SYNTHESIS AND REACTIONS OF 3-AMINOTHIAZOLIDIN-2-THION-4-ONE DERIVATIVES.

6.* THIAZOLO[4,3-b][1,3,4]THIADIAZOLES

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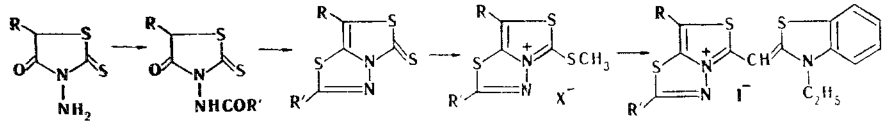
New thiazolo[4,3-b][1,3,4]thiadiazole derivatives were synthesized. The redistribution of the electron density in their molecules during photoexcitation was analyzed by the methods of quantum chemistry.

Within the framework of the further study of condensed systems with a thiazole ring synthesized from 3-amino-2-thioxo-4-thiazolidinone [1, 2] it seemed of interest to obtain new thiazolo[4,3-b][1,3,4]thiadiazole derivatives, to study their chemical transformations, and to investigate this class of compounds by the theoretical methods of quantum chemistry with comparison of the results with the corresponding data for their isoelectronic analogs, viz., thiazolo[4,3-b][1,2,4]triazoles.

From 3-aminorhodanines Ia-c by the usual methods [3] we obtained 3-acylaminorhodanines IIb-e, which, by the action of phosphorus pentasulfide in analogy with [4, 5], were converted to thiazolothiadiazoles IIIb-e. It follows from data from the PMR spectra of the synthesized compounds that, regardless of the substituent in the 7 position, they, like the previously obtained derivatives IIIa,f,g [4, 5], are probably protonated at the sulfur atom of the thione group. Their reaction with alkylating agents also takes place at the same center. Thus, for example, 5-(methylthio)thiazolothiadiazoles IVb-e are formed by the action of methyl p-toluenesulfonate. The reaction of tosylates IVb-e with 2-methyl-3-ethylbenzothiazolium iodide in the same way as in the case of monomethylidynecyanine Va gave its analogs Vb-e.



I a–c II a–g III a–g IV a–g V a–g

I—V a R=H, R′=C_6H_5; b R=CH_3, R′=C_6H_5; c R=R′=C_6H_5; II—V d R=H, R′=p-$C_6H_4NO_2$; e R=H, R′=p-$C_6H_4OCH_3$; f R=H, R′=NHC_6H_5, g R=H, R′=CH_3

The spectral characteristics of thiazolothiadiazole derivatives III-V are compared in Table 1. It is apparent from the data in Table 1 that, as in the thiazolotriazole series, replacement of the methyl group in the 7 position of the phenyl ring leads to a shift of the absorption maxima of solutions of the corresponding compounds to the long-wave region of the spectrum.

The introduction of electron-donor or electron-acceptor substituents in the phenyl ring bonded to the carbon atom in the 2 position in the thiazolothiadiazole series leads to greater, respectively, hypso- and bathochromic shifts of the absorption maxima of the band corresponding to the first electron transition than in the case of the analogous thiazolotriazoles. This can evidently be explained by the fact that they are less planar because of the steric hindrance that is present in the thiazolotriazole molecules [1, 2].

In order to ascertain the atoms on which the first π–π* transition is localized in the examined thiazolothiadiazole and thiazolotriazole derivatives we subjected model thiones III

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*See [1] for Communication 5.

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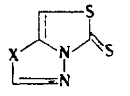
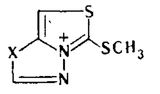
TABLE 1. Data from the Absorption Spectra of Methanol Solutions of Thiazolothiadiazoles III-V

R	R′	Compound	λ_{max}, nm (lg ε)	Compound	λ'_{max}, nm (lg ε)	Compound	λ_{max}, nm (lg ε)
H	C_6H_5	IIIa	266 (3,30), 400 (2,79)	IVa	280 (3,20), 357 (2,60)	Va	478 (3,69)
CH_3	C_6H_5	IIIb	270 (3,39), 410 (2,90)	IVb	260 (3,38), 360 (2,48)	Vb	493 (3,70)
C_6H_5	C_6H_5	IIIc	280 (3,47), 355 (3,19), 420 (2,98)	IVc	294 (3,37), 362 (2,88), 3,84 (2,90)	Vc	511 (3,73)
H	p-$C_6H_4NO_2$	IIId	285 (3,30), 440 (2,56)	IVd	289 (3,44), 365 (2,68)	Vd	495 (3,50)
H	p-$C_6H_4OCH_3$	IIIe	300 (3,54), 396 (3,02)	IVe	317 (3,36), 350 (3,05)	Ve	476 (3,73)
H	NHC_6H_5	IIIf	288 (3,42), 352 (3,16)	IVf	262 (3,10), 317 (3,29)	Vf	444 (3,84)
H	CH_3					Vg	452 (2,60)

