PMR SPECTRA AND ELECTRONIC STRUCTURES OF THE NEUTRAL BASES AND CATIONS OF THIAZOLO[3,2-a]-BENZIMIDAZOLE AND ITS METHYL DERIVATIVES

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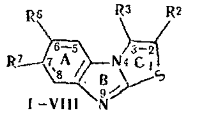
The PMR spectra of the neutral bases and cations of methyl derivatives of thiazolo[3,2-a]-benzimidazole were studied. The dependence of the chemical shifts on the acid concentration was examined. The investigated system is protonated and N-methylated at the N_9 atom. The structure of the conjugated cation corresponds to considerable delocalization of the effective positive charge to the heteroatoms of the thiazole ring. A satisfactory linear correlation between the corrected chemical shifts and the π-electron densities, calculated by the simple MO LCAO method using a coulombic integral for the sulfur atom, $h_{\ddot{S}} = 0.9$, and the parameters of the Pullman system for the remaining heteroatoms, was observed.

We have previously examined the electronic structures, PMR spectra, and reactivities of heteroaromatic systems of the imidazo[5,1-b]benzimidazole type [1]. This paper is devoted to a study of the similar three-ring thiazolo[3,2-a]benzimidazole system:



I–VIII

I $R^2 = R^3 = R^6 = R^7 = H$;
II $R^2 = CH_3$, $R^3 = R^6 = R^7 = H$;
III $R^2 = R^6 = R^7 = H$, $R^3 = CH_3$;
IV $R^2 = R^3 = CH_3$, $R^6 = R^7 = H$;
V $R^2 = R^3 = H$, $R^6 = R^7 = CH_3$;
VI $R^2 = H$, $R^3 = R^6 = R^7 = CH_3$;
VII $R^2 = R^6 = R^7 = CH_3$, $R^3 = H$;
VIII $R^2 = R^3 = R^6 = R^7 = CH_3$

We have measured the PMR spectra of the unsubstituted compound and a number of the corresponding methyl derivatives (II–VIII).* The dependence of the chemical shifts on the acidity of the media was studied, and the parameters of the PMR spectra of the protonated forms of the I and VI molecules were determined. The spectra of the hydrochlorides and methiodides of I, VI, and V were measured. The correlation between the chemical shifts and the PMR spectra of the neutral base and cation of I and the π-electron densities, calculated by the simple MO LCAO method, was examined.

The parameters of the spectra of neutral bases I–VIII are presented in Table 1. The signals of the protons of the thiazole ring (C), which appear as two doublets with a spin–spin coupling constant of 4.5 Hz, are readily isolated in the spectrum of thiazolo[3,2-a]benzimidazole (I). The assignment of these signals to the 2-H and 3-H protons is a consequence of a comparison of the spectrum of I with the spectra of 3- and 2-methyl derivatives (III, VI, II, and VII). The protons of the unsubstituted benzene ring (A) form an ABCD system, the spectrum of which, however, yields to an approximate first-order interpretation. Thus, the two weak-field doublets with a small additional splitting can be ascribed to the 5-H and 8-H protons in the "peri" position relative to the N_4 and N_9 atoms. The second multiplet, which has the form of two overlapped split triplets, is assigned to the 6-H and 7-H protons.

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*See [2] for the methods used to synthesize the compounds.

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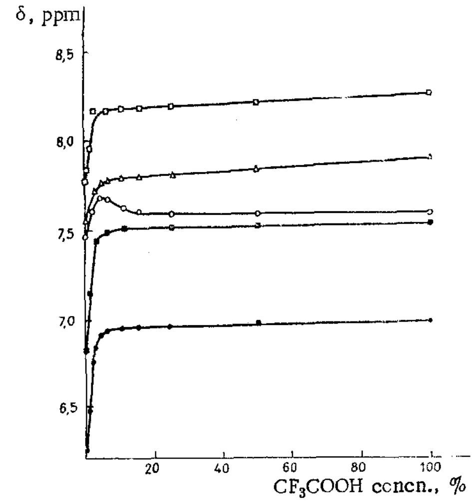


Fig. 1. Dependence of the chemical shifts of the protons on the acid concentration for thiazolo[3,2-a]benzimidazole (I) and 3,6,7-trimethylthiazolo[3,2-a]benzimidazole (VI): ■ for 2-H; □ for 3-H (I); ● for 2-H, Δ for 5-H, and ○ for 8-H (VI).

