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TETRAKIS(THIADIAZOLO)PORPHYRAZINES. 3*. ACID–BASE PROPERTIES AND STABILITY OF TETRAKIS-3,4-(1,2,5-THIADIAZOLO)-PORPHYRAZINE IN SULFURIC ACID SOLUTIONS

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AM1 calculations gave the proton affinities of different types of donor sites in tetrakis-3,4-(1,2,5-thiadiazolo)porphyrazine, $H_2\{[SN_2)_4PA\}$, and protonation of the meso-nitrogen atoms was found to be favored. A spectrometric study showed that the basicity of the meso-nitrogen atoms of the porphyrazine macrocycle is strongly diminished and these atoms in CF_3CO_2H are involved in an incomplete acid–base interaction (ABI) to give acid solvates, while a complete ABI (protonation) is found only in the presence of sulfuric acid. The basicity constants of the meso-nitrogen atoms were determined spectrophotometrically in $CF_3CO_2H–H_2SO_4$. The kinetics of decomposition of the macrocyclic chromophore in concentrated sulfuric acid was studied and a possible mechanism for this process was proposed.

Keywords: porphyrazines, 1,2,5-thiadiazole, AM1 calculations, basic properties, proton affinity, electronic absorption spectra.

Porphyrazines (H_2PA) are compounds with multiple basic sites, in which the donor sites, namely, two internal pyrrolenine nitrogen atoms and four bridging *meso*-nitrogen atoms, are found in a single conjugated macrocyclic π-system and their basic properties are highly interrelated and mutually dependent [3, 4]. Additional donor sites also capable of participating in an acid–base interaction (ABI) appear in the conjugated system upon the fusion of nitrogen heterocycles in the β,β-positions of the pyrrole rings as found, for example, in known tetra(pyridino)- or tetra(pyrazino)porphyrazines, $H_2\{(Py)_4PA\}$ and $H_2\{(Pyz)_4PA\}$ [5]. In recent work [1], we obtained the first porphyrazine with fused 1,2,5-thiadiazole rings, namely, tetrakis-3,4-(1,2,5-thiadiazolo)porphyrazine, $H_2\{(SN_2)_4PA\}$ (Fig. 1). In the present work, we studied the basic properties of this compound.

$H_2\{(SN_2)_4PA\}$ has very low solubility in neutral solvents such as chlorobenzene and dichloromethane. The solubility is significantly enhanced in basic or proton-donor solvents due to strong specific solvation of acidic and basic sites in this molecule. Thus, very strong solvation of the N–H bonds is found in pyridine, leading to formation of a pyridinium salt, $2Py\cdot H_2\{(SN_2)_4PA\}$ [1].

* Communications 1 and 2, see ref. [1, 2].

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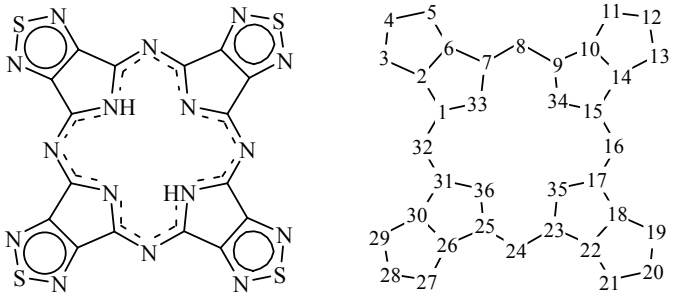

Fig. 1. Structural formula of tetrakis-3,4-(1,2,5-thiadiazolo)porphyrazine, $H_2\{(SN_2)_4PA\}$, and numbering system used.

