

CYANINE DYES FROM NAPHTHO[1,2-6]THIAZOLO-  
[3,2-d][1,4]THIAZINE

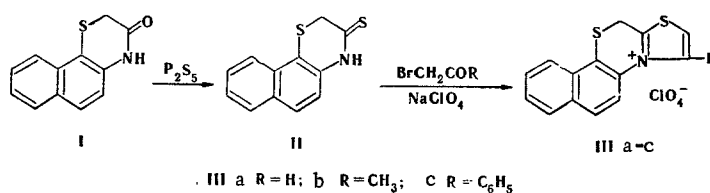
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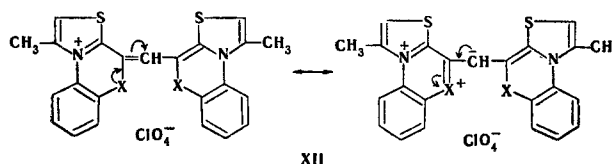
Deeply colored cyanine dyes have been synthesized from the previously unknown 3-methyl-12H-naphtho[1,2-b]thiazolo[3,2-d][1,4]thiazinium salts. It is assumed that the deep color of the new cyanines is connected with the conversion of the nonaromatic 1,4-thiazine ring in the dye molecule into an aromatic thiazine ring with three double bonds in a six-membered ring.

A series of cyanine dyes from derivatives of thiazolo[2,3-c][1,4]benzothiazine has been described previously [1]. These dyes proved to be more deeply colored compounds than the corresponding thiacyanines.

In order to obtain deeply colored cyanines we have made the thiazolobenzothiazine molecule more complicated by introducing another benzene ring into it. By condensing potassium 2-amino-1-thionaphthoxide [2] with monochloroacetic acid in an alkaline medium we obtained compound (I) [3]. By reaction with phosphorus pentasulfide, this compound was converted into the thioxo derivative (II) and from this by reaction with  $\alpha$ -bromo carbonyl compounds (where R = H, in the form of an acetal) we obtained the quaternary salts (III).



In the salts obtained, the methylene group in position 12 proved to be sufficiently active to permit the synthesis by the usual methods of dyes of interest to us (VI-XI, Table 1). These dyes are colored somewhat more deeply than the analogous dyes from 1-methylthiazolo[2,3-c][1,4]benzothiazinium salts (IV) [1] and considerably more deeply than the dyes from 2,4-dimethyl-3-phenylthiazolium salts (V) [4] (Table 1). The calculated deviations for the unsymmetrical dyes showed that the basicity of the thiazolo-naphthothiazine nucleus in the dyes approximates to that of a quinoline nucleus. Compounds (VI-XI) can be considered as cyanines in which the hydrogen atom in the  $\alpha$  position of the polymethine chain has been replaced by a naphthylthio group, and this is fixed in the plane of the dye molecule.



X=O,  $\lambda_{\max}$  756 nm [5]; X=S,  $\lambda_{\max}$  654 nm [1]; X=Se,  $\lambda_{\max}$  626 nm [6].

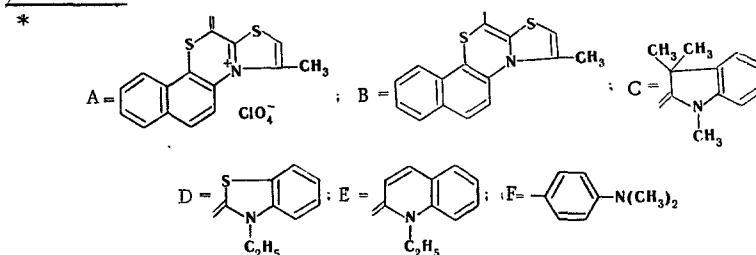
Similar compounds are known in the literature. Thus, for example, dyes of the general formula (XII) are far more deeply colored than the N,N'-diphenylthiazolocyanine unsubstituted in the polymethine chain ( $\lambda_{\max}$  566 nm) [4].

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TABLE 1. Characteristics of the Dyes Synthesized

Comp.	Formula*	mp, °C	$\lambda_{\text{max}}$ nm (ethanol)	Deviation, nm	Empirical formula	S, %		$\lambda_{\text{max}}$ of analogous dye, nm		Yield, %
						found	calc.	from IV	from V	
VI	A=CH B	237	668	—	$\text{C}_{31}\text{H}_{27}\text{ClN}_2\text{O}_4\text{S}_4$	19,6	19,7	654	566	40
VII	A=CHCH=CH B <sup>†</sup>	247	750	—	$\text{C}_{38}\text{H}_{23}\text{BrN}_2\text{S}_4$	19,4	19,5	—	657	34
VIII	A=CHCH=C	212	586	21	$\text{C}_{28}\text{H}_{25}\text{ClN}_2\text{O}_4\text{S}_2$	11,3	11,6	580	534	85
IX	A=CHCH=D	177	611	3	$\text{C}_{26}\text{H}_{21}\text{ClN}_2\text{O}_4\text{S}_2$	17,1	17,2	609	558	61
X	A=CHCH=E	223	637	0,5	$\text{C}_{28}\text{H}_{23}\text{ClN}_2\text{O}_4\text{S}_2$	11,3	11,6	630	589	58
XI	A=CHF	231	524	115	$\text{C}_{24}\text{H}_{21}\text{ClN}_2\text{O}_4\text{S}_2$	13,0	12,8	—	504	81