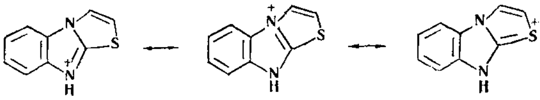
Two singlets of the protons in the 5- and 8-positions are observed in the spectra of V-VIII. The singlet at stronger field is related to 5-H. This assignment follows from the observed shift of this signal to weak field due to the steric effect of the CH_3 group in the 3-position (by comparison of the spectrum of VII with the spectra of VI and VIII).

The shielding of the protons in thiazolo[3,2-a]benzimidazole (I) increases in the order 8-H < 3-H ≈ 5-H < 6-H ≈ 7-H < 2-H. The electron-donor effect of the methyl groups has a considerable effect on the shielding of the adjacent protons but is extremely weakly transmitted from the C ring to the A ring.

The protonation of I and VI was studied in mixtures of methylene chloride and trifluoroacetic acid containing from 0 to 100% of the latter. The greatest changes in the chemical shifts are observed for acid concentrations from 0 to 10% (see Fig. 1). An increase in the acid concentration from 10 to 100% results in relatively small changes in the chemical shifts, and all of the dependences obtained in this region are close to linear. From the character of the changes in the chemical shifts, it can be concluded that both compounds form monocations in trifluoroacetic acid, and a practically completely protonated form is present in 10% acid. The chemical shifts of cations Ib and VIb were obtained by extrapolation of the linear portions of the graphs to zero acid concentration. In Table 2 these values are compared with the chemical shifts of the protons in the spectra of the hydrochlorides (C) and methiodides (D) of I, V, and VI, measured in a mixture consisting of 10% trifluoroacetic acid and 90% methylene chloride. The assignment of the signals to the 5-H and 8-H protons in the cations was made on the basis of a comparison of the spectra of Vb and VIb.

Proceeding from the concepts regarding the π-electron structure of thiazolo[3,2-a]benzimidazole, it can be assumed that the compounds are protonated and N-methylated at the N_9 atom, since the unshared pair of electrons of the heteroatoms in the 1- and 4-positions are part of the aromatic π system, and their participation in salt formation is hindered. These concepts are in agreement with data on the protonation of azaindolizines [3]. The experimental confirmation of salt formation at the N_9 atom in thiazolo[3,2-a]benzimidazoles follows, for example, from a comparison of the spectra of methiodides VD and VID. The close values of the chemical shifts of the protons of the benzene ring (5-H and 8-H) in the spectra of VD and VID indicate that N-methylation of these compounds is directed at the same position. The addition of a CH_3 group to N_4 is apparently excluded, since in VI this is not only energetically unfavorable but also sterically hindered. In addition, the signal of $N\text{-}CH_3$ is found at approximately the same field in the spectra of VD (4.12 ppm) and VID (4.09 ppm). If methylation of V and VI had occurred at N_4, the steric effect of the $C_3\text{-}CH_3$ group in VID would have led to a shift in this signal to weak field.

Protonation of the investigated compounds leads to a shift in the signals of all of the protons to weak field. The greatest changes in the chemical shift are sustained by the protons of the thiazole ring ($\Delta\delta_2$ = 0.65-0.69 ppm, $\Delta\delta_3$ = 0.47 ppm). The shielding of the protons of the benzene ring is considerably less reduced: $\Delta\delta_5$ = 0.24 ppm, $\Delta\delta_8$ = 0.17 ppm. These results indicate that the structure of the conjugated cation of thiazolo[3,2-a]benzimidazole corresponds to considerable delocalization of the positive charge to the heteroatoms of the thiazole ring:



The chemical shifts in the PMR spectra of the base and cation of thiazolo[3,2-a]benzimidazole were compared with the electronic structure indexes calculated by the simple MO LCAO method using several variants of the heteroatom parameters (Table 3).

