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Proton-Transfer Complexes of β-Substituted β,β-Fused Tetraazaporphyrins

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Abstract—The problems concerning the formation of complexes with proton transfer of β-substituted β,β-fused tetraazaporphyrins in a system dimethyl sulfoxide–chlorobenzene (benzene) are considered. The problems of their structure are discussed. The reactivity of the proton-transfer tetraazaporphyrin complexes in the reaction with metal acetates was studied. The stability of the proton-transfer tetraazaporphyrin complexes depending on the basicity of the environment and the nature of the substituents in the macrocycle is analyzed.

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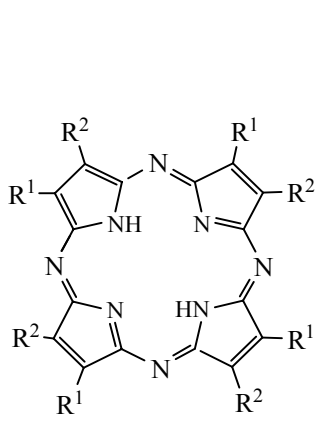
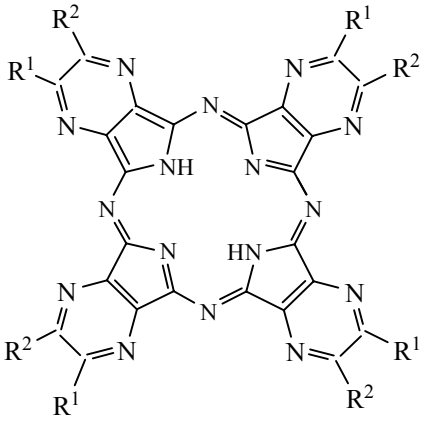
Tetraazaporphyrins represent a new class of macrocyclic compounds becoming more widely used in nonlinear optics, catalysis, redox processes, and medicine due to their unusual structure and unique properties. They exhibit semiconductor and liquid crystal properties and are considered as promising materials in sensor devices. A thorough examination of the state of tetraazaporphyrins in various media largely determines not only their successful practical application, but also permits expanding the range of useful properties of these macrocycles.

Thanks to the acid properties of the endocyclic NH-bonds, tetraazaporphyrins in a proton-acceptor environment enter into the interactions with organic bases not typical of porphyrins, to form complexes with proton transfer. These complexes vary by kinetic stability and reactivity in the reactions with metal salts.

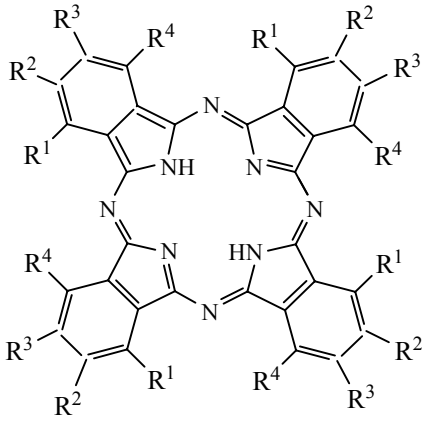
The laws of the formation of the proton transfer complexes in the system of tetraazaporpyrin–dimethylsulfoxide–chlorobenzene (benzene). The acid–base interaction of β-substituted tetraazaporphyrins [H_2TapR], and β,β-fused tetraazaporphyrins [H_2Tap(Pyz)$_4$R], [H_2Pc(NO$_2$)$_4$(*t*-Bu)$_4$] with dimethyl sulfoxide (DMSO) in chlorobenzene (benzene) is observed only in the conditions of considerable excess of DMSO [1–7].



[H_2TapR]



[H_2Tap(Pyz)$_4$R]



[H_2Pc(NO$_2$)$_4$(*t*-Bu)$_4$]

R^1 = H, R^2 = Br [H_2TapBr$_4$]; R^1 = H, R^2 = Cl [H_2TapCl$_4$]; R^1 = R^2 = 4-NO$_2$-C$_6$H$_4$ [H_2Tap(C$_6$H$_4$NO$_2$)$_8$]; R^1 = *t*-Bu, R^2 = H [H_2Tap(Pyz-*t*-Bu)$_4$]; R^1 = R^2 = Ph [H_2Tap(PyzPh$_2$)$_4$]; R^1 = R^2 = Et[H_2Tap(PyzEt$_2$)$_4$]; R^1 = NO$_2$, R^2 = R^4 = H, R^3 = *t*-Bu.

