B. A mixture of 0.215 g (0.5 mmole) of salt III and 0.08 g (0.5 mmole) of N-ethyl-2-thioxo-4-thiazolidinone was dissolved by heating in a mixture of 10 ml of acetonitrile and 1 ml of pyridine. The precipitate that formed after the addition of 0.1 ml of triethylamine was removed by filtration and washed with acetonitrile.

No melting-point depression was observed for a mixture of the products obtained by methods A and B.

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CONDENSED HETEROCYCLES WITH A THIAZOLE RING.
18.* PYRIDO(QUINOLINO)THIAZOLOPYRAZINES

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UDC 547.789.6'831.78'825.07

Derivatives of new condensed heterocyclic systems – pyrido- and quinolino[1',2':3,2]thiazolo[4,5-b]pyrazines – were synthesized by condensation of 2,3-dichloropyrazine with 2-mercaptopyridine and 2-mercaptoquinolines.

Derivatives of new heterocyclic systems – azino[1',2':3,2]thiazolo[4,5-b]quinoxalinium salts [2], which can be used in the synthesis of cyanine dyes – are formed in the condensation of 2,3-dichloroquinoxaline with 2-mercaptopyridine and 2-mercapto-4-R-quinolines. Since it was found that, as compared with known analogs [3], the absorption maxima in the electronic spectra of such dyes are shifted to the red part of the spectrum, it seemed of interest to make a more detailed study of the dependence of the color indices of the new type of cyanines on the structure of the terminal heteroresidue.

In order to obtain new condensed heterocyclic systems with a nodal nitrogen atom that contain a thiazolo azinium fragment, we studied the reaction of 2,3-dichloropyrazine with 2-mercaptopyridine and 2-mercapto-4-R-quinolines and observed that perchlorates I and IIa, b, respectively, are readily formed when the reaction is carried out in acetic acid (see scheme on following page).

Signals that are characteristic only for condensed heterocycles that contain a quaternary nitrogen atom are observed in the PMR spectra of these compounds. As expected, the signal of the proton in the 9 position shows up at weakest field in the spectrum of salt I (10 ppm, α-pyridinium proton). However, the signal of the proton in the 1 position is observed at even

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*See [1] for Communicaton 17.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1276-1278, September, 1990. Original article submitted July 21, 1988; revision submitted February 5, 1990.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formul	mp, °C	UV spectrum, λ_{max}, nm	Yield, %	Compound*	Empirical formula	mp, °C	UV spectrum, λ_{max}, nm**	Yield, %
I	$C_9H_6ClN_3O_4S$	290	350	80	IV	$C_{23}H_{17}ClN_4O_4S_2$	300	575	60
IIa	$C_{13}H_8ClN_3O_4S$	294	378	85	VI	$C_{27}H_{21}ClN_4O_4S$	300	665	75
IIb	$C_{14}H_{10}ClN_3O_4S$	255	375	72	VIII	$C_{29}H_{17}ClN_6O_4S_2$	163	793	45
III	$C_{23}H_{19}ClN_4O_4S$	298	620	77	IX	$C_{37}H_{21}ClN_6O_4S_2$	300	837	48

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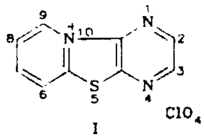
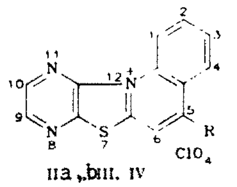
*According to the data in [2], λ_{max} is 561 nm for VII.

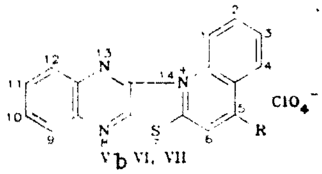
**The spectra of IV and IX were measured in DMF.



I

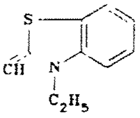


IIa, b III, IV



Vb VI, VII

IIa R=H; II, Vb R=CH_3; III, VI R= $-CH=CHC_6H_4N(CH_3)_2$; IV, VII R=$-CH$

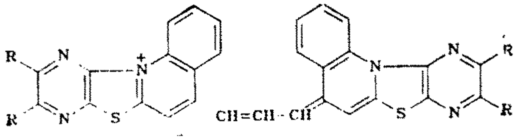


weaker field (10.5 ppm) in the spectra of quinolinothiazolopyrazines IIa, b. In addition, it was found unexpectedly that the signal of the proton in the 6 position of the I cation (the β position relative to the onium center) is observed at weaker field than the signal of the proton in the 7 position (the γ position).

In comparing the electronic spectra of I and IIa, b (Table 1) and pyrido- (400 nm) and quinolino[1',2':3,2]thiazolo[4,5-b]-quinoxalinium (414 nm) salts [2] it is apparent that additional benzannelation of the pyrido(quinolino)thiazolopyrazinium molecules leads to bathochromic shifts of their long-wave absorption maxima by 50 and 65 nm, respectively.

Methyl-substituted salt IIb reacts readily with p-dimethylaminobenzaldehyde, and 3-ethyl-2-benzothiazoliosulfonate to give respectively, styryl III and monomethinecyanine IV. From an analysis of the spectral data for III and IV and their benzo analogs VI and VII, which were obtained from perchlorate Vb, it is apparent that, in this case, the effect of benzannelation is ambiguous. In fact, whereas a solution of thiacyanine IV is more deeply colored by 14 nm than its benzo homolog VII, the situation is reversed for styryls III and VI – for dye VI the bathochromic shift is 45 nm. This effect may be due to both the different effective lengths (L) in the dyes and (or) their electron-donor characters (Φ) [4]. In addition, a knowledge of these parameters for the terminal fragments in cyanines makes it possible to form a judgment beforehand regarding the possible range of practical use of investigated substances.