TABLE 1. PMR Spectra of Thiazolo[3,2-a]benzimidazole and Its Methyl Derivatives in $CDCl_3$

Comp.	R^2	R^3	R^6	R^7	Chemical shifts, ppm										J, Hz			
					2-H	3-H	5-H	6-H	7-H	8-H	$2\text{-}CH_3$	$3\text{-}CH_3$	$6\text{-}CH_3$	$7\text{-}CH_3$	$J_{2,3}$	$J_{2\text{-}CH_3,3}$	$J_{2,3\text{-}CH_3}$	$J_{2\text{-}CH_3,3\text{-}CH_3}$
I	H	H	H	H	6,73	7,61	7,58	7,19		7,70	—	—	—	—	4,5	—	—	—
II	CH_3	H	H	H	—	7,26	7,51	7,23		7,73	2,34	—	—	—	—	2,5	—	—
III	H	CH_3	H	H	6,27	—		7,72 7,19			—	2,65	—	—	—	—	2,5	—
IV	CH_3	CH_3	H	H	—	—		7,66 7,18			2,21	2,45	—	—	—	—	—	1,0
VI	H	CH_3	CH_3	CH_3	6,18	—	7,40	—	—	7,47	—	2,50	2,25	2,25	—	—	2,5	—
VII	CH_3	H	CH_3	CH_3	—	7,18	7,19	—	—	7,49	2,35	—	2,30	2,30	—	2,5	—	—
VIII	CH_3	CH_3	CH_3	CH_3	—	—	7,36	—	—	7,46	2,24	2,46	2,33	2,33	—	—	—	1,0

TABLE 2. Chemical Shifts of Protons of the Neutral Bases (A), Trifluoroacetates (B), Hydrochlorides (C), and Methiodides (D) of Thiazolo[3,2-a]benzimidazoles

Comp.	Comp. form	Medium	Chemical shifts, ppm			
			2-H	3-H	5-H	8-H
I	A	CH_2Cl_2	6,83	7,72	7,7	
	B	CH_2Cl_2/CF_3COOH	7,52	8,19	7,96	7,86
	B	CF_3COOH	7,57	8,28	8,00	7,89
	C	CH_2Cl_2/CF_3COOH	7,51	8,18	7,98	
	D	CH_2Cl_2/CF_3COOH	7,68	8,40	8,12	7,80
V	B	CH_2Cl_2/CF_3COOH	7,42	8,07	7,69	7,63
	B	CF_3COOH	7,52	8,20	7,82	7,63
	D	CH_2Cl_2/CF_3COOH	7,61	8,28	7,85	7,52
VI	A	CH_2Cl_2	6,28	—	7,54	7,47
	B	CH_2Cl_2/CF_3COOH	6,93	—	7,78	7,64
	B	CF_3COOH	7,04	—	7,92	7,64
	C	CH_2Cl_2/CF_3COOH	6,94	—	7,77	7,69
	D	CH_2Cl_2/CF_3COOH	7,13	—	7,83	7,55

TABLE 3. Parameters for the Heteroatoms*

Computation variant†	Coulombic integrals			Band integrals		
	$h_{\ddot{N}}$	$h_{\dot{N}}$	$h_{\ddot{S}}$	$K_{C\ddot{N}}$	$K_{C\dot{N}}$	$K_{C\ddot{S}}$
I	1,5	0,5	0,0	0,8	1,0	0,6
II	1,0	0,4	0,0	0,9	1,0	0,6
III	1,5	0,5	0,9	0,8	1,0	0,6
IV	1,0	0,4	0,6	0,9	1,0	0,6
V	1,0	0,4	0,9	0,9	1,0	0,6

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*A supplementary induction parameter ($h_{C_\alpha} = 0.1h_{\dot{X}}$ and $0.05h_{\ddot{X}}$) was introduced for all of the carbon atoms that form a bond with a heteroatom ($C_\alpha-X$).