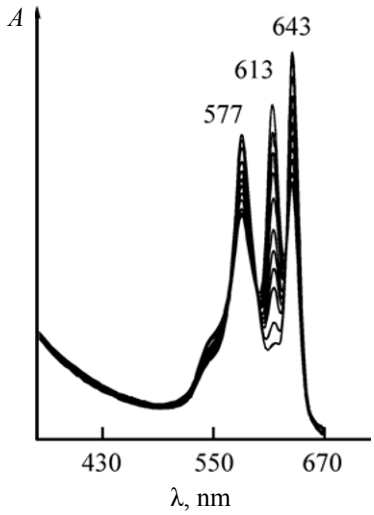


Fig. 1. Changes in the electron absorption spectrum of H_2TapBr_4 in the presence of DMSO within 20 min at c_{DMSO} 2.58 M in chlorobenzene and T = 323 K.

The spectral changes accompanying these reactions do not depend on the nature of the substituents in the macrocycle, nor on the nature of the solvent (Fig. 1). They point to a change in the symmetry of the H_2TapR, $H_2Tap(Pyz)_4R$ and $H_2Pc(NO_2)_4(t\text{-}Bu)_4$] as a result of changes in energy of the molecular π-orbitals [8]. In the process of acid–base interactions involving tetraazaporphyrins the energies of the lowest unoccupied molecular orbital π_1* and the highest occupied molecular orbital π_1 increases, while the energies of the highest occupied molecular orbital π_2 and lowest unoccupied molecular orbital π_2* do not undergo significant changes. The reduced energy difference between the highest occupied molecular orbitals π_1 and π_2, and degeneration of the two lowest unoccupied molecular orbitals $\pi_{1,2}$* (Fig. 2) leads to an increase in the effective symmetry of the π-chromophore of the molecule from D_{2h} to D_{4h} (Fig. 1). This indicates that the β-substituted and β,β-fused tetraazaporphyrins in the presence of DMSO exhibit the properties of dibasic NH-acids and form complexes with proton transfer $H_2TapR{\cdot}2DMSO$, $H_2Tap(Pyz)_4R{\cdot}2DMSO$ and $H_2Pc(NO_2)_4(t\text{-}Bu)_4{\cdot}2DMSO$.

In these complexes the hydrogen atoms bound with the molecules of dimethyl sulfoxide and the endocyclic nitrogen atoms are located axially above and below the plane of the macrocycle along the fourth order symmetry axis, which is a prerequisite for compliance with D_{4h} symmetry of the charge distribution [9]. The degree of proton transfer from the NH-acid to an

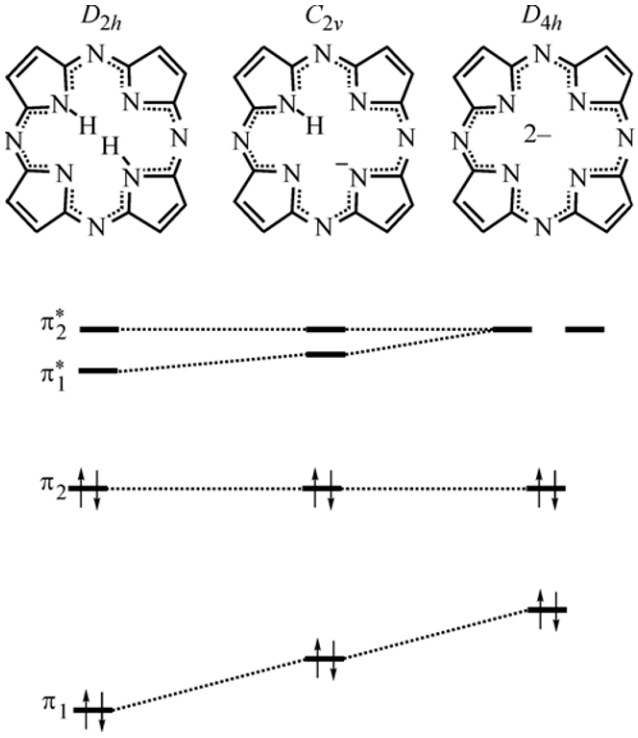
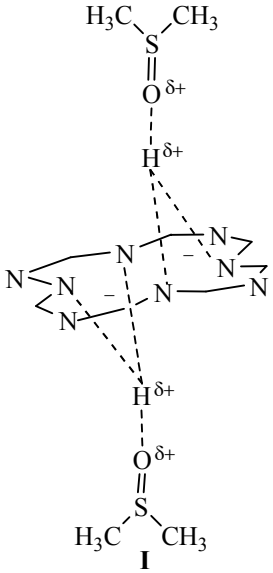


