SYNTHESIS AND REACTIONS OF AZIDES OF HETEROCYCLIC COMPOUNDS

III.* CYANINE DYES BASED ON AZIDES OF BENZOTHIAZOLE AND BENZIMIDAZOLE

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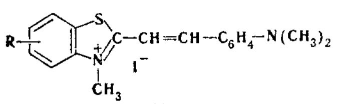
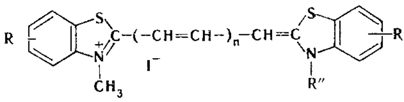
Cyanine dyes containing azido groups in the 5 or 6 position of the benzazole ring were obtained from quaternary salts of azides of benzothiazole and benzimidazole. The introduction of an azido group into the dye molecule results in a considerable bathochromic effect.

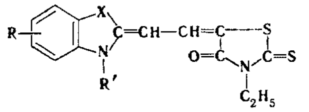
5-Azido- (I) and 6-azido-2-methylbenzothiazole methiodides (II) and 5-azido-1-phenyl-2-methyl- (III) and 6-azido-1,2-dimethylbenzimidazole ethiodides (IV), which were described in [2], were used for the synthesis of cyanine dyes containing azido groups in the 5 or 6 position of the benzazole ring.



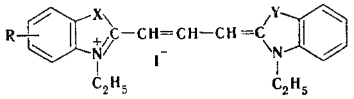
V, VI



VII-XII



XIII, XIV, XIX, XX



XV-XVIII

V $R=5\text{-}N_3$; VI $R=6\text{-}N_3$; VII $R=5\text{-}N_3$, $R'=H$, $R''=C_2H_5$, $n=0$; VIII $R=6\text{-}N_3$, $R'=H$, $R''=C_2H_5$, $n=0$; IX $R=R'=5\text{-}N_3$, $R''=CH_3$, $n=1$; X $R=R'=6\text{-}N_3$, $R''=CH_3$, $n=1$; XI $R=5\text{-}N_3$, $R'=H$, $R''=CH_3$, $n=1$; XII $R=6\text{-}N_3$, $R'=H$, $R''=CH_3$, $n=1$; XIII $R=5\text{-}N_3$, $R'=CH_3$, $X=S$; XIV $R=6\text{-}N_3$, $R'=CH_3$, $X=S$; XV $R=5\text{-}N_3$, $X=N\text{-}C_6H_5$, $Y=S$; XVI $R=6\text{-}N_3$, $X=N\text{-}CH_3$, $Y=S$; XVII $R=5\text{-}N_3$, $X=N\text{-}C_6H_5$, $Y=CH=CH$; XVIII $R=6\text{-}N_3$, $X=N\text{-}CH_3$, $Y=CH=CH$; XIX $R=5\text{-}N_3$, $R'=C_2H_5$, $X=N\text{-}C_6H_5$; XX $R=6\text{-}N_3$, $R'=C_2H_5$, $X=N\text{-}CH_3$

In contrast to the quaternary salts of benzothiazole azides, the quaternary salts of the benzimidazole azides do not form symmetrical carbocyanines in either acetic anhydride or pyridine. When we carried out the reaction in nitrobenzene, the azide quaternary salts decomposed.

On the basis of data from the IR spectra of the cyanine dyes (V-XX), it can be concluded that on passing from quaternary salts to cyanine dyes the azido group in the latter is retained and participates in the conjugation system. The IR spectra of the cyanine dyes contain bands of the asymmetrical stretching vibrations of the azido group at 2105-2123 cm^{-1} (Tables 1 and 2).

To clear up the question of the effect of the azido group on the color of the cyanine dyes we used dyes of the benzothiazole series, for which styryls (V, VI), monomethylidynecyanines (VII, VIII), symmetrical (IX, X) and unsymmetrical (XI, XII) carbocyanines, and merocyanines (XIII, XIV) were obtained. We were unable to obtain this series for imidacyanines. From a comparison of the absorption maxima of the dyes that we obtained and the corresponding unsubstituted dyes the following conclusions can be drawn. The introduction of an azido group into the benzazole ring of the cyanine dye leads to a considerable shift in the

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*See [1] for communication II.