According to the literature [5,6], the unusually deep coloration of these dyes is due to a tendency to the transformation of the oxazine, thiazine, and selenazine rings into aromatic rings with three double bonds in a six-membered ring, which must enhance the electronic action of the oxygen, sulfur, and selenium atoms and, consequently, their capacity for deepening the color, as well. The dyes from the salt (IIIb), in particular the symmetrical carbocyanines (VI) and (VII), form one more example of this type of electronic transitions connected with the aromatization of the thiazine ring.

## EXPERIMENTAL

**3,4-Dihydro-2H-naphtho[1,2-b][1,4]thiazine-3-thione (II).** A mixture of 5.45 g (25 mmoles) of (I) [3] and 2.67 g (12 mmoles) of phosphorus pentasulfide in 35 ml of pyridine was heated with stirring at 100°C for 50 min, and the red-brown solution was poured into 200 ml of water. An oil separated out which gradually solidified. Yield 5.6 g (95%). For purification, a benzene solution of compound (II) was passed through a column of alumina. Yellow plates, mp 206°C (from toluene). Found, %: S 27.7.  $\text{C}_{12}\text{H}_9\text{NS}_2$ . Calculated, %: S 27.7.

**12H-Naphtho[1,2-b]thiazolo[3,2-d][1,4]thiazinium Perchlorate (IIIa).** To a solution of 1 g (4.2 mmoles) of (II) in 50 ml of benzene was added 1.8 g (9 mmoles) of bromoacetaldehyde and the mixture was boiled for 1 h. The dark resinous product was dissolved in water, the solution was treated with activated carbon, and the required salt was precipitated with sodium perchlorate. Yield 0.2 g (13%), yellow needles with mp 228°C (from water). Found, %: S 17.9.  $\text{C}_{14}\text{H}_{10}\text{ClNO}_4\text{S}_2$ . Calculated, %: S 18.0.

**3-Methyl-12H-naphtho[1,2-b]thiazolo[3,2-d][1,4]thiazinium Perchlorate (IIIb).** A mixture of 4 g (16.8 mmoles) of (II) and 3.3 g (24 mmoles) of bromoacetone in 200 ml of benzene was boiled for 1 h. The dark gray precipitate was washed with benzene. Yield 1.3 g (20%). The compound obtained was converted into the perchlorate — colorless plates with mp 216°C (from ethanol). Found, %: Cl 10.5; S 17.3.  $\text{C}_{15}\text{H}_{12}\text{ClNO}_4\text{S}_2$ . Calculated, %: Cl 10.4; S 17.4.

**3-Phenyl-12H-naphtho[1,2-b]thiazolo[3,2-d][1,4]thiazinium Perchlorate (IIIc)** was obtained in a similar manner to (IIIa) from (II) and bromoacetophenone with a yield of 22%. Light-yellow crystals with mp 219°C (from ethanol). Found, %: S 14.8.  $\text{C}_{20}\text{H}_{14}\text{ClNO}_4\text{S}_2$ . Calculated, %: S 14.8.

**Bis[3-methyl-12H-naphtho[1,2-b]thiazolo[3,2-d][1,4]thiazine-(12)]monomethinecyanine Perchlorate (VI).** A mixture of 0.185 g (0.5 mmole) of (IIIb) and 0.18 g (1.2 mmole) of diethoxymethyl acetate [7] in 3 ml of pyridine was boiled for 10 min. After cooling, the dye was filtered off and was washed with ethanol and ether. Yield 0.12 g.

**Bis[3-methyl-12H-naphtho[1,2-b]thiazolo[3,2-d][1,4]thiazine-(12)]trimethinecyanine Bromide (VII).** A mixture of 0.18 g (0.5 mmole) of (IIIb) in the form of the bromide and 0.18 g (1 mmole) of  $\beta$ -ethoxyacrolein diethyl acetal in 5 ml of pyridine was boiled for 5 min. After cooling, the dye was filtered off and was washed with hot water, ethanol, and ether. Lustrous green needles. Yield 0.11 g.

The unsymmetrical dyes (VIII-XI, Table 1) were obtained by condensing (IIIb) with the appropriate formyl derivatives in acetic anhydride and were purified by recrystallization from acetic acid.

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