The solubility is enhanced in proton-donor media (carboxylic acids) due acidic solvation of the donor nitrogen atoms (the intracyclic pyrrolenine (N_{pyr}), *meso*-nitrogen (N_{meso}), and thiadiazole nitrogen atoms (N_{het}). In strong proton-donor media such as mineral acids, proton transfer to a donor site within the solvation shell can occur through transsolvation to give hydrogen-bonded associated species and ion–ion associated species (complete ABI) and dissociation of the ionic associated species to give an ionized protonated form along with acid solvation (incomplete ABI):

$$\underset{}{B: + HA} \rightleftharpoons \underset{\substack{\text{acidic}\\\text{associated}\\\text{species}}}{B{:}\cdots HA} \rightleftharpoons \underset{\substack{\text{hydrogen-bonded}\\\text{associated}\\\text{species}}}{B{:}\cdots H^{\delta+}\cdots A^{\delta-}} \rightleftharpoons \underset{\substack{\text{ion-ion}\\\text{associated}\\\text{species}}}{B{:}H^{+}\cdots A^{-}} \rightleftharpoons \underset{\text{protonated form}}{B{:}H^{+} + A^{-}}$$

Since all the acidic and basic sites of $H_2\{(SN_2)_4PA\}$ are found in a single macrocyclic π-chromophore, ABI processes strongly affect the shape and position of the bands in the electronic absorption spectra (EAS). A study of the dependence of the EAS of porphyrazines on acidity and ionizing capacity of the solvent permitted us to localize the ABI processes and measure the basic properties [3, 6].

The EAS of $H_2\{(SN_2)_4PA\}$ in neutral solvents show a splitted *Q*-band ($\lambda(Q_x)$ = 653, $\lambda(Q_y)$ = 641 nm), which is typical for porphyrazines with D_{2h} symmetry of the π-chromophore (Fig. 2, spectrum *1*). The splitting $\Delta E(Q)$ = 290 cm^{-1} is much less than in unsubstituted H_2PA or phthalocyanine H_2Pc ($\Delta E(Q)$ = 2180 and 730 cm^{-1}, respectively [7]). This discrepancy is attributed to the strong electron-withdrawing effect of the fused thiadiazole fragments and, as a consequence, strengthening of the intramolecular hydrogen bonds in the internal cavity of the macrocycle. No splitting of the long-wavelength *Q*-band is found in the EAS of the pyridinium salt $2Py{\cdot}H_2\{(SN_2)_4PA\}$ (Fig. 2, spectrum *2*) and this EAS becomes similar to the corresponding spectra of metal complexes with D_{4h} symmetry.

The EAS of solutions of $H_2\{(SN_2)_4PA\}$ in formic acid and trifluoroacetic acid (Fig. 2, spectrum *3*) feature a slight hypsochromic shift of the *Q*-bands ($\lambda(Q_x)$ = 647, $\lambda(Q_y)$ = 634 nm in formic acid and $\lambda(Q_x)$ = 645, $\lambda(Q_y)$ = 629 nm in CF_3CO_2H) and increase in $\Delta E(Q)$ = 320-390 cm^{-1}. The maximum of the *Q*-band in concentrated aqueous sulfuric acid (Fig. 2, curve *4*) is shifted bathochromically to $\lambda(Q_x)$ = 661-662 nm and $\lambda(Q_y)$ = 639-641 nm ($\Delta E(Q)$ = 470 cm^{-1}). When the sulfuric acid concentration is increased from 90 to 100%, the Q_y band becomes less pronounced and converts to a shoulder (Fig. 2, spectrum *5*). In 35% oleum, the *Q*-band maximum is shifted further bathochromically to 676 nm (Fig. 2, spectrum *7*). In chlorosulfonic acid, the *Q*-band is broadened and has a maximum at about 670 nm (Fig. 2, spectrum *6*).

