CONDENSED HETEROCYCLIC COMPOUNDS CONTAINING A THIAZOLE RING.

12.* DERIVATIVES OF THIAZOLO[3,4-b][1,2,4]TRIAZINE

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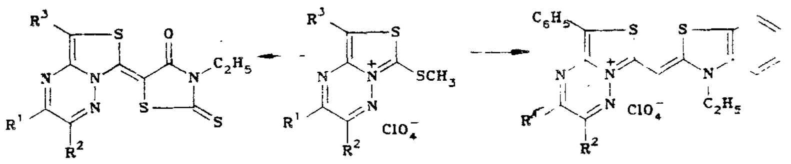
UDC 547.798.6'873:771.78:541.147:2:
543.422

Unsymmetrical monomethinecyanine dyes, containing a benzothiazole residue, were obtained from thiazolotriazine. To interpret the nature of the main absorption bands and localize the electronic transitions, the transition energies and electronic distribution of the first and second excited states of several model compounds were calculated by the self-consistent field method.

Salts of thiazolo[3,4-b][1,2,4]triazine of structures Ia-f have been reported [2]. In a search for new optical sensitizing agents for silver halide photographic emulsions, we have synthesized cyanine dyes basedon these compounds, and we have studied their spectral characteristics.

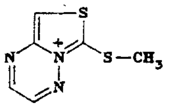


VIIa-f, VIIIf Ia-f, VIf IXa,d-f

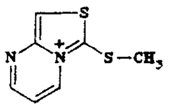
I, VII $R^3=C_6H_5$; VI, VIII $R^3=H$; a $R^1=R^2=CH_3$; b $R^1=C_6H_5$, $R^2=H$; c $R^1=H$, $R^2=C_6H_5$; d $R^1=C_6H_5$, $R^2=CH_3$; e $R^1=CH_3$, $R^2=C_6H_5$; f $R^1=R^2=C_6H_5$

A study of the absorption spectra of solutions of the perchlorates Ia-f showed that they absorb in the visible part of the spectrum (Table 1), while the position of the absorpti maxima depends largely on the nature of the substituents R^1 and R^2.

To interpret the nature of the absorption bands in substituted thiazolotriazine molecule a quantum-chemical calculation of the electron distribution in the ground state and the first excited state was approximated for the cation of the model compound II by the self-consistent field method and included the calculation of singly excited states.



II



III

The results obtained are given in Fig. 1 as a diagram of the electron density distribution at the atoms of the condensed system for the transition of the molecule to the first excited state. The long-wave band in the spectrum of thiazolotriazine II was due to the transfer of electron density from the thiazole to the triazine ring. The exocyclic sulfur atom and the carbon atom at position 8 make an especially large contribution to the total electron transfer. A qualitatively similar map of electron density distribution was obtained from an analysis [3] of molecular quantum-chemical calculations for excitation of the thiazol· [3,4-b]pyrimidine cation III.

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*For Communication 11, see [1].

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1693-1697, December, 1986. Original article submitted July 15, 1985.

0009-3122/86/2212-1373$12.50 © 1987 Plenum Publishing Corporation

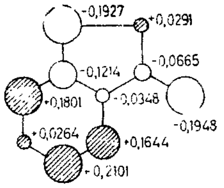

Fig. 1. Change in electron density on transition to the first excitation state for the model compound II.

TABLE 1. Absorption Spectra of Synthesized Compounds

Compound	λ_{max}, nm (lg ε)	Compound	λ_{max}, nm (lg ε)	Compound	λ_{max}, nm (lg ε)
Ia	324 (3,94); 425 (3,78)	VIIa	446 (4,44); 560 (3,72)	IXa	438 (4,50); 505 (4,19)
Ib	333 (4,37); 468 (3,68)	VIIb	460 (4,63); 650 (3,60)	—	
Ic	303 (4,40); 457 (3,57)	VIIc	451 (4,47); 640 (3,54)	—	
Id	329 (4,24); 447 (3,71)	VIId	453 (4,60); 604 (3,44)	IXd	448 (4,72); 522 (3,79)
Ie	329 (4,27); 446 (3,74)	VIIe	452 (4,60); 595 (3,43)	IXe	449 (4,69); 510 (3,75)
If	339 (4,38); 470 (3,69)	VIIf	458 (4,54); 645 (3,60)	IXf	454 (4,71); 555 (3,87)
VIf	317 (4,36); 420*	VIIIf	447 (4,54); 590 (3,45)	—	

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*Inflection.

Similarly, the effect of substituents in a number of previously studied compounds of type III showed that electronically similar substituents in the triazine ring of the condensed system II produced qualitatively similar effects on the color. For example, as seen from the data in Table 1, substitution of hydrogen atoms at positions 2 or 3 (compounds Ib, c) by electron-donor methyl groups causes the color to become more intense.

