CYANINE DYES FROM THIAZOLOMORPHOLINIUM AND THIAZOLODIHYDRO-THIAZINIUM SALTS

V. P. Khilya, G. P. Kutrov, and F. S. Babichev

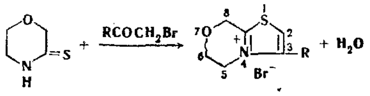
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 6, pp. 1043–1047, 1967

UDC 547.78+547.867.4+547.869.2:543.422.6+668.8

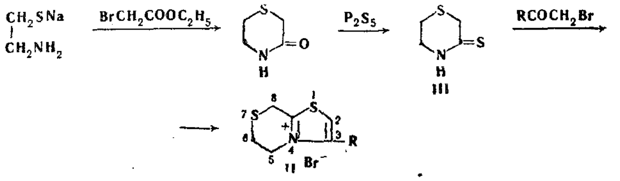
Cyanine dyes have been synthesized from previously unknown thiazolo [3, 2-c] morpholinium and thiazolo[3, 2-c] dihydrothiazinium salts, and their absorption spectra have been determined.

In the development of the previously described syntheses of cyanine dyes with electron-donating substituents in the polymethine chain included in a ring [1], in the present work we have obtained analogous dyes from thiazolo [3, 2-c] morpholinium salts I and thiazolo [3, 2-c] dihydrothiazinium salts II.

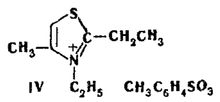
The initial thiazolo [3, 2-c] morpholinium salts were synthesized by condensing morpholine-3-thione with α-halo ketones.



Similarly, the salts II were formed from 1, 4-thiazane-3-thione (III).



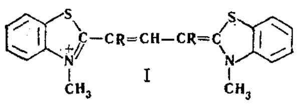
In the bicyclic salts I and II, the methylene groups is position 8, which are conjugated with the positively charged nitrogen atom, are active. The activity of these groups is fairly high and cyanine dyes can be obtained from them by the usual methods. However, the ethyl tosylate derivative of 2-ethyl-4-methylthiazole (IV), in which the methylene group is not included in the ring, does not undergo cyanine condensations at all.



IV

As can be seen from the information in the table, the absorption maxima of the cyanine dyes from salts I and II are displaced substantially into the long-wave region of the spectrum as compared with the absorption maxima of the analogous thiazolocyanines unsubstituted in the polymethine chain. The observed bathochromic effect must be ascribed, as in the case of cyanine dyes from dihydrooxazino- and dihydrothiazinobenzothiazolium salts [1], to the effect of electron-donating substituents (O and S) forming part of a cyclic system in active positions of the chain.

Thiazolocyanines with alkoxy or aryloxy groups or alkylthio or arylthio groups in the 6, 8 positions of the chain were previously unknown; however, such dyes have been obtained in the thiacyanine series. It was found that deepening of the color is caused only by phenoxy groups in the 8, 10 positions (λ_{max} 589 nm) and the introduction of phenylthio groups in the same positions of the chain even led to a slight heightening of the color (λ_{max} 552 nm).



I

R	λ_{max}, nm
H	558
OC_6H_5	589[2]
SC_6H_5	552[3]

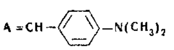
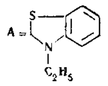
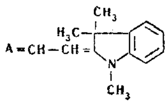
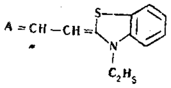
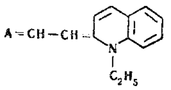
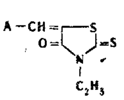
In the symmetrical dyes (**IX–XII, XIX, XX**), the atom of oxygen and the atom of sulfur also cause a deepening of the color, the greater displacement of the absorption maximum being found in dyes with oxygen atoms (74 and 79 nm in the monomethine cyanines).

In the styryl dyes (V, VI) and in the unsymmetrical carbocyanines with nuclei of low basicity (XIII–XVI), compounds containing a sulfur atom as substituent have a deeper coloration. The observed relationship can be explained by the assumption of the lower basicity of the thiazole nucleus in the dyes from thiazolo [3, 2-c] thiazinium salts as compared with the basicity of the same nucleus in thiazolo [3, 2-c] morpholinium salts. The fall in basicity may be connected with the capacity of the sulfur atom for exhibiting electron-accepting properties in some cases [4, 5]. Using the same arguments that were given previously in relation to the cyanine dyes from dihydrooxazino- and dihydrothiazinobenzothiazolium salts [1], from 2, 3-polymethylenebenzothiazolium salts [6, 7], and from 2, 3-polymethylenethiazolium salts [8], it can be shown that there is no steric hindrance in the chains of the dyes obtained and that it is impossible to explain their deep coloration in this way.