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TABLE 1. Cyanine Dyes from Benzothiazole Azides

Compound	λ_{max}, nm	log ε	λ_{max} of the dye without an azido group, nm (log ε)	Empirical formula	$\nu_{as}N_3$, cm^{-1}
V*	540	4,70	528 (5,04)[6]	12	2123
VI*	535	4,74	528 (5,04)[6]	7	2116
VII	430	4,97	422 (4,91)[7]	8	2115
VIII	434	4,91	422 (4,91)[7]	12	2105
IX*	576	5,15	558 (5,15)[8]	18	2114
X*	580	5,15	558 (5,15)[8]	22	2110
XI*	566	5,07	558 (5,15)[8]	8	2120
XII*	570	5,09	558 (5,15)[8]	12	2114
XIII*	530	4,78	521 (4,96)[6]	9	2114
XIV*	536	4,79	521 (4,96)[6]	15	2120

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*See [2] for the synthesis of the dyes.

TABLE 2. Cyanine Dyes from Benzimidazole Azides

Compound	mp, °C	Empirical formula	Found, %		Calc. %		λ_{max} nm	lg ε	λ_{max} of the dye w/o azide group, nm	Bathochromic shift, nm	ν_{as} N$_3$, cm^{-1}	Yield, %
			N	S	N	S						
XV	214—215	$C_{27}H_{25}IN_6S$	14,6	5,6	14,2	5,4	522	5,03	517[9]	5	2110	60
XVI	210—212	$C_{22}H_{23}IN_6S$	16,0	6,2	15,8	6,0	522	—	500[9]	22	2115	40
XVII	—	$C_{29}H_{23}IN_6$	14,0	—	14,3	—	574	4,97	559[9]	15	2110	50
XVIII	—	$C_{24}H_{25}IN_6$	16,2	—	16,0	—	534	4,92	521[9]	13	2112	57
XIX	169—170	$C_{22}H_{20}N_6OS_2$	18,8	13,9	18,9	13,9	524	5,13	511[9]	5	2110	34
XX	198—200	$C_{17}H_{18}N_6OS_2$	21,6	16,4	21,9	16,1	526	—	511[9]	15	2110	45

absorption maximum to the long-wave portion of the spectrum, and this shift is somewhat greater for thiacyanines than for imidacyanines. Two azido groups in the 5,5' or 6,6' positions of the thiacarbocyanine cause a bathochromic effect that is twice that of one azido group in the 5 or 6 position (Table 1). The absorption maxima of the cyanine dyes containing an azido group in the 6 position of the benzothiazole ring differ only slightly from the absorption maxima of the 5-azido derivatives.

In [3] it is noted that the slight difference in the color of the 5,5'- and 6,6'-substituted thiacarbocyanines is associated with the equal possibility of conjugation of the substituents with the polymethine chain of the dye through both the nitrogen atom and the sulfur atom. The sulfur atom of the thiazole ring is an electron conductor only with respect to electron-donor substituents and does not participate at all or participates only weakly in conjugation if there is an electron-acceptor substituent in these positions [4]. The absence of conjugation through the sulfur atom for electron-acceptor substituents explains the great difference in the color of thiacarbocyanines that contain electron-acceptor substituents in the 5,5' and 6,6' positions. The small difference in the absorption maxima of thiacarbocyanines that contain azido groups in the 5,5' and 6,6' positions provides a basis for assuming that the azido group acts as an electron-donor substituent in this case. In numerical value its bathochromic effect approaches the effect of the acetamido group [4]. The acetamido group does not cause deviations when it is introduced into one ring of the thiacarbocyanine [5]. We observe the same thing when an azido group is introduced into one benzothiazole ring of the dye.

It is known that the color of merocyanines is shifted bathochromically when the basicity of the heterocyclic residue bonded to the rhodanine ring by a polymethine chain increases. Thiamerocyanines containing an azido group as a substituent are more deeply colored (by 9-15 nm) than the unsubstituted dyes, and this is an indirect confirmation of the fact that the azido group acts as an electron-donor substituent. The similarity, in an optical respect, of thiacarbocyanines that contain an azido group in the 5,5' and 6,6' positions can be explained by the equal possibility of conjugation of the azido group in these dyes through both the nitrogen atom and the sulfur atom.