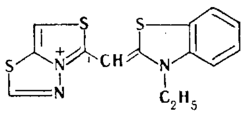
and VI, methylthio-substituted salts IV and VII, and dye V to quantum-chemical calculation:



III, VI



IV, VII



V

III, IV X=S; VI, VII X=N–CH_3

It is apparent from Fig. 1a that electron density is transferred from the thiazole to the thiadiazole ring in thione molecule III during excitation, whereas this sort of transfer is not observed for cation IV (Fig. 1b). Moreover, the electron density increases on some of the atoms of cation IV on transition to the excited state, whereas, on the other hand, it decreases on the same atoms in thione III. Thus, for example, the carbon atom in the 5 position in the cation in the ground state is somewhat electron-impoverished (charge $\Delta z^\circ = z_{core} - q^\circ = +0.0472$), which is due to the presence adjacent to it of atoms that provide the π-electron system of the molecule with atomic orbitals with great orbital electronegativity and with core charge $z_{core} = 2$. The electron density on this atom increases markedly ($\Delta z^* = -0.3029$) on passing to the excited state. In thione III the same atom in the ground state bears negative charge ($\Delta z^0 = -0.4966$), since in this case the orbital electronegativity of the p electrons of the exocyclic sulfur atom ($z_{core} = 1$) is significantly lower than the analogous value for the unshared pair of the sulfur atom ($z_{core} = 2$) in cation IV. The electron density decreases somewhat during excitation.

A marked change in the electron density occurs in the 2 and 7 positions of the III and IV molecules (Fig. 1, diagrams a and b), which indicates that the spectra of the corresponding molecules should be very sensitive to the effect of the substituents in the indicated positions. The sign of the shift of the absorption band when substituents are introduced should be the same for both thione III and salt IV, since the sign of the change in the electron density is the same for both cases in the corresponding positions. Such changes in the absorption spectra are actually observed (Table 1).

It is apparent from a comparison of the electron redistribution in the thiazolothiazole series (Fig. 1, diagrams c and d) that there are no fundamental differences between these systems. The nature of the absorption bands and their sensitivity to the effect of substituents should therefore be the same, which is also confirmed by the experimental data [1, 2]. The difference in the orbital electronegativities of the nitrogen and sulfur atoms in the 1 position of the corresponding condensed systems leads only to different numerical values of the change in the electron density during excitation, i.e., to somewhat different shifts in the spectra of the substituted molecules. The calculated absorption maxima for the model compounds (III 422, VI 418, IV 367, VII 343, and V 466 nm) are close to the experimental values.

In conclusion, let us note that the changes in the electron densities in the case of excitation of III, IV, VI, and VIII are comparable to those for the polymethine chain of dyes (Fig. 1e). However, the first transition in the case of dyes is localized primarily on the atoms of the polymethine "Kuhn chain," whereas the changes in the electron densities on the atoms of the remainder of the molecule are several times smaller.

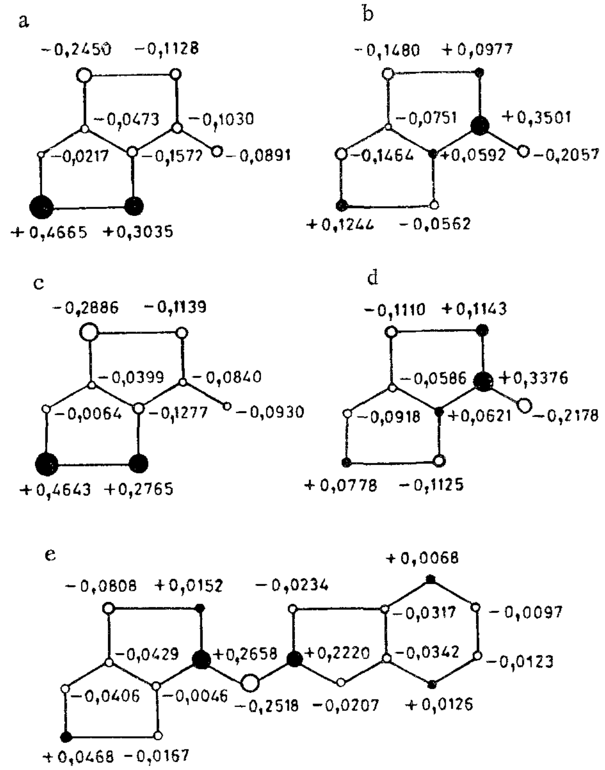


Fig. 1. Change in the electron density on passing to the first excited state (q^*-q^0) for model molecules: a) III; b) IV; c) VI; d) VII; e) V.

