 g (1 mmole) of p-dimethylaminobenzaldehyde and 2 ml of acetic anhydride were added, and the mixture was refluxed for 2 min. A solution of 0.12 g (1 mmole) of sodium perchlorate in 3 ml of acetic acid was added to the hot solution, and the dye was removed by filtration and washed with alcohol and ether.

1-Oxo-2-(1-oxidothiazolyl[3,2-a]quinolinio-2-methylene)-1,2-dihydrothiazolo[3,2-*a*]-quinolinium Perchlorate (X). A mixture of 0.22 g (1 mmole) of (2-quinolylthio)acetic acid, 15 ml of acetic acid, and 0.2 g (1.33 mole) of ethyl orthoformate was heated at 60°C for 2 min, after which 0.22 g (1 mmole) of (2-quinolylthio)acetic acid and 2 ml of acetic anhydride were added, and the mixture was heated at 100°C for 10 min. A solution of 0.12 g (1 mmole) of sodium perchlorate in 5 ml of acetic acid was added, and the precipitate was removed by filtration and washed with alcohol and ether.

5-(3-Methylbenzothiazolinylidene-2-methyl)-2-(1,3,3-trimethyl-3H-indolio-2-vinyl)-thiazolo[3,2-*a*]quinolinium 1-Oxide Perchlorate (XI). A 0.05-g (0.5 mmole) sample of triethylamine and 0.1 g (0.3 mmole) of 3-methyl-2-methylthiobenzothiazolium methylsulfate were added to a solution of 0.17 g (0.3 mmole) of dye VIIIb in 20 ml of acetic anhydride, and the mixture was heated at 100°C for 30 min. The resulting precipitate was removed by filtration and washed with alcohol and ether.

5-(1,3,3-Trimethyl-3H-indolinylidene-2-methyl)-2-(1,3,3-trimethyl-3H-indolio-2-vinyl)-thiazolo[3,2-*a*]quinolinium 1-Oxide Perchlorate (XII). This compound was obtained as in the preceding experiment from VIIIb and 1,3,3-trimethyl-2-methylthio-3H-indolium perchlorate.

5-(1,3,3-Trimethyl-3H-indolinylidene-2-propenyl)-2-(1,3,3-trimethyl-3H-indolio-2-vinyl)thiazolo[3,2-*a*]quinolinium 1-Oxide Perchlorate (XIII). A mixture of 0.25 g (0.5 mmole) of dye VIIIb, 0.09 g (0.5 mmole) of 1,3,3-trimethyl-2-formylmethylene-3H-indoline, and 6 ml of acetic anhydride was heated at 90°C for 30 min, after which 10 ml of ether was added, and the precipitate was removed by filtration and washed with alcohol and ether.

1-Oxo-1,2-dihydro-2-(p-dimethylamino)benzylidene-5-(p-dimethylaminophenylvinyl)thiazole[3,2-*a*]quinolinium Perchlorate (XIV). A solution of 0.3 g (2 mmole) of p-dimethylaminobenzaldehyde in 1.5 ml of acetic acid was added to a solution of 0.23 g (1 mmole) of (4-methyl-2-quinolylthio)acetic acid in 5 ml of acetic acid, the mixture was heated to the boiling point, and 2 ml of acetic anhydride was added dropwise. A solution of 0.12 g (1 mmole) of sodium perchlorate in 2 ml of acetic acid was added dropwise to the hot solution, and the dye was removed by filtration and washed with alcohol and ether.

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PMR SPECTRA AND STRUCTURES OF 2H,6H-2,6-DIMETHYL-4-AMINO-1,3,5-DITHIAZINE AND ITS DERIVATIVES

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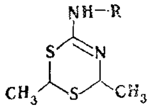
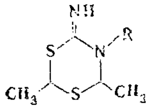
An analysis of the PMR spectra of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine, its acyl derivatives, and 2H,3H,6H-2,6-dimethyl-4-amino-1,3,5-thiadiazine in various solvents and in the presence of $Eu(FOD)_3$ [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)$_3$europium] confirms the structure assigned to it and makes it possible to prefer a cis orientation of the methyl substituents in the half-chair conformation.

The heterocyclization of divinyl sulfide with thiourea leads to a nitrogen-containing heterocycle, to which the 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine structure (Ia) was assigned on the basis of IR and PMR spectroscopic data [1].



I-V a

or



I-V b

Ia,b R = H; IIa,b R = $COCH_3$; IIIa,b R = COC_3H_7; IVa,b R = COC_6H_5; Va,b R = $SO_2C_6H_4CH_3$

A great deal of attention is currently being directed to the study of the structure of heterocyclic derivatives of thiourea, which can exist in tautomeric forms [2]. However, the available data are not devoid of contradictions and do not always give an unambiguous answer to the question of the structures of the tautomers [2]. A universal approach to the solution of this problem has not yet been developed.

In the present paper we set forth the results of a study of the structures of heterocycle I and its derivatives II-V, as well as 6H-2,6-dimethyl-4-amino-2,3-dihydro-1,3,5-thiadiazine (VI), by means of PMR spectroscopy (see Table 1). In particular, we studied their tautomerism and cis—trans isomerism.

In examining the question of tautomerism we proceeded from the fact that if two tautomeric forms, viz., amino (a) and imino (b) forms, exist, solvents with different properties should have different effects on the position of the tautomeric equilibrium and, consequently, on the parameters of the PMR spectra of mixture of the tautomers (a and b). The chemical shifts (δ, in parts per million) of the signals of the protons of the methylidyne groups and the methyl groups bonded to them in heterocycles I-VI, the J_{CH-CH_3} spin—spin coupling constants, and the δ values of the signals of the protons bonded to the nitrogen atom are presented in Table 1. The data in Table 1 constitute evidence that replacement of CCl_4 by CD_3OD and d_6-DMSO affects the δ value but only within the limits that are usually produced by a change in the character of the intermolecular interaction of a substance with a solvent [3]; the J_{CH-CH_3} constant remains unchanged in this case.

It also follows from Table 1 that replacement of one of the hydrogen atoms bonded to the nitrogen atom by CO—CH_3 (II), COC_3H_7 (III), COC_6H_5 (IV), and $SO_2C_6H_4CH_3$ (V) groups leads

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