† The same parameters, except for the coulombic integral for the N_9 atom, which was taken as $h_{\overset{+}{-N}} = 2.0$ in all of the variants, were used to calculate the cation.

The calculation leads to the following qualitative results that are general for the entire examined interval of heteroatom parameters. The excess π-electron densities are localized on the carbon atoms in the 2-, 3-, 5-, 6-, 7-, and 8-positions; the maximum negative π charges are localized on C_2 and C_3. Protonation of the molecule at N_9 leads to an appreciable stabilization of the π system; the total π-electron energy (E_π) and the delocalization energy (E_D) increase substantially in the cation. Transition from the base to the cation is accompanied by the most significant decrease in the electron density in the thiazole ring (C). Moreover, the bond orders in this ring ($\rho_{1,2}$, $\rho_{1,12}$, $\rho_{3,4}$, and $\rho_{4,12}$) increase, but the bond orders in the imidazole ring (C) ($\rho_{4,10}$, $\rho_{9,11}$, and $\rho_{9,12}$) decrease. These results are in qualitative agreement with the concepts regarding the structure of the conjugated cation based on examination of the spectra.

TABLE 4. Corrections for the Effect of Ring Currents in Thiazolo[3,2-a]benzimidazole, Calculated Relative to the Effect of Ring Currents in Benzene

Position	$\Delta\sigma_{rc}$, ppm	
	base	cation
2	0,02	−0,13
3	−0,34	−0,50
5	−0,82	−0,86
8	−0,71	−0,73

In addition to this, variation of the parameters showed that several qualitative conclusions regarding the distribution of the π-electron density in the system depend on the relative values of the coulombic integrals for the heteroatoms in the 1- and 4-positions.* The dependence is distinctly displayed, particularly in the relative values of the electron density on the carbon atoms of the thiazole ring. Variant I, which takes the maximum difference in the $h_{\ddot{N}}$ and $h_{\ddot{S}}$ values ($\Delta h = 1.5$) into account, leads to the maximum difference in the electron densities on C_2 and C_3, and $q_\pi^{(3)} > q_\pi^{(2)}$. The considerably greater decrease in the electron density on C_3 than on C_2 on passing from the base to the cation also corresponds to this variant. The decrease in the difference between $h_{\ddot{N}}$ and $h_{\ddot{S}}$, regardless of their absolute values, leads to equalization of the π-electron densities on the C_2 and C_3 atoms in the base and to an increase in the fraction of π charge taken up from C_2 on protonation of the molecule. Finally, the redistribution of the π-electron density on the C_2 and C_3 atoms in the neutral molecule [$q_\pi^{(2)} > q_\pi^{(3)}$] and the substantially greater lowering of the electron density on C_2 than on C_3 on passing from the base to the cation correspond to the closest $h_{\ddot{N}}$ and $h_{\ddot{S}}$ values ($\Delta h = 0.1$). Thus, the latter computational variant leads, at least qualitatively, to the best correspondence between the results and the experimental data.

To obtain a more well-grounded selection of parameters for the calculation of the investigated system within the π-electron approximation, we examined the quantitative correlation between the chemical shifts of the protons and the π-electron densities on the adjacent carbon atoms in the base and cation, calculated for each parameter variant. To do this, we proceeded from the general concepts [7] regarding the existence of a linear dependence between the component of the chemical shift of the proton, caused by perturbation of the π-electron system of the molecule, and the "induced" π-electron charge on the adjacent carbon atom:

$$\Delta\sigma_{(\pi)} = a \cdot \Delta q_\pi. \tag{1}$$

The determination of the $\Delta\sigma_{(\pi)}$ values from the experimental values of the chemical shifts, even within a crude approximation that ignores the interaction between the π and σ electrons of the molecules, requires allowance for the steric factors caused by the magnetic anisotropy and electrical fields of the atoms and bonds far removed from the nucleus under consideration. The consideration of these factors in several condensed heteroaromatic systems was examined in detail in [8, 9] and reduces to an approximate estimate of the following effects: 1) the ring currents, 2) the paramagnetic anisotropy and electric field of the dipoles of the unshared pairs of electrons of the heteroatoms, and 3) the electrical field of the π charges of the molecule.