Fig. 2. Changes in the highest occupied molecular orbital and lowest unoccupied molecular orbitals in the process of acid–base interaction of the tetraazaporphyrin macrocycle [8].

acceptor center of the base is limited to the stage of formation of H-complex (H-associate **I**) [3–7].



I

The reaction of the acid–base interaction of the tetrabromotetraazaporphin (H_2TapBr_4) and tetrachlorotetraazaporphin (H_2TapCl_4) with dimethyl sulfoxide in chlorobenzene is described by the kinetic equation (1):

Table 1. Kinetic parameters of acid-base interactions of tetraazaporphyrins with dimethylsulfoxide in chlorobenzene [3][a]

Tetraazaporphyrin	T, K	$k\times10^5$, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1}K^{-1}
H_2TapBr_4	298	3.47	24	250
	323	7.40		
	333	9.50		
	343	12.30		
H_2TapCl_4	298	5.30	26	237
	313	8.80		
	323	11.25		
	333	16.00		

[a] $[H_2TapBr_4] = [H_2TapCl_4] = 0.5\times10^{-5}$ M, [DMSO] = 3.88 M.

$$H_2TapHal_4 + 2DMSO \rightarrow H_2TapHal_4\cdot 2DMSO,$$

$$Hal = Br \text{ and } Cl,$$

$$-d[H_2TapHal_4]/d\tau = k[H_2TapHal_4][DMSO]. \quad (1)$$

Here k is the second order rate constant.

The limiting stage of the process is of bimolecular nature, and the intermolecular proton transfer from the NH groups of $H_2TapHal_4$ to DMSO proceeds in two steps [1, 3]:

$$H_2TapHlg_4 + DMSO \xrightarrow{k_1} H_2TapHlg_4\cdot DMSO, \quad (2)$$

$$H_2TapHlg_4\cdot DMSO + DMSO \xrightarrow{k_2} H_2TapHlg_4\cdot 2DMSO. \quad (3)$$

The reaction (2) shall decrease the molecular symmetry from D_{2h} to C_{2v} (Fig. 2), resulting in the blue shift of the longwave components of Q_x band in the electron absorption spectrum [8]. However, at a large excess of DMSO the decrease in the $H_2TapHal_4$ concentration occurs with the preservation of a clear isobestic points without the appearance in the reaction system of an intermediate spectral form $H_2TapHal_4\cdot$ DMSO (Fig. 1). Consequently, $k_1 < k_2$ or $k_1 \approx k_2$.

