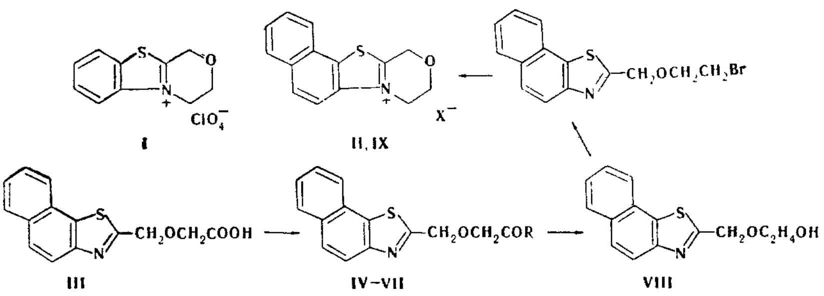
CYANINE DYES FROM 8,9-DIHYDRO-11H-NAPHTHO-[2',1':4,5]THIAZOLO[2,3-c][1,4]OXAZINIUM SALTS

V. P. Khilya and G. I. Galatsan

UDC 668.8'541.651:547.789.6'867

The condensation of the anhydride of diglycolic acid with 2-aminothionaphthol has given naphtho[2,1-d]thiazol-2-ylmethoxyacetic acid, from which esters and the amide and hydrazide have been obtained. The lithium tetrahydroaluminate reduction of the methyl ester of the acid has given a carbinol which has been converted by reaction with phosphorus tribromide and subsequent heating into 8,9-dihydro-11H-naphtho[2',1':4,5]thiazolo-[2,3-c][1,4]oxazinium bromide. From this quaternary salt have been synthesized cyanine dyes, the deep coloration of which is due to the strong electron-donating action of the substituent in the α position of the polymethine chromophore.

The cyanine dyes obtained previously [1] from 3,4-dihydro-1H-benzothiazolo[2,3-c][1,4]oxazinium salts (I) have been tested for their sensitizing action on silver halide emulsions. The results of the tests showed that these dyes have no advantages over industrial sensitizers. However, according to a Belgian patent [2], these dyes are valuable highly intensive sensitizers for color film. The addition to the emulsions of stabilizers containing mercapto groups further increases the activity of these sensitizers. In view of these statements of the patent, we have undertaken the synthesis of benzo derivatives of these cyanines from salts of structure (II). For this purpose, by condensing diglycolic anhydride with potassium 2-aminothionaphthoxide under the conditions described by Kiprianova et al. [3] we obtained naphtho[2,1-d]-thiazol-2-ylmethoxyacetic acid (III), the esterification of which in methanol or ethanol in the presence of dry hydrogen chloride led to the methyl or ethyl ester (IV or V, respectively). The latter were used to obtain the amide (VI), the hydrazide (VII), and the alcohol (VIII). Compound (VIII) was converted into the bromide from which, by intramolecular alkylation, the quaternary salt (IX), and then (II), were obtained.



II–X = ClO_4; IX X = Br; IV R = OCH_3; V R = OC_2H_5; VI R = NH_2; VII R = $NHNH_2$

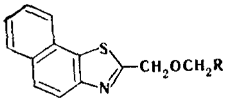
The methylene group in position 11 of the salt (II) proved to be fairly active, which permitted the synthesis by the usual methods of styryls, symmetrical and unsymmetrical carbocyanines, dicarbocyanines, and merocyanines. Table 2 gives information on the dyes obtained (X–XVI), which may be considered as thiacyanines substituted in the polymethine chain in which the $-CH_2CH_2O-$ substituent is included in a ring and is therefore fixed in one plane with the naphthothiazole nucleus and the polymethine chromophore.

As can be seen from Table 2, the absorption maxima of the cyanine dyes from salt (II) are displaced considerably into the long-wave part of the spectrum as compared with the absorption maxima of the

---

T. G. Shevchenko Kiev State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1258–1261, September, 1973. Original article submitted July 20, 1972.

TABLE 1



Comp.	R	mp, °C	Empirical formula	Found, %	Calc., %	$R_f \cdot 10^2$† A	$R_f \cdot 10^2$† B	$R_f \cdot 10^2$† C	Yield, %
III	COOH	186	$C_{14}H_{11}NO_3S$*	S 11,4	S 11,7	0	2	0	54
IV	$COOCH_3$	85	$C_{15}H_{13}NO_3S$	S 11,2	S 11,2	52	64	59	55
V	$COOC_2H_5$	68	$C_{16}H_{15}NO_3S$	S 10,7	S 10,6	58	66	62	56
VI	$CONH_2$	180	$C_{14}H_{12}N_2O_2S$	N 10,4	N 10,3	14	31	14	64
VII	$CONHNH_2$	176	$C_{14}H_{13}N_3O_2S$	N 14,5	N 14,5	5	12	9	34
VIII	CH_2OH	95	$C_{14}H_{13}NO_2S$	S 12,4	S 12,4	—	35	15	52

---

*Found, %: N 5.2. Calculated, %: N 5.1.