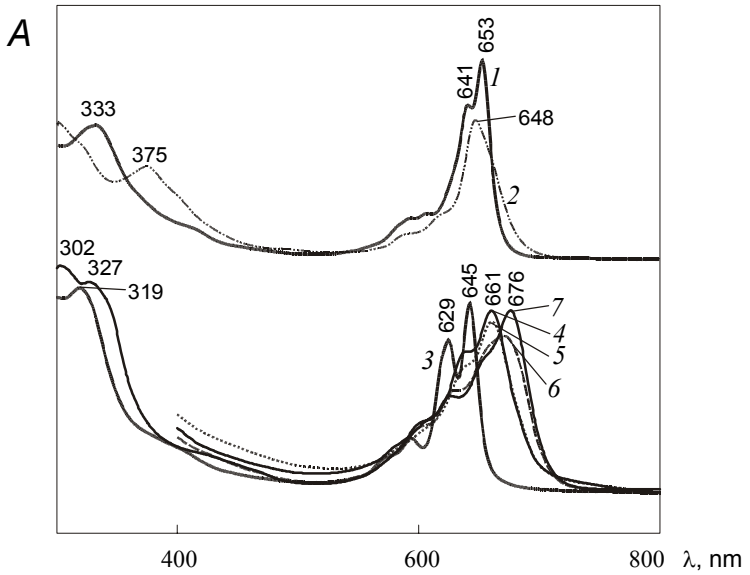

Fig. 2. EAS of $H_2\{(SN_2)_4PA\}$ in chlorobenzene (*1*), pyridine (*2*), CF_3CO_2H (*3*), (*c* 96%) aqueous H_2SO_4 (*4*), 100% H_2SO_4 (*5*), $ClSO_3H$ (*6*), and 35% oleum (*7*).

We should note that the macrocycle is unstable in concentrated aqueous sulfuric acid and undergoes rapid decomposition to give colorless products (Fig. 3). The rate of decomposition is virtually independent of the sulfuric acid concentration in the range from 92 to 98% (see Table 1). However, the stability of macrocycle becomes much greater in 100% H_2SO_4 and, especially, in oleum.

The spectral changes occurring upon ABI with the donor sites in the porphyrazine molecule are described qualitatively rather well using a simple four-orbital model for the EAS of protonated porphyrazine species [3, 6]. According to this model, complete ABI with the *meso*-nitrogen atoms N_{meso} in porphyrazines should lead to a bathochromic shift of the *Q*-bands. A hypsochromic shift may be observed theoretically upon protonation of the internal cyclic pyrrolenine nitrogen atoms N_{pyr}, as, for example, in the case of porphyrins and their *meso*-monoaza derivatives [3, 4, 6].

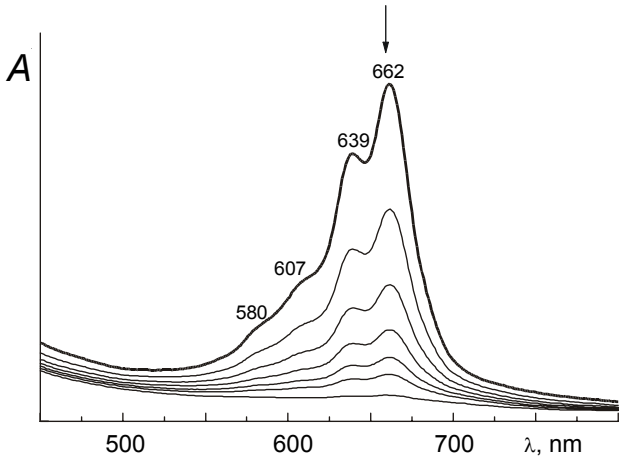

Fig. 3. Change in EAS of a solution of $H_2\{(SN_2)_4PA\}$ in aqueous H_2SO_4 (*c* 94%) over time.