We calculated the ring-current effect from the equation [10]

$$\sigma_{rc} = 0.63 \sum_i K_n{}^i \cdot \left(\frac{a_n{}^i}{a_б}\right)^2 \cdot I_n, \tag{2}$$

where K_n are the values found from the tables of Johnson and Bovey [11] for the corresponding distances of the ring protons from the center of each ring, a_n is the radius of the corresponding ring, a_b is the radius of the benzene ring, I_n is the intensity of the currents in the ring in units of the intensity of the currents in the benzene ring, and 0.63 is an empirical constant [12]. The interatomic distances in the three-ring system were assumed to be equal to the CC and CH bond lengths in benzene. In estimating the intensities of the ring currents we proceeded from the following assumptions. The ratio of the current intensities in the A and B rings of the benzimidazole fragment of the molecule was assumed to be equal to the ratio of the current intensities in six- and five-membered indole (or benzimidazole†) rings, but equal to the ratio of the

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*We felt that it was expedient to carry out the variation within the framework of the standard scales of the Pullman [4] and Streitwieser [5] parameters using also the value $h_{\ddot{S}} = 0.9$ [6]. When this was done, as seen from Table 3, the calculation reduced fundamentally to variation of the coulombic integrals for the heteroatoms in the 1- and 4-positions.

†Aza-substitution has virtually no effect on the ring currents [9, 13].

TABLE 5. Corrections for the Effect of the Field of π Charges in Thiazolo[3,2-a]benzimidazole ($\Delta\sigma_E q_\pi$)

Computational variant	Base				Cation			
	2-H	3-H	5-H	8-H	2-H	3-H	5-H	8-H
I	−0,98	−0,86	0,34	0,13	−1,18	−0,93	0,25	0,19
II	−1,02	−1,04	0,31	0,23	−1,19	−1,09	0,17	0,15
III	−0,63	−0,74	0,21	0,15	−0,82	−0,89	0,24	0,24
IV	−0,71	−0,93	0,24	0,18	−0,86	−1,07	0,24	0,15
V	−0,70	−0,86	0,22	0,15	−0,89	−1,04	0,22	0,23

TABLE 6. Calculated and "Observed" Distribution of π-Electron Density in Thiazolo[3,2-a]benzimidazole

Computa. variant	Comp. form*	Position	$\Delta\sigma^{cor}$, ppm	a_{av}, ppm / charge	Δq^{obs}_{π}	Δq^{cal}_{π}	Mean square deviation
I	N	2	1,49	10,8	−0,138	−0,078	0,043
		3	0,85		−0,079	−0,145	
		5	0,16		−0,015	−0,016	
		8	0,54		−0,050	−0,054	
	C	2	1,05		−0,097	−0,073	
		3	0,50		−0,046	−0,094	
II	N	2	1,53	8,7	−0,176	−0,115	0,031
		3	1,03		−0,118	−0,146	
		5	0,19		−0,022	−0,024	
		8	0,44		−0,051	−0,057	
	C	2	1,06		−0,122	−0,106	
		3	0,66		−0,076	−0,110	
III	N	2	1,14	16,1	−0,071	−0,051	0,017
		3	0,73		−0,045	−0,070	
		5	0,29		−0,018	−0,015	
		8	0,52		−0,032	−0,035	
	C	2	0,69		−0,043	−0,033	
		3	0,46		−0,029	−0,053	
IV	N	2	1,28	12,4	−0,103	−0,086	0,010
		3	0,95		−0,077	−0,086	
		5	0,28		−0,023	−0,021	
		8	0,57		−0,046	−0,042	
	C	2	0,83		−0,067	−0,074	
		3	0,65		−0,052	−0,064	
V	N	2	1,22	13,0	−0,094	−0,085	0,005
		3	0,92		−0,071	−0,063	
		5	0,26		−0,020	−0,021	
		8	0,49		−0,038	−0,040	
	C	2	0,73		−0,056	−0,055	
		3	0,64		−0,049	−0,056	