EXPERIMENTAL

The IR spectra of KBr pellets were recorded with a UR-10 spectrometer. The UV spectra of ethanol solutions were recorded with an SF-4 spectrophotometer.

(3-Methyl-5-azido-2-benzothiazolyl) (3'-Ethyl-2'-benzothiazolyl)monomethylidynecyanine Iodide (VII). A mixture of 0.33 g (1 mmole) of 5-azido-2-methylbenzothiazole methiodide, 0.38 g (1 mmole) of 2-methylmercaptobenzothiazole ethyltosylate, and 1 mmole of triethylamine in absolute ethanol was refluxed for

30 min. The dye began to precipitate as the mixture was heated. The mixture was cooled, and the precipitate was removed by filtration and washed with alcohol to give 0.28 g (45%) of a product with mp 262-264° (dec., from ethanol). Found %: N 14.3; S 13.0. $C_{18}H_{16}IN_5S_2$. Calculated %: N 14.2; S 13.0.

(3-Methyl-6-azido-2-benzothiazolyl) (3'-Ethyl-2'-benzothiazolyl)monomethylidynecyanine Iodide (VIII). This compound was similarly obtained from 0.33 g (1 mmole) of 6-azido-2-methylbenzothiazole and 0.38 g (1 mmole) of 2-methylmercaptobenzothiazole ethyltosylate. The yield of product with mp 225-228° (dec., from ethanol) was 0.32 g (56%). Found %: N 14.1; S 13.2. $C_{18}H_{16}IN_5S_2$. Calculated %: N 14.2; S 13.0.

Unsymmetrical Carbocyanines XV and XVI. These dyes were obtained by heating equimolecular amounts of the corresponding quaternary salts (III or IV) with 3-ethyl-2-formylmethylenebenzothiazoline in acetic anhydride. The resulting dyes were removed by filtration, washed with alcohol and ether, and crystallized from alcohol (Table 2).

Unsymmetrical Carbocyanines XVII and XVIII. These compounds were obtained by heating equimolecular amounts of the appropriate quaternary salt (III or IV) and 2-ω-acetanilidovinylquinoline in acetic anhydride in the presence of triethylamine. The dyes were purified by chromatography of chloroform solutions of them with a column filled with activity II aluminum oxide (Table 2).

Merocyanines XIX and XX. These dyes were obtained by heating equimolecular amounts of the corresponding ethiodides (III or IV) with acetanilidomethylene-N-ethylrhodanine in ethanol in the presence of triethylamine. The products were purified by chromatography of chloroform solutions of them on activity II aluminum oxide (Table 2).

LITERATURE CITED

1. I. A. Ol'shevs'ka, V. Ya. Pochinok, N. A. Pasmurtseva, and N. F. Parkhomenko, Visnik Kiivs'k. Univ., Ser. Khim., No. 14, 61 (1973).
2. I. A. Ol'shevskaya, V. Ya. Pochinok, and L. F. Avramenko, Khim. Geterotsikl. Soedin., 898 (1968).
3. E. D. Sych and L. P. Umanskaya, Zh. Obshch. Khim., 33, 80 (1963).
4. E. D. Sych, Ukr. Khim. Zh., 18, 159 (1952).
5. A. I. Kiprianov, Doctoral Dissertation [in Russian], Kharkov (1940).
6. A. I. Kiprianov and F. A. Mikhailenko, Zh. Obshch. Khim., 31, 781 (1961).
7. A. I. Kiprianov and I. K. Ushenko, Zh. Obshch. Khim., 20, 135 (1950).
8. A. I. Kiprianov and F. A. Mikhailenko, Zh. Obshch. Khim., 31, 786 (1961).
9. A. V. Stetsenko and L. I. Filileeva, Ukr. Khim. Zh., 32, 853 (1966).