TABLE 1. Kinetic Parameters of the Decomposition of $H_2\{(SN_2)_4PA\}$ in Concentrated Aqueous H_2SO_4

Concentration of H_2SO_4, %	Concentration of H_3O^+, mol/l	log $[H_3O^+]$	T, K	$k_{ef} \cdot 10^3$, s^{-1}	E_a, kJ/mol	$-\Delta S^{\neq}$, J/(mol·K)
92.03	6.62	0.82	288	4.17 ± 0.07	47 ± 3	135 ± 10
			298	8.41 ± 0.45		
			308	14.93 ± 1.43		
92.90	6.14	0.79	288	4.41 ± 0.15	47 ± 7	135 ± 14
			298	9.41 ± 0.94		
			308	15.78 ± 0.95		
93.75	5.72	0.75	288	4.29 ± 0.27	50 ± 5	125 ± 17
			298	9.21 ± 0.87		
			308	16.59 ± 0.49		
94.47	5.27	0.72	288	4.55 ± 0.01	47 ± 1	133 ± 2
			298	8.86 ± 0.54		
			308	16.52 ± 0.43		
95.61	4.4	0.64	288	4.75 ± 0.11	43 ± 9	150 ± 25
			298	9.77 ± 0.36		
			308	15.04 ± 0.61		
96.68	3.5	0.54	288	4.58 ± 0.17	44 ± 8	145 ± 23
			298	9.50 ± 0.62		
			308	15.12 ± 0.75		
97.78	2.22	0.34	288	4.58 ± 0.11	46 ± 2	138 ± 7
			298	8.61 ± 0.43		
			308	15.93 ± 0.61		
Mean value			288	4.47 ± 0.39	46 ± 9	137 ± 30
			298	9.11 ± 1.02		
			308	15.70 ± 0.89		

However, in this case, the splitting of the *Q*-band should be diminished (monoprotonation) or disappear entirely due to enhanced symmetry of the π-chromophore. Furthermore, as noted recently for diazaporphyrins and porphyrazines [4], a bathochromic shift of the *Q*-band is found rather than a hypsochromic shift upon the protonation of two N_{pyr} atoms to give a symmetrical dication. This behavior is in contrast to findings for porphyrins themselves. A hypsochromic shift of the *Q*-band may result from ABI with the nitrogen atoms of the thiadiazole fragments N_{het}, since it enhances their electron-withdrawing effect on the porphyrazine macrocycle. However, the acidic properties of HCO_2H and CF_3CO_2H with Hammett acid function H_0 = -2.22 and -3.03, respectively [8, 9] are clearly insufficient for protonation of the thiadiazole nitrogen atoms (pK_a = -4.9 for 1,2,5-thiadiazole [10]). Thus, only incomplete ABI with all the donor sites is presumably observed in 100% CF_3CO_2H, *e.g.*, the acid solvation of these sites, which is accompanied by a solvatochromic effect (hypsochromic shift) and leads to weakening of the intramolecular hydrogen bonding (increased splitting of the *Q*-band). It is interesting to note that the presence of water in CF_3CO_2H enhances the solvatochromic effect. Thus, if the commercial sample of CF_3CO_2H is not additionally purified by distillation over concentrated sulfuric acid, the Q_x-band is observed at 642 nm, while the Q_y-band is found at 624 nm ($\Delta E(Q)$ = 450 cm^{-1}).

We performed a spectrophotometric titration of $H_2\{(SN_2)_4PA\}$ in CF_3CO_2H–H_2SO_4. Increased acidity produced by adding sulfuric acid to CF_3CO_2H leads to a bathochromic shift of the *Q*-bands ($\lambda(Q_x)$ = 657, $\lambda(Q_y)$ = 634 nm, $\Delta E(Q)$ = 550 cm^{-1}). Clear isosbestic points are also observed (Fig. 4). This type of spectral evolution indicates complete ABI (protonation) at one of the *meso*-nitrogen atoms under these conditions.