From quantum-chemical calculation data it also follows that, as in [3], substitution of the phenyl group at position 8 by a hydrogen atom should lead to an appreciable increase in color. To confirm this, the perchlorate VIf was synthesized from the hydrazone IV and the cyanomethylbenzenesulfonate V; the structure of the product was confirmed by IR and PMR spectral data

$$\underset{IV}{C_6H_5C(=O)C(C_6H_5)=NNHCS_2CH_3} + \underset{V}{C_6H_5SO_3CH_2CN} \longrightarrow VIf$$

The PMR spectrum contains signals with chemical shifts 2.53 (3H), 7.03 (10H), and 7.90 (1H) ppm from the methylthio group and the aromatic protons. The IR spectrum contains absorption bands due to the stretching vibrations of the C=C and C=N bonds (1515 and 1610 cm^{-1}) while absorption bands from the C=O, N–H, and C≡N groups of the starting components (1640, 3210, 2220 cm^{-1}) [2] were absent.

A comparison of the spectra (Fig. 2) of compound VIf and its 8-phenylsubstituted analog If shows that the long-wave absorption band of a solution of the salt VIf is considerably displaced toward the short-wave region of the spectrum and appears as a point of inflection.

Further investigation showed that the salts Ia-f and VIf readily react with nucleophilic reagents, such as 3-ethylrhodanine and 2-methyl-3-ethylbenzothiazole p-toluenesulfonate with formation of the corresponding zeromethinemerocyanines VII and VIII and monomethinecyanines IX. It should be noted that in the monomethinecyanine series only the 2,3,8-trisubstituted thiazolotriazine derivatives were isolated and analyzed.

The visible part of the spectra of solutions of the synthesized dyes (Table 1) showed two bands: an intense short-wave band (438-460 nm) and a considerably smaller long-wave band (505-555 nm for monomethinecyanines and 560-645 nm for zeromethinemerocyanines). It is interesting that the short-wave bands of monomethinecyanines and zeromethinemerocyanines lie approximately in the same region, near to the absorption maximum of solutions of the starting salts I, and their position is practically independent of the nature of the substituent on the thiazolotriazine ring, while the position of the long-wave band is determined precisely by these substituents. This relationship is also observed for the absorption spectra of solutions of the starting thiazolotriazine salts I and VI.

It should be noted that the presence of two bands in the visible region of the absorption bands was reported earlier [4] for solutions of thiazolo[3,4-a]pyrimidine dyes X, but here the long-wave and short-wave bands were of approximately equal intensity.

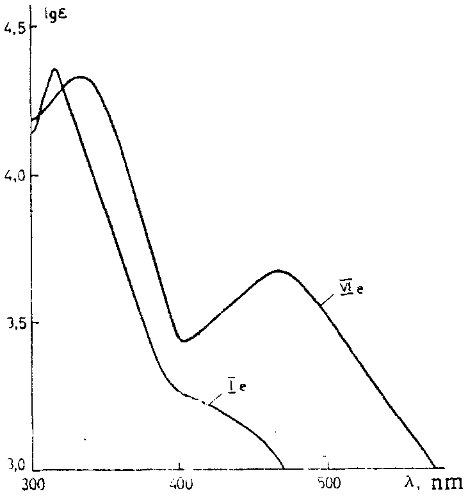

Fig. 2. Absorption curves for thiazolotriazines VIf and If (in acetonitrile).

TABLE 2. Physical Data for Synthesized Compounds

Compound	mp, °C*	Found, %		Empirical formula	Calculated, %		Yield, %
		N (Cl)	S		N (Cl)	S	
VIf	262—263	(8,2)	14,5	$C_{18}H_{14}ClN_3O_4S_2$	(8,1)	14,7	25
VIIa	273—274	13,8	24,2	$C_{18}H_{16}N_4OS_3$	14,0	24,0	85
VIIb	253—254	12,4	21,5	$C_{22}H_{16}N_4OS_3$	12,5	21,4	90
VIIc	268—269	12,5	21,1	$C_{22}H_{16}N_4OS_3$	12,5	21,4	90
VIId	265—267	12,4	20,5	$C_{23}H_{18}N_4OS_3$	12,1	20,8	88
VIIe	271—272	12,4	20,6	$C_{23}H_{18}N_4OS_3$	12,1	20,8	84
VIIf	274—275	10,5	18,3	$C_{28}H_{20}N_4OS_3$	10,7	18,3	38
VIIIf	306—307	12,3	21,0	$C_{22}H_{16}N_4OS_3$	12,5	21,4	52
IXa	175—176	(6,9)	12,3	$C_{23}H_{21}ClN_4O_4S_2$	(6,9)	12,4	79
IXd	322—324	(6,3)	11,0	$C_{28}H_{23}ClN_4O_4S_2$	(6,0)	11,1	57
IXe	315—317	(6,2)	10,9	$C_{28}H_{23}ClN_4O_4S_2$	(6,0)	11,1	67
IXf	326—327	(5,4)	9,8	$C_{33}H_{25}ClN_4O_4S_2$	(5,5)	10,0	92

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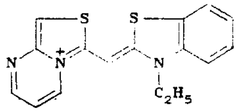
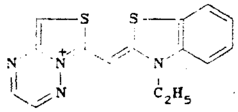
*Compound VIf was crystallized from a mixture of acetic acid and formic acid (5:1); VIIa, f from nitromethane; VIIIf from alcohol and DMFA (2:1).