EXPERIMENTAL

Morpholine-3-thione. A mixture of 12.5 g of 3-morpholone [9] and 25 g of phosphorus pentoxide was carefully ground and was heated with 200 ml of benzene for 1 hr. After this, the hot benzene solution was decanted from the viscous mass and cooled, whereupon morpholine-3-thione deposited. Yield 6.3 g (43%), colorless needles, mp 122° C (from benzene). Found, %: S 27.34; 27.19. Calculated for C_4H_7NOS, %: S 27.34.

Characteristics of the Dyes Synthesized

Compound	Formula*	Anion	X	R	Mp, °C	λ_{max}, nm	Bathochromic displacement***, λ_{max}, nm	Deviation of λ_{max}, nm	Empirical formula	S, %		Yield, %
										Found	Calculated	
V		ClO$_4$	O	CH$_3$	218	492	12	128	$C_{16}H_{19}ClN_2O_5S$	8.03; 8.15	8.28	64
VI		ClO$_4$	S	CH$_3$	232	502	22	114	$C_{16}H_{19}ClN_2O_4S$	16.00; 15.93	15.80	55
VII		ClO$_4$	O	C$_6$H$_5$	277	453	—	—	$C_{21}H_{19}ClN_2O_5S_2$	13.17; 13.25	13.33	49
VIII		Br	S	C$_6$H$_5$	229	486	—	—	$C_{20}H_{17}BrN_2S_3$	20.68; 20.76	20.84	56
IX	A=CH—B	Br	O	CH$_3$	244	630	74	—	$C_{15}H_{17}BrN_2S_2$	15.63; 15.82	15.97	85
X		ClO$_4$	S	CH$_3$	249	622	66	—	$C_{15}H_{17}ClN_2O_4S_2$	27.94; 28.12	28.20	81
XI		ClO$_4$	O	C$_6$H$_5$	189	638	79	—	$C_{25}H_{21}ClN_2O_6S_2$	11.90; 11.85	11.76	54
XII		Br	S	C$_6$H$_5$	249	630	71	—	$C_{25}H_{21}BrN_2S_4$	22.61; 22.71	23.00	64
XIII		ClO$_4$	O	C$_6$H$_5$	235	554	—	38	$C_{25}H_{25}ClN_2O_5S$	6.46; 6.52	6.40	71
XIV		I	S	C$_6$H$_5$	250	564	—	20	$C_{25}H_{25}IN_2S_2$	11.72; 11.88	11.79	48
XV		ClO$_4$	O	CH$_3$	237	568	—	27	$C_{18}H_{19}ClN_2O_5S_2$	14.14; 14.27	14.47	74
XVI		ClO$_4$	S	CH$_3$	228	578	—	13	$C_{18}H_{19}ClN_2O_4S_3$	20.48; 20.67	20.90	45
XVII		ClO$_4$	O	CH$_3$	245	617	—	0.5	$C_{20}H_{21}ClN_2O_5S$	7.22; 7.12	7.33	41
XVIII		ClO$_4$	S	CH$_3$	246	610	—	3.5	$C_{20}H_{21}ClN_2O_4S_2$	13.98; 14.10	14.15	50
XIX	A=CH—CH=CH—B	ClO$_4$	O	C$_6$H$_5$	192	730	—	—	$C_{27}H_{23}ClN_2O_5S_2$	11.27; 11.31	11.23	52
XX		ClO$_4$	S	C$_6$H$_5$	249	722	—	—	$C_{27}H_{23}ClN_2O_4S_4$	20.96; 20.84	21.20	78
XXI		—	O	CH$_3$	306	578	38	7	$C_{13}H_{14}N_2O_3S_2$	$C_{13}H_{14}N_2O_2S_3$	29.47	86
XXII		—	S	CH$_3$	285	572	32	9	$C_{13}H_{14}N_2OS_4$	37.12; 37.08	37.42	54

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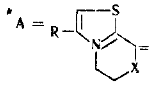
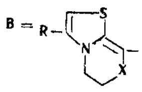
* ; 

**Dyes XIII and XV were recrystallized from a mixture of ethanol and water (1:2), XXI and XXII from isopropanol, and the others from ethanol.

***In comparison with the analogous dyes unsubstituted in the chain.

1, 4-Thiazane-3-thione (III). A mixture of 4.6 g of 1, 4-thiazin-3-one [10] and 1.8 g of phosphorous pentasulfide was heated with 25 ml of toluene at 100° C for 30 min and the toluene solution was filtered hot from the viscous mass. After cooling, the filtrate deposited substance III. Yield 2.45 g (51%), needles, mp 141°–142° C (from ethanol). Found, %: S 47.78; 47.92. Calculated for $C_4H_7NS_2$, %: S 48.12.