Localization of the first step in the protonation of $H_2\{(SN_2)_4PA\}$ on one of the *meso*-atoms is also indicated by the results of a quantum-chemical calculation. The semiempirical AM1 method has been used to calculate heats of formation and proton affinities of various nitrogen compounds [11, 12]. We used this method

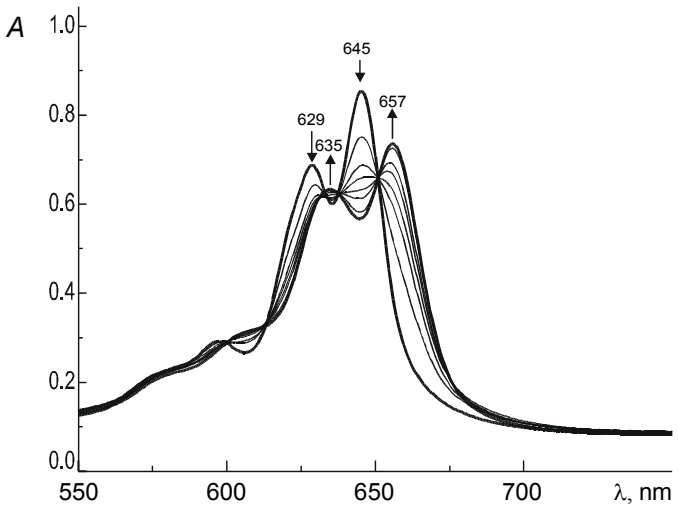

Fig. 4. Change in the EAS of $H_2\{(SN_2)_4PA\}$ in CF_3CO_2H–H_2SO_4 with H_0 = -3.03, -3.4, -3.92, -4.09, -4.21, -4.83, -5.28.

to compare the stabilities of monoprotonated forms of $H_2\{(SN_2)_4PA\}$ (Table 2). We found that the protonation at one of the *meso*-nitrogen atoms in the first ABI step (Fig. 5a) is favored over protonation at the thiadiazole nitrogen atoms (by 22 and 39 kJ/mol for the thiadiazole rings fused to the pyrrole (Fig. 5b) and pyrrolenine rings, respectively). Protonation of the intracyclic pyrrolenine nitrogen atoms N_{pyr} is also less advantageous (by 31 kJ/mol) than at a *meso*-nitrogen atom and, furthermore, leads to a breakdown in the planarity of the macrocycle (Fig. 5c). We should note that the calculation results indicate that the proton affinity of the *meso*-nitrogen atoms of the porphyrazine macrocycle is reduced by 37 kJ/mol upon fusion of the 1,2,5-thiadiazole fragments, while the thiadiazole nitrogen atoms increase their basicity by 16 kJ/mol. The proton affinities of various porphyrazines calculated for the gas phase are in good accord with the experimental data for solutions in proton-donor media.

Using known Hammett acidity functions H_0 for H_2SO_4–CF_3CO_2H [9, 13, 14], we determined the basicity constant for a *meso*-nitrogen atom in $H_2\{(SN_2)_4PA\}$, pK_{a1} = -4.06±0.15. The tangent to the curve describing the logarithm of $\log I_n$ *vs*. H_0 is close to unity (tan α = 1.02), which indicates the involvement of only one donor site in the complete ABI in this step. The value found for pK_{a1} for $H_2\{(SN_2)_4PA\}$ is less than the corresponding value for unsubstituted porphyrazine H_2PA (pK_{a1} = +0.15 [15]) and phthalocyanine H_2PctBu_4 (pK_{a1} = +0.86 [16]). These findings are in accord with the calculated proton affinities of these compounds and indicate that the fused 1,2,5-thiadiazole fragments, in contrast to benzene rings, have a strong electron-withdrawing effect on the porphyrazine macrocycle. On the other hand, the value of p*K*a1 for $H_2\{(SN_2)_4PA\}$ is higher than for tetrakis(2,3-pyridino)porphyrazine $H_2\{(2,3Py)_4PA\}$ (pK_{a1} = -8.2 [17, 18]). This result is related to the circumstance that protonation of the nitrogen atoms of the fused heterocycles precedes protonation of the *meso*-nitrogen atoms of the porphyrazine macrocycle (pK_a = +5.21 for pyridine *vs*. pK_{a1} = -4.9 for 1,2,5-thiadiazole) for $H_2\{(^{2,3}Pyr)_4PA\}$, in contrast to $H_2\{(SN_2)_4PA\}$ and the value of pK_{a1} = -8.2 characterizes, in essence, the basicity of the *meso*-nitrogen atoms in the tetracation of $H_2\{(^{2,3}PyH^+)_4PA\}$. The calculation results for $H_2\{(^{2,3}Py)_4PA\}$ indicate that the proton affinity of the pyridine nitrogen atoms is higher than for the *meso*-nitrogen atoms (Table 2).