In order to explain the nature and localization of the electron transitions corresponding to the color of the thiazolotriazine dyes, a diagram of the redistribution of electron density in the cation of the model monomethinecyanine XI was drawn:


X


XI

The change in electron density at the atoms for the first and second π—π*-transitions are given in Fig. 3. It can be seen that, in the molecule XI, the first transition depends mainly on the transfer of electron density from the carbon atom of the polymethine chain to the triazine nucleus (Fig. 3a), while the second π—π*-transition (Fig. 3b) is mainly localized at the atoms of the methine chain and at the carbon atom at position 8. There is a difference in the localization of electron transitions between the compounds we have studied and their structural analogs X [4], where the first electron transition corresponding to the long-wave absorption band is localized on the atoms of the methine chain, while the secon is due to the transfer of electron density from the carbon atom of the polymethine chain and the carbon at position 8 of the pyrimidine ring.

The results of the calculations agree with experimental data. Thus, for example, the magnitude of the change in electronic density at atoms $C_{(2)}$ and $C_{(3)}$ of the thiazolotriazine ring of the dye XI is considerably greater for the transition to the first excitation state; this agrees with the observation that the position of the long-wave absorption maximum is more sensitive to the position of substituents in the molecule than that of the short-wave maximum.

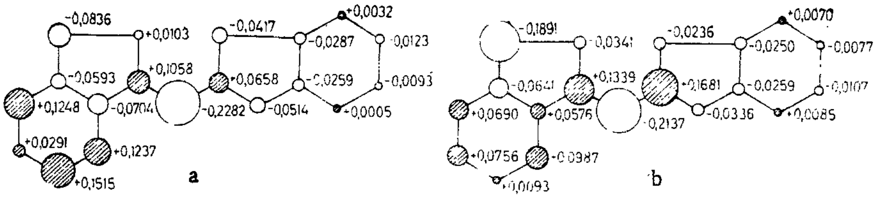


Fig. 3. Change in electronic density on transition of the molecule of the model dye XI to the first (z) and second (b) excitation states.

EXPERIMENTAL

Electronic spectra were obtained on an SF-8 spectrometer using acetonitrile as solvent, IR spectra were recorded on a UR-10 spectrometer (KBr pellets), PMR spectra were obtained on a BS-467 (60 MHz) in trifluoroacetic acid (internal standard – HMDS). Quantum chemical calculations were carried out in approximation PPP as in [3]. Physicochemical data for the dyes prepared in this work are given in Table 2.

Perchlorate of 6-Methylthio-2,3-diphenylthiazolo[3,4-b][1,2,4]triazine (VIf). A mixture of 0.31 g (1 mmole) of benzyl methyldithiohydrazonate and 0.21 g (1.1 mmole) of cyanomethylbenzenesulfonate was heated for 30 min at 100°. The mixture was dissolved in 25 ml of acetic acid, 1 ml of 57% hydrochloric acid added, the product filtered off, and recrystallized.

2-Thioxo-3-ethyl-5-(2,3-dimethyl-8-phenyl-6H-thiazolo[3,4-b][1,2,4]triazin-6-ylidene)thzolidinon-4 (VIIa). A mixture of 0.36 g (1 mmole) of the perchlorate Ia and 0.16 g (1 mmole) of 3-ethylrhodanine was heated to boiling in 15 ml of alcohol and 0.1 g (1 mmole) of triethylamine added. The precipitate which separated on cooling was filtered off and recrystallized.

Zeromethinemerocyanines VIIb-f and VIIIf were obtained by the same method from the corresponding salts.

Perchlorate of 2,3-Dimethyl-8-phenyl-6-[(3-ethyl-2(3H)-benzothiazolyidene)methyl]thiazolo[3,4-b][1,2,4]triazine (IXa). A mixture of 0.36 g (1 mmole) of 2-methyl-3-ethylbenzothiazole p-toluenesulfonate, 0.35 g (1 mmole) of perchlorate Ia and 15 ml of alcohol were heated to boiling and 0.1 g (1 mmole)of triethylamine was added. After cooling, the material was filtered off and recrystallized.

Monomethinecyanines IXd-f were obtained analogously from the corresponding salts Id-f.

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