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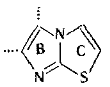
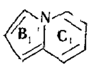
*N is the neutral base, and C is the cation.

current intensities in the B_1 and C_1 rings of the isoelectronic indolisine system in the B and C rings of the imidazothiazole fragment:

$$\frac{i_B}{i_C} \approx \frac{i_{B_1}}{i_{C_1}}$$





Redistribution of the double bond in the imidazothiazole fragment during protonation of the molecule should lead to redistribution of the currents in the B and C rings:

$$\frac{i_C}{i_B} \approx \frac{i_{B_1}}{i_{C_1}}$$

The relative intensities of the ring currents can be found from the relative chemical shifts caused by the ring currents [14]. To estimate these values, we used data on the effect of ring currents in indole and indolisine [9]. By further assuming that the currents in five-membered heteroaromatic rings are close to the currents in benzene [14], we used the following intensities of the currents in the rings of the investigated system (in units of the ring currents in benzene) in the calculation: $I_A = 1.3$, $I_B = 1.0$, and $I_C = 0.9$ in the

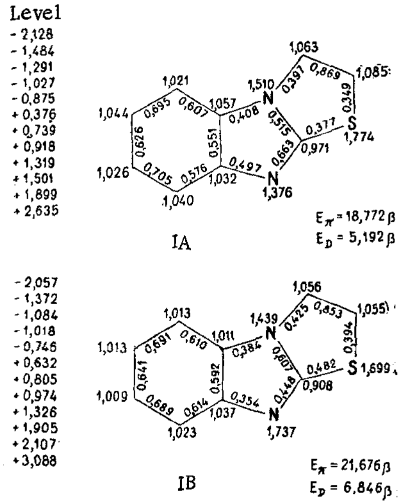


Fig. 2. Molecular diagrams of the neutral base (IA) and cation (IB) of thiazolo[3,2-a]benzimidazole (see Table 3, variant V, for the parameters).

base, and $I_A = 1.3$, $I_B = 1.0$, and $I_C = 1.1$ in the cation. The chemical shifts caused by the ring currents and calculated from Eq. (2) are presented in Table 4.

Evaluation of the contributions of magnetic anisotropy and the electrical field of the dipoles of the unshared pairs of electrons of the heteroatoms in complex systems is extremely problematic. Since the unshared pairs of heteroatoms in the 1- and 4-positions are a part of a conjugated π system, it can be assumed that the contribution of the paramagnetic anisotropy of these atoms is relatively small, while the electrical field effect, which depends on the degree of delocalization of the electron pairs, is taken into account in the calculation of the effect of the field of the π charges of the molecule. The calculation of the effect of the magnetic anisotropy of the nitrogen atom of the "pyridine" type (N_9) is complicated because of the absence of experimental data on the energies of the n → π* transitions in the investigated compounds. Since the experimental values of these energies in condensed nitrogen-containing heterocycles usually range from 3.2 to 3.8 eV [15], one can take $\Delta E^{n\to\pi^*} = 3.5$ eV for rough estimates. Under this assumption, our calculation by the Pople method [16]† led to the following values of the paramagnetic components of the tensor of local susceptibility on the N_9 atom ($\cdot 10^{-6}$):

$$(\chi_{N}{}^{p})_{zz}=6.4;\quad (\chi_{N}{}^{p})_{xx}=16.2;\quad (\chi_{N}{}^{p})_{yy}=9.9.$$

In the dipole approximation, the effect of paramagnetic anisotropy of the N_9 atom leads to deshielding of the 8-H proton in the neutral molecule by a factor of $\Delta\sigma_{\chi}^{N} = -0.21$ ppm and has virtually no effect on the chemical shifts of the remaining protons.