ABI with the nitrogen atoms of the fused 1,2,5-thiadiazole fragments probably becomes possible in media with H_0 < -7, i.e., when the concentration of H_2SO_4 in CF_3CO_2H is greater than 1 mol/l and in aqueous sulfuric acid (*c* > 80%). This is reflected in the EAS by broadening, loss of structure, and a slight bathochromic shift of the *Q*-band maximum from 657 to 662 nm. The instability of the macrocyclic chromophore in this acid form, especially in aqueous sulfuric acid (*c* 80-98%) is also probably related to

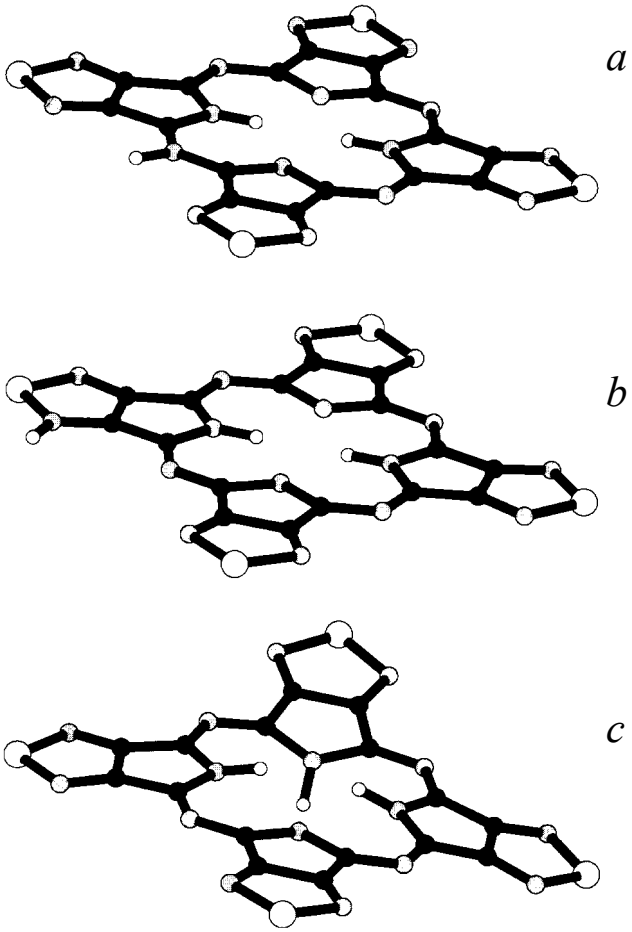

Fig. 5. Structure of monoprotonated forms of $H_2\{(SN_2)_4PA\}$ optimized by an AM1 calculation: *a*) 8,33,35-$H_2\{(SN_2)_4PA\}H^+$, *b*) 3,33,35-$H_2\{[(SN_2)_4H]PA\}^+$, *c*) 33,34,35-$H_3\{(SN_2)_4PA\}^+$.