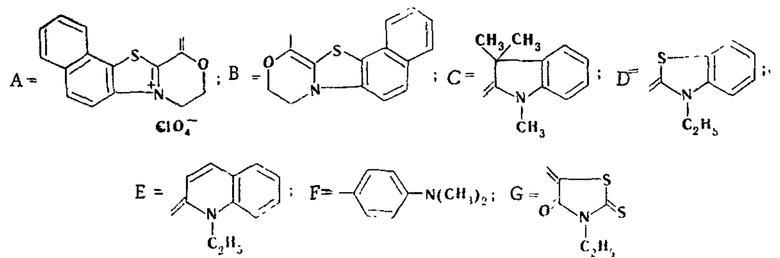
†Solvent systems for chromatography: A, ethyl acetate; B, dichloroethane–methanol (9 : 1); C, dichloroethane–methanol (95 : 5).

TABLE 2. Characteristics of the Dyes Synthesized

Comp.	Formula*	mp, °C	λ max, nm, EtOH	Deviation, nm	Bathochromic shift, nm†		Empirical formula	S, %		Yield, %
					$\Delta\lambda_1$	$\Delta\lambda_2$		found	calc.	
X	A=CHB ‡	278	676	—	38	118	$C_{29}H_{21}BrN_2O_2S_2$	10,9	11,2	23
XI	A=CHCH=CHB ‡	270	772	—	34	122	$C_{31}H_{23}BrN_2O_2S_2$	11,2	10,9	60
XII	A=CHCH=C	207	592	19	19	50	$C_{27}H_{25}ClN_2O_5S$	6,3	6,1	79
XIII	A=CHCH=D	257	611	7	16	53	$C_{25}H_{21}ClN_2O_5S_2$	12,0	12,1	54
XIV	A=CHCH=E	275	640	0,5	19	62	$C_{28}H_{23}ClN_2O_5S$	5,9	5,8	36
XV	A=CHF	350	548	95	8	18	$C_{23}H_{21}ClN_2O_5S$	6,9	6,8	63
XVI	BCH=G	284	584	25	14	60	$C_{20}H_{16}N_2O_2S_3$	23,1	23,3	69

---

*



†$\Delta\lambda_1$, in comparison with the analogous dyes from salt (I); $\Delta\lambda_2$, in comparison with the analogous dyes from 2-methylbenzothiazole ethiodide.

‡ Bromide.

analogous thiacyanines unsubstituted in the polymethine chain. As in the case of the dyes from salt (I), the observed bathochromic effect must be ascribed to the electron-donating action of the oxygen atom forming part of a cyclic system, since there is no steric hindrance in the molecules of these dyes. This conclusion, in particular, follows from the fact that in this series of dyes a normal vinylene difference of 96 nm (X and XI) is observed. The absorption curves of the dyes obtained have narrow and sharp absorption maxima resembling in shape the absorption curves of the cyanine dyes from 2-methylbenzothiazole ethiodide. This similarity, and also Stuart–Briegleb models, confirm the coplanarity of the molecules of the new dyes.

The calculated deviations for the unsymmetrical dyes show that the basicity of the heterocyclic nucleus in the molecules of the dyes from the salt (II) is almost equal to the basicity of a quinoline nucleus.

EXPERIMENTAL

The chromatography of compounds (III-VIII) was performed on plates in a thin layer of Merck silica gel G, and the spots were revealed with iodine vapor (Table 1).

2-Naphtho[2,1-d]thiazol-2-ylmethoxyacetic Acid (III). To a freshly prepared hot (50°C) melt of potassium 2-amino-1-thionaphthoxide obtained from 25 g (0.11 mole) of β-naphthylenethiazthionium hydroxide [4, 5] were added 20 ml of glacial acetic acid and 13.2 g (0.11 mole) of finely ground diglycolic anhydride [6]. After the end of the exothermic reaction, the mixture was heated at 100°C for 30 min, and then a 10% solution of caustic potash was added to give an alkaline reaction and the mixture was filtered. The decolorized filtrate was neutralized with hydrochloric acid to Congo Red. The product that deposited was crystallized from acetic acid. Yield 16 g.