Taking the dipole moment of the unshared pair of electrons of the N_9 atom as 1.6 D and placing the center of the dipole at a distance of 1 Å from the nitrogen atom [8, 9], we estimated the electrical field effect, which also makes a substantial contribution only to the shielding of the proton in the 8-position ($\Delta\sigma_{E}^{N} = -0.19$ ppm).

The effect of the field of π charges of the molecule was calculated from the equation

$$\Delta\sigma_E(q_\pi) = -13.92\cdot 10^{-6}\sum_i \Delta q_\pi{}^i\cdot r_i{}^{-2}\cdot\cos\alpha_i + 17.05\cdot 10^{-6}\sum_i (\Delta q_\pi{}^i\cdot r_i{}^{-2})^2, \tag{3}$$

obtained from the general Buckingham equation [18] with Muscher coefficients [19]. The results are presented in Table 5.

The $\Delta\sigma^{cor}$ values were calculated (with allowance for the above examined effects) from the experimental values of the chemical shifts of the protons of the base (2-H, 3-H, 5-H, and 8-H) and the cation (2-H and 3-H) of thiazolo[3,2-a]benzimidazole (I), found relative to the chemical shifts of the protons in benzene (7.26 ppm) measured under similar conditions. The average values of the a coefficient in Eq. (1) for each of the computational variants were found from the ratio between these values and the π-electron charges on carbon atoms in the corresponding positions of the neutral molecule and cation. The calculated (Δq_π^{cal}) and "observed" (Δq_π^{obs}) π-electron charges calculated from Eq. (1) are compared in Table 6. The a_{av} values for all of the computational variants lie in a reasonable interval of values (8.7-16.1 ppm/charge). The "observed" distribution of π-electron density in the neutral base, found for the entire range of a_{av} values, corresponds to the sequence

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† The computational procedure is described in detail in [8, 9, 17]. In our calculation we used the average value of the energy of excitation for the remaining transitions ($\Delta E_{av} = 10$ eV) and the averaged values of the matrix elements of the charges and bond orders calculated for all parameter variants.

$$\Delta q_{\pi(2)} > \Delta q_{\pi(3)} > \Delta q_{\pi(8)} > \Delta q_{\pi(5)}.$$

Only variant V, which involves the use of the coulombic integrals for the S_1 and N_4 atoms that are closest in value, leads to the same sequence of relative π-electron densities. The quantitative correlation between the calculated and "observed" π-electron densities improves successively as the difference between $h_{\ddot{N}}$ and $h_{\ddot{S}}$ decreases. The mean square deviation of the Δq_{π}^{cal} values from Δq_{π}^{obs} decreases by one order of magnitude in the examined range of $\Delta h_{\ddot{N},\ddot{S}}$ values (0.1-1.5).

Thus the results of the calculation obtained using the Streitwieser parameters [5] (Table 3, variant I) are in poorest agreement with the relative chemical shifts of the protons in the base and cation of thiazolo-[3,2-a]benzimidazole (I). Variation of the coulombic integral for the sulfur atom within the framework of the scale of the Pullman parameters [4] (Table 3, variants II, IV, and V) leads to completely satisfactory correlation between the π-electron densities and the chemical shifts for $h_{\ddot{S}} = 0.9$. The molecular diagrams, energy levels, and delocalization energies of the neutral molecule and cation of I, calculated for this parameter variant, are presented in Fig. 2. It should be noted that the relative values of the corresponding indices of electronic structure in the base and cation, calculated with these parameters, agree satisfactorily with the observed changes in the PMR spectra on protonation of the investigated compounds.

EXPERIMENTAL

The PMR spectra of solutions in deuterochloroform, methylene chloride, and methylene chloride–trifluoroacetic acid containing various amounts of trifluoroacetic acid (from 0 to 100 vol.%) were measured with a JNM-4H-100 spectrometer. All of the measurements were made at the same concentration of the investigated substance in solution (0.17 M). The chemical shifts were measured on the δ scale relative to tetramethylsilane as the internal standard.

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