protonation of the thiadiazole rings. The decomposition reaction is first-order relative to porphyrazine concentration but its effective rate constant (k_{ef}) is virtually independent of the concentrations of sulfuric acid and the hydroxonium ion, H_3O^+. The decomposition of the porphyrazine macrocycle in aqueous sulfuric acid usually proceeds as a hydroprotolytic reaction and its rate increases with increasing concentration of the H_3O^+ ion, i.e., with a decrease in the sulfuric acid concentration in the Brand region (90-98%). The decomposition reaction is second-order relative to H_3O^+ for H_2PA [19], third-order for $H_2\{(^{2,3}Py)_4PA\}$ [18], and fourth-order for H_2Pc [20]. Berezin [20] considers that the rate-limiting step for the hydroprotolytic decomposition of the porphyrazine macrocycle is attack of the hydroxonium ion at the α-carbon atom of the pyrrole rings. We may presume that the observed differences in the kinetics of the decomposition of the macrocycle in $H_2\{(SN_2)_4PA\}$ are related the circumstance that the rate-limiting step in this case is cleavage of the protonated 1,2,5-thiadiazole ring accompanied by further rapid decomposition of the porphyrazine macrocycle. Indeed, the effective rate constant for the decomposition of $H_2\{(SN_2)_4PA\}$ in 92-98% sulfuric acid, k_{ef}^{298} is 2-15 times less than for H_2PA under the same conditions. In contrast, the rate of decomposition of the macrocycle in H_2Pc and $H_2\{(^{2,3}Py)_4PA\}$, in which the fused rings are resistant to cleavage, is 3-5 orders of magnitude less than for $H_2\{(SN_2)_4PA\}$. We should note that the decomposition of the porphyrazine macrocycle in $H_2\{(SN_2)_4PA\}$ is characterized by lower activation energy (E_a = 46±9 kJ/mol) and more negative activation entropy ($\Delta S^{\neq}$ = -137±30 J/(mol·K)) than

TABLE 2. Calculated and Experimental Basicity Parameters for Porphyrazines: Heats of Formation (ΔH_f) and Proton Affinity (ΔH_{BH+}) from an AM1 Calculation and Experimental Basicity Constants pK_a.

Base and its protonated form	Heat of formation ΔH_f, kJ/mol	Proton affinity ΔH_{BH+}, kJ/mol	Localization of ABI	Base constant pK_a
1,2,5-Thiadiazole	207.9			-4.9
1,2,5-Thiadiazolium	912.6	831.7	N_{het}	
H_2PA	1174.6			-0.15
H_2PAH^+	1804.1	906.9	N_{meso}	
H_2Pc	1332.1			+0.86
H_2PcH^+	1926.8	941.7	N_{meso}	
33,35-$H_2\{(SN_2)_4PA\}$	1994.3			-4.06
8,33,35-$H_2\{(SN_2)_4PA\}H^+$	2660.6	866.7	N_{meso}	
33,34,35-$H_3\{(SN_2)_4PA\}^+$	2691.6	839.0	N_{pyr}	
3,33,35-$H_2\{[(SN_2)_4H]PA\}^+$	2682.8	847.8	N_{het}	
11,33,35-$H_2\{[(SN_2)_4H]PA\}^+$	2700.0	830.6	N_{het}	
$H_2\{(^{2,3}Py)_4PA\}$	1547.5			-8.2
$H_2\{(^{2,3}Py)_4PA\}H^+$	2155.1	928.8	N_{meso}	
$H_2\{[(^{2,3}Py)_4H]PA\}^+$	2145.7	938.1	N_{het}	

found for H_2PA (E_a = 65 kJ/mol, $\Delta S^{\neq}$ = -103 J/(mol·K) [19]). This result indicates the enhanced importance of solvation and is in accord with the proposed mechanism, in which the rate-limiting step is cleavage of the protonated thiadiazole ring in the acid solvate.