TABLE 2. Data on the Properties of the Synthesized Compounds

Compound	mp,* °C	Found, %			Empirical formula	Calculated, %			Yield, %
		Hal	N	S		Hal	N	S	
IIb	132—133	—	10,6	24,2	$C_{11}H_{10}N_2O_2S_2$	—	10,5	24,1	87
IIc	141—142	—	8,5	19,7	$C_{16}H_{12}N_2O_2S_2$	—	8,6	19,6	95
IId	173—175	—	14,2	21,7	$C_{10}H_7N_3O_4S_2$	—	14,1	21,5	90
IIe	164—165	—	9,8	22,8	$C_{11}H_{10}N_2O_3S_2$	—	9,9	22,7	96
IIIb	192—193	—	10,6	36,3	$C_{11}H_8N_2S_3$	—	10,6	36,4	59
IIIc	210—211	—	8,6	29,2	$C_{16}H_{10}N_2S_3$	—	8,6	29,4	45
IIId	275—276	—	14,2	32,4	$C_{10}H_5N_3O_2S_3$	—	14,2	32,5	40
IIIe	193—194	—	10,1	34,1	$C_{11}H_8N_2OS_3$	—	10,0	34,3	20
IVb	225—226	9,3	—	25,4	$C_{12}H_{11}ClN_2O_4S_3$	9,4	—	25,4	80
IVc	259—260	8,2	—	21,9	$C_{17}H_{13}ClN_2O_4S_3$	8,1	—	21,8	97
IVd	216—217	8,8	—	23,5	$C_{11}H_8ClN_3O_6S_3$	8,7	—	23,4	95
IVe	203—204	9,0	—	24,2	$C_{12}H_{11}ClN_2O_5S_3$	9,0	—	24,3	70
Vb	268—269	23,8	—	18,1	$C_{21}H_{18}IN_3S_3$	23,7	—	17,9	60
Vc	263—264	21,3	—	16,1	$C_{26}H_{20}IN_3S_3$	21,3	—	16,1	89
Vd	272—273	22,4	—	16,8	$C_{20}H_{15}IN_4O_2S_3$	22,4	—	17,0	76
Ve	298—299	21,3	—	16,4	$C_{21}H_{18}IN_3OS_3\cdot$ $\cdot C_2H_5OH$	21,3	—	16,1	72

*The compounds were crystallized: IId, IIIb, IVe, and Vb from alcohol, and IIb,c,e from benzene. Compound IIIe was purified by chromatography on Al_2O_3 and subsequent crystallization from alcohol. The remaining compounds were crystallized from alcohol–dimethylformamide: IIIc (1:1); IIId 1:2, IVb 6:1, IVc 3:2, IVd 10:1, Vc 5:1, Vd 2:1, and Ve 4:1.

EXPERIMENTAL

The quantum-chemical calculations were made by the method in [6]. The parameters for the sulfur atom of the thione group with core charge $z_{core} = 1$ were as follows: $U_\mu = -9.63$ eV, $\gamma_{11} = 8.94$ eV, and $\beta_{CS} = -1.95$ eV. The electronic spectra of solutions of the compounds in methanol were recorded with SF-8 and SF-10 spectrophotometers. The PMR spectra of solutions in CF_3COOH were measured with a Tesla BS-467 spectrometer.

3-Acylaminorhodanines IIb-e (Table 2). A mixture of 0.1 mole of the corresponding aminorhodanine, 0.1 mole of the acid chloride, and 20 ml of dry distilled benzene was refluxed for 3 h. The next day, the precipitated acylation product was removed by filtration.

7-Methyl-2-phenyl-5H-thiazolo[4,3-b][1,3,4]thiazole-5-thione (IIIb) (Table 2). A mixture of 0.53 g (2 mmole) of 5-methyl-3-benzamido-2-thioxo-4-thiazolidinone, 0.44 g (2 mmole) of phosphorus pentasulfide, and 10 ml of dry distilled dioxane was refluxed for 1 h, after which the solution was decanted, and the precipitate was refluxed with a fresh portion of dioxane. The dioxane solution was evaporated, and the reaction product was crystallized. The yield was 0.31 g (59%).

Thiazolothiadiazolethiones IIIc-e. These compounds were similarly obtained.

7-Methyl-2-phenyl-5-(methylthio)thiazolo[4,3-b][1,3,4]thiazolium Perchlorate (IVb) (Table 2). A mixture of 0.53 g (2 mmole) of thione IIIb and 0.74 g (4 mmole) of methyl p-toluenesulfonate was heated at 110°C for 2 h, after which the resulting solid melt was triturated with acetone and ether, and the reaction product was removed by filtration. The yield was 0.72 g (78%). A sample was converted to the perchlorate for analysis.

Salts IVc-e. These compounds were similarly obtained.

7-Methyl-2-phenyl-5-[(3-ethylbenzothiazolin-2-ylidene)methyl]thiazolo[4,3-b][1,3,4]thiadiazolium Iodide (Vb). A mixture of 0.45 g (1 mmole) of 7-methyl-2-phenyl-5-(methylthio)-thiazolo[4,3-b][1,3,4]thiadiazolium tosylate and 0.31 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium iodide was dissolved in 5 ml of absolute alcohol by heating, and 0.1 g (1 mmole) of triethylamine was added. The dye was removed by filtration and washed with alcohol. The yield was 0.32 g (60%).

Monomethylcyanines Vc-e. We obtained similar results.

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