Methyl Ester of (III) (IV). A suspension of 7 g (25 mmoles) of (III) in 120 ml of methanol was saturated with dry hydrogen chloride until the solid matter had dissolved, and was then boiled for 3 h. The residue after the alcohol had been distilled off was made alkaline with sodium carbonate solution. The precipitate that deposited was filtered off and washed with water until mineral salts had been eliminated completely. The yield of (IV) was 4 g; colorless plates (from heptane).

The ethyl ester of (III) (V) was obtained similarly to compound (IV).

The Amide of (III) (VI). A mixture of 0.5 g (17 mmoles) of (IV) and 10 ml of dry methanol was saturated with ammonia and was left for 2-3 days. The precipitate was filtered off and crystallized from ethanol. Thin colorless needles. Yield 0.3 g.

Hydrazide of (III) (VII). A mixture of 0.5 g (17 mmoles) of (IV) and 0.5 ml of 85% hydrazine hydrate was heated at 100°C for 45 min, and then 15 ml of dry methanol was added (complete dissolution) and heating was continued for another 2 h. The (VII) was crystallized from ethanol. Yield 0.17 g.

2-Naphtho[2,1-d]thiazol-2-ylmethoxyethanol (VIII). A solution of 2.2 g (7.6 mmoles) of (IV) in 25 ml of tetrahydrofuran was added dropwise to a stirred solution of 0.17 g (4.4 mmoles) of lithium tetrahydroaluminate in 50 ml of tetrahydrofuran at −50°C, the mixture was stirred at −50°C for another 1 h, and then 15 ml of moist ether was added dropwise at −30°C and a solution of 1.2 g of caustic soda in 7 ml of water at −20°C. After the removal of the aluminum hydroxide, the filtrate was diluted with ether, washed with water, and dried with sodium sulfate. The residue after the distillation of the ether was crystallized from a mixture of heptane and carbon tetrachloride. Light-yellow needles. Yield 1.4 g.

8,9-Dihydro-11H-naphtho[2',1'-4,5]thiazolo[2,3-c][1,4]oxazinium Perchlorate (II). To a solution of 0.8 g (3 mmoles) of (VIII) in 20 ml of carbon tetrachloride at −15°C, 1.1 g (4 mmoles) of phosphorus tribromide was added dropwise. The solvent was distilled off, the mixture was heated at 100°C for 1 h and cooled, and 15 ml of water was added followed by sodium carbonate solution to an alkaline reaction. The oil that separated out was extracted with ether and dried with calcium chloride. The residue after the distillation of the ether was heated in xylene at 130-140°C for 2 h 30 min. The bromide (IX) formed was washed on the filter with xylene and with ether. Yield 0.58 g (56%). The action of $NaClO_4$ in water on the (IX) gave (II) in the form of plates with mp 298°C (from water). Found, %: Cl 10.6; S 9.6. $C_{14}H_{12}ClNO_5S$. Calculated, %: Cl 10.4; S 9.4.

Bis{8,9-dihydro-11H-naphtho[2',1':4,5]thiazolo[2,3-c][1,4]oxazine-(11)}monomethinecyanine Bromide (X). A mixture of 0.18 g (1.2 mmole) of diethoxymethyl acetate and 0.18 g (0.55 mmole) of (IX) in 3 ml of pyridine was heated to the boil. The dye formed precipitated instantaneously. Heating was continued for another 10 min. After cooling, the dye was filtered off and was crystallized from acetic acid. Yield of (X) 0.04 g.

Bis{8,9-dihydro-11H-naphtho[2',1':4,5]thiazolo[2,3-c][1,4]oxazine-(11)}trimethinecyanine Bromide (XI). A mixture of 0.12 g (0.37 mmole) of (IX) and 0.12 g (0.82 mmole) of β-ethoxyacrolein diethyl acetal in 5 ml of pyridine was rapidly heated to the boil. A precipitate of dye deposited immediately, and this was filtered off and was washed on the filter with hot water and with small amounts of ethanol and ether. Yield of (XI) 0.11 g.

The dyes (XII-XVI) were obtained by general methods.

LITERATURE CITED

1. F. S. Babichev and V. P. Khilya, Zh. Organ. Khim., 1, 562 (1965).
2. Belgian Patent No. 650,828 (1965); Chem. Abstr., 64, 17760 (1966).
3. L. A. Kiprianova, D. K. Yarovoi, É. Shchetsinskaya, and F. S. Babichev, Ukr. Khim. Zh., 30, 859 (1964).
4. V. M. Zubarovskii, Zh. Obshch. Khim., 17, 613 (1947).
5. V. M. Zubarovskii and S. N. Fidel', Zh. Obshch. Khim., 21, 2064 (1951).
6. R. Anschütz and F. Biernaux, Ann. Chem., 273, 64 (1893).