Despite the lack of dependence of the decomposition rate on the hydroxonium ion concentration, the presence of such ions in the reaction medium and, thus, in the solvation shell of the macrocycle, is necessary both for cleavage of the 1,2,5-thiadiazole fragment and the subsequent decomposition of the porphyrazine macrocycle. The macrocycle in $H_2\{(SN_2)_4PA\}$ is stable in chlorosulfonic acid and oleum, in which, in contrast to aqueous sulfuric acid, there are no H_3O^+ ions. Under these conditions, protonation of a second *meso*-nitrogen atom becomes possible, leading to a bathochromic shift of the *Q*-band to 676 nm (Fig. 2, spectra 4-7). Using the values of the acidity function H_0 for these media gave pK_{a2} = -13±1. The difference between pK_{a1} and pK_{a2}, characterizing protonation of the first and second *meso*-nitrogen atoms in $H_2\{(SN_2)_4PA\}$, is 10 orders of magnitude, in contrast to only 2-3 orders of magnitude for phthalocyanines. This results from protonation of the thiadiazole nitrogen atoms in intermediate steps.

Thus, we have experimentally found that 1,2,5-thiadiazole fragments, displaying pronounced σ- and π-electron-withdrawing properties relative to the porphyrazine macrocycle, have a significant effect on the acid–base properties of this macrocycle, leading to enhanced acid properties of the intracyclic N–H bonds and sharp drop in the basicity of the *meso*-nitrogen atoms.

EXPERIMENTAL

A sample of tetrakis-3,4-(1,2,5-thiadiazolo)porphyrazine, $H_2\{(SN_2)_4PA\}$, was prepared according to our previous procedure [1].

A series of solutions was prepared for the spectrophotometric titration with concentration 10^{-5} M $H_2\{(SN_2)_4PA\}$ in acid media with different acidity, CF_3CO_2H–H_2SO_4, oleum, and chlorosulfonic acid. Chemically-pure grade oleum and 96% sulfuric acid were used to prepare 100% sulfuric acid by the conductometric method. Pure-grade samples of chlorosulfonic acid and trifluoroacetic acid were distilled (CF_3CO_2H was distilled over 96% H_2SO_4 to dry the sample). The prepared solutions were placed in a cell at

constant 298 K and the EAS were taken on a Hitachi U-2000 spectrophotometer. The basicity constants pK_{ai} were calculated using the Hammett formula using the optical density at the wavelength of the absorption maximum of the neutral (or acid) form and the ratio $I_n = (A_0 - A)/(A - A_\infty)$:

$$pK_{ai} = H_0 + \log I_n.$$

The acidity functions H_0 for the acid media were taken from Pal'm [21].

In the study of the decomposition kinetics, a sample of $H_2\{(SN_2)_4PA\}$ was dissolved in aqueous H_2SO_4 (*c* 92-98%) and the solution was placed in a spectrophotometric cell. After prior thermostatting, the time dependence of the change in optical density at the long-wavelength absorption band was measured. The effective decomposition rate constant was calculated using the following equation:

$$k_{ef} = (1/\tau)\ln[(A - A_\infty)/(A_0 - A_\infty)].$$

The quantum-chemical calculations were performed using the Hyperchem 4.5 program. The geometrical structure of the starting molecule was initially optimized by the MM^+ molecular mechanics method. Then, final optimization was carried out by a semiempirical AM1 calculation in the unlimited Hartree–Fok basis and the heat of formation $\Delta H_f(B)$ was found. The optimization conditions (convergence limit $4.18\cdot10^{-4}$ kJ/mol, gradient $4.18\cdot10^7$ kJ/mol·m) were achieved using the Polak–Ribiere method. The calculation for $\Delta H_f(BH^+)$ was carried out analogously for various monoprotonated forms. The proton affinity ΔH_{BH+} was determined using the following formula [11, 12]:

$$\Delta H_{BH+} = \Delta H_f(H^+) + \Delta H_f(B) - \Delta H_f(BH^+).$$

In this case, as in the work of Dewar [11, 12], the experimental value $\Delta H_f(H^+)$ = 1534.9 kJ/mol was used.

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