In this connection we also synthesized symmetrical carbocyanines VIII and IX from the corresponding methyl-substituted salts IIb and Vb.



VIII, IX

VIII R=H; IX R + R=$-(CH=CH)_2-$

As compared with the maxima of the bands of the corresponding trimethinecyanine from a quaternary salt of lepidine [5], the maxima of the absorption bands of solutions of dyes VIII and IX are shifted to the long-wave part of the spectrum by 88 and 130 nm, respectively.

The relative basicities of the heteroresidues in the synthesized dyes were calculated by the method of deviations of styryls [5]. The deviations ($\Delta\lambda_{max}$) are 80 and 55 nm for perchlorates III and VI, while the deviation for the styryl based on lepidine is 110 nm. Consequently, with respect to its electron-donor character, the quinolinothiazolopyrazine residue approaches the quinaldine residue ($\Delta\lambda$ = 80 nm), while the quinolinothiazoloquinoxaline residue approaches the benzothiazole residue ($\Delta\lambda$ =

58 nm). The effect of the structure of the heteroresidue on the positions of the absorption maxima of different types of dyes hence becomes understandable.

However, the reasons for such a marked change in the L and, particularly, Φ values in the case of benzannelation are not clear, since the pyrazine and quinoxaline molecules have similar basicities [6], i.e., one should also have expected a similar effect on the color index. A substantial change in the bond orders and the distribution of the charges in both the thiazole and quinoline fragments of the molecule, which is also manifested in a change in Φ and L, evidently occurs in the case of benzannelation of the pyrazine ring in the heteroresidue. Thus, the problem of the interrelationship between the chemical structure of the terminal groupings and the color indices of dyes in the investigated series requires that research on condensed heterocycles be continued.

EXPERIMENTAL

The electronic spectra of solutions of the compounds in acetonitrile were obtained with an SF-8 spectrophotometer. The PMR spectra of solutions in d_6-DMSO were obtained with a WP-100 SY spectrometer (100 MHz) with tetramethylsilane (TMS) as the internal standard.

The results of elementary analysis for N and Cl (S) were in agreement with the calculated values.

Pyrido[1',2':3,2]thiazolo[4,5-b]pyrazinium Perchlorate (I). A mixture of 0.6 g (4 mmoles) of 2,3-dichloropyrazine, 0.45 g (4 mmoles) of 2-mercaptopyridine, and 6 ml of acetic acid was refluxed for 5 min, after which 0.5 g (4 mmoles) of sodium perchlorate or 1 ml (5 mmoles) of 58% perchloric acid was added. The precipitated product was removed by filtration, washed with acetic acid, and crystallized from CH_3COOH. PMR spectrum: 9.24 (1H, d), 9.14 (1H, d), 9.06 (1H, d, J = 6 Hz), 8.75 (1H, t), 8.26 (1H, t), 10.05 ppm (1H, d, J = 6 Hz).

5-R-Quinolino[1',2':3,2]thiazolo[4,5-b]pyrazinium Perchlorates IIa, b. These compounds were obtained in the same way as I from the corresponding 2-mercapto-4-R-quinolines. PMR spectrum of IIa: 9.28 (2H, s), 9.23 (1H, d, J = 9 Hz), 9.00 (1H, d), 8.59 (1H, d), 8.13 (1H, t), 8.41 (1H, t), 10.50 ppm (1H, d). PMR spectrum of IIb: 3.09 (3H, s), 9.24 (2H, s), 8.89 (1H, s), 8.65 (1H, d, J = 9 Hz), 8.13 (1H, t), 8.39 (1H, t), 10.54 ppm (1H, d).

5-(p-Dimethylamino)styrylquinolino[1',2':3,2]thiazolo[4,5-b]pyrazinium Perchlorate (III). A mixture of 0.35 g (1 mmole) of perchlorate IIb, 0.15 g (1 mmole) of p-dimethylaminobenzaldehyde, and 8 ml of acetic anhydride was refluxed for 3 min, after which it was cooled, and the precipitated product was removed by filtration and washed with hot acetic anhydride. The yield was 0.37 g.

5-[3-Ethyl-2(3H)-benzothiazolylidene]methylquinolino[1',2':3,2]thiazolo[4,5-b]pyrazinium Perchlorate (IV). A mixture of 0.35 g (1 mmole) of perchlorate IIb, 0.24 g (1 mmole) of 3-ethyl-2-benzothiazoliosulfonate, and 5 ml of DMF was heated to the boiling point and treated with 0.1 g (1 mmole) of triethylamine. The mixture was maintained at 120°C for 5 min, after which it was cooled, and the product was removed by filtration and washed successively with acetic anhydride and hot acetic acid. The yield was 0.3 g.

5-(p-Dimethylaminostyryl)quinolino[1',2':3,2]thiazolo[4,5-b]quinoxalinium Perchlorate (VI). This compound was obtained in the same way as styryl III from perchlorate Vb.

5-[3-(5,12-Dihydro-5-quinolino[1',2':3,2]thiazolo[4,5-b]pyrazinylidene)-1-propenyl]quinolino-[1',2':3,2]thiazolo[4,5-b]pyrazinium Perchlorate (VIII). A mixture of 0.7 g (1 mmole of perchlorate IIb, 0.2 g (1 mmole) of diphenylformamidine, and 5 ml of acetic anhydride was heated to the boiling point and treated with 0.1 g (1 mmole) of triethylamine. The mixture was refluxed for 2 min, after which it was cooled, and the precipitated product was removed by filtration. The yield was 0.3 g.

Compound IX was similarly obtained from perchlorate Vb [2].

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