8H-3-Methylthiazolo[3, 2-c] morpholinium bromide (I, R = CH_3). A solution of 2.34 g of morpholine-3-thione in 100 ml of benzene was added to a solution of 5.48 g of bromoacetone in 50 ml of benzene. The reaction mixture became turbid and an oil rapidly separated out. The mixture was boiled in the water bath for 30 min and, after cooling, the solid reaction product was filtered off and washed with benzene. Yield 4.6 g (97%), prisms, mp 216° C (decomp., from ethanol). Found, %: S 13.22; 13.44; Br 33.39; 33.43. Calculated for $C_7H_{10}BrNOS$, %: S 13.55; Br 33.83.

Two grams of the above bromide was converted into the perchlorate with a yield of 78%. Needles, mp 177° C (from ethanol). Found, % S 12.22; 12.36. Calculated for $C_7H_{10}ClNO_5S$, %: S 12.54.

8H-3-Phenylthiazolo[3, 2-c]morpholinium bromide (I, R = C_6H_5). From 2.34 g of morpholine-3-thione and 4 g of bromoacetophenone in 150 ml of benzene (boiled for 1 hr) was obtained 5.76 g (96%) of the bromide. Needles mp 226° C (decomp, from ethanol). Found, %: S 10.80; 10.93; Br 26.43; 26.63. Calculated for $C_{12}H_{12}BrNOS$, %: S 10.75; Br 26.79.

Two grams of the bromide was converted into the perchlorate with a yield of 81%. Lustrous plates, mp 205° C (decomp., from ethanol). Found, %: S 10.23; 10.27. Calculated for $C_{12}H_{12}ClNO_5S$, %: S 10.09.

8H-3-Methyl-5, 6-dihydrothiazolo[3, 2-c]-1, 4-thiazinium bromide (II, R = CH_3). A mixture of 2 g of 1, 4-thiazane-3-thione and 2 g of bromoacetone in 10 ml of acetone was boiled for 10 min. After cooling, the bromide that had deposited was filtered off and washed with ethanol and ether. Yield 2.9 g (83%), needles, mp 212° C (from ethanol). Found, %: S 25.64; 25.59. Calculated for $C_7H_{10}BrNS_2$, %: S 25.43.

8H-3-Phenyl-5, 6-dihydrothiazolo[3, 2-c]-1, 4-thiazinium bromide (II, R = C_6H_5) was obtained similarly to the preceding substance. Yield 57%, needles, mp 232° C (decomp., from ethanol).

Below, syntheses of dyes of each type are given as examples.

8-(p-Dimethylaminobenzylidene)-8H-3-methylthiazolo[3, 2-c] morpholinium perchlorate (V). A mixture of 0.24 g of the bromide I and 0.15 g of p-dimethylaminobenzaldehyde in 4 ml of acetic anhydride was boiled for 15 min. After cooling, an aqueous ethanolic solution of sodium perchlorate was added to the dye solution. The crystals that deposited were filtered off, washed with water, with a small amount of ethanol, and with ether, and recrystallized from ethanol.

Bis (8H-3-methylthiazolo[3, 2-c] morpholine-8) monomethinecyanine bromide (IX). A mixture of 0.3 g of the bromide (I, R = CH_3) and 0.3 g of dimethylformamide dimethyl acetal in 3 ml of pyridine containing 3 drops of triethylamine was heated at 120° C for 15 min. The crystals of dye that deposited after cooling (fine blue needles with a metallic luster) were filtered off, washed with ethanol and ether, and recrystallized from ethanol.

(8H-3-Phenylthiazolo[3, 2-c] morpholine-8)-(1', 3', 3'-trimethylindolenine-2') dimethinecyanine perchlorate (XIII). A mixture of 0.3 g of 8H-3-phenyl-thiazolo[3, 2-c] morpholinium perchlorate, 0.23 g of 1, 3-trimethyl-2-formyl-methyleneindolenine, and 3 ml of acetic anhydride was heated at 100°–110° C for 15 min. The dye was washed with water, aqueous ethanol, and ether.

Bis (8H-3-phenylthiazolo[3, 2-c] morpholine-8) trimethinecyanine perchlorate (XIX). A mixture of 0.4 g of the bromide (I, R = C_6H_5), 0.4 g of β-ethoxyacrolein diethyl acetal, and 4 ml of pyridine was boiled for 1 min. The dye formed directly and precipitated in the form of green needles. After cooling, the dye was filtered off and was washed with ethanol and with ether.

3-Ethyl-5-(8'H-3'-methylthiazolo[3', 2'-c] morpholin-8'-methylene) thione-2-thiazolone-4 (XXI). A mixture of 0.35 g of the bromide (I, R = CH_3), 0.45 g of 3-ethyl-5-acetanilidomethylenerhodanine, 5 drops of triethylamine, and 10 ml of absolute ethanol was boiled for 10 minutes. After cooling, the dye was filtered off, washed with 50 ml of hot water, with ethanol, and with ether, and was recrystallized from propanol.

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28 February 1966 Kiev State University