The data in Table 1 show that the reaction of H_2TapBr_4 and H_2TapCl_4 with dimethylsulfoxide in an inert low-polar chlorobenzene is characterized by unusually low values of the rate constants that is not typical of the simple enough liquid-phase acid–base systems [10]. The reason for this phenomenon is connected with the macrocyclic effect, which includes electronic (polarization) and steric components [11]. Thus, the tetraaza-substitution in the porphyrin molecule followed by an introduction to the pyrrole rings of four atoms of bromine (chlorine) considerably increases the polarity of the endocyclic NH bonds [12] and indicates the increasing role of electronic component of the macrocyclic effect. In contrast, continuous π,π-overlap over the 16-membered macrocycle (C_8N_8), ithe inclusion of *n*-electron pairs of the endocyclic nitrogen atoms and halogens in the *n*π-conjugation, as well as the increase in the number of π-electrons in the conjugated system of the macrocycle due to the nitrogen *meso*-atoms contributes to the increase in aromaticity and a decrease in the conformational "flexibility" of the $H_2TapHal_4$ molecules. The higher conformational rigidity, the greater the effect of the spatial screening of the protons of endocyclic NH-groups by the atoms and the π-electrons, Thus, despite the pronounced acidity of tetrahalo-substituited tetraazaporphyrins, the removal of the NH protons by the DMSO molecules from the macrocycle plane occurs in unfavorable steric conditions, which is reflected in the kinetic parameters of the process. At the same time, the nature of the halogen in the $H_2TapHal_4$ has no effect on the values of k^{298}, E_a, and $\Delta S^{\neq}$ (Table 1), since the action of bromine and chlorine on the reaction center is transferred to the semi-isolated $C_\beta{=}C_\beta$ bonds not only by the induction mechanism, but also on account of the effect of *n*π-conjugation with the macrocycle [13]. Inductive (*–I*) effect increases in going from the bromine to chlorine atom, which increases the polarity of the endocyclic NH bonds. On the contrary, the +*C*-effect, while growing in the same manner, reduces the protonation of the NH bonds due to the increased electron density on the endocyclic nitrogen atoms. This results in leveling of the electronic effects of halogen atoms on the acidity of H_2TapBr_4 and H_2TapCl_4, and thus these effects are not observed in the acid–base interactions.

Unlike H_2TapBr_4 and H_2TapCl_4, the reaction of octa(*p*-nitrophenyl)tetraazaporphin [$H_2Tap(C_6H_4NO_2)_8$] [4], tetra(5-*tert*-butylpyrazino)tetraazaporphin [H_2Tap(Pyz-*t*-Bu)$_4$] [7], octaethyltetrapyrazinoporphin [H_2Tap(PyzEt$_2$)$_4$] [7, 14], octaphenyltetrapyrazinoporphin [$H_2Tap(PyzPh_2)_4$] [6, 14] and tetra(3-nitro-5-*tert*-butyl) phthalocyanine [$H_2Pc(NO_2)_4(t\text{-}Bu)_4$] [5] with dimethyl sulfoxide in benzene is extremely fast, with the rate immeasurable by conventional kinetic methods.

The proton transfer complexes of the β-substituted β,β-fused tetraazaporphyrins formed in the course of the acid–base interaction in the system of DMSO–chlorobenzene (benzene), as well as in 100% DMSO are stable and do not decompose in time [3, 7].

Reactivity of the proton transfer complexes of tetraazaporphyrins at the contact with a metal acetate. The high kinetic stability of the proton transfer complexes of tetraazaporphyrins with DMSO allowed studying their reactivity in the reactions with the metal acetates $M(OAc)_2$, M = Cu, Ni, Co, Zn, Cd, Mg.

In DMSO, the formation of metallocomplexes of tetrabromtetraazaporphin, tetrachlorotetraazaporphin, and octa(*p*-nitrophenyl)tetraazaporphin occurs almost instantly at mixing the freshly prepared solutions [4, 15, 16].

$$H_2TapHal_4{\cdot}2DMSO + M(OAc)_2 \rightarrow MTapHal_4 + 2\,HOAc + 2DMSO,$$

$$H_2Tap(C_6H_4NO_2)_8{\bullet}2DMSO + M(OAc)_2 \rightarrow MTap(C_6H_4NO_2)_8 + 2\,HOAc + 2DMSO.$$

The process is accompanied by a color change of solution and blue shift of the maximum absorption bands of $H_2TapHal_4{\cdot}2DMSO$ and $H_2Tap(C_6H_4NO_2)_8{\cdot}2DMSO$ (Table 2).

In contrast, the formation of $MgTapHal_4$ from $H_2TapHal_4{\cdot}2DMSO$ and $Mg(OAc)_2$ in DMSO proceeds in time [15]. The reaction is described by the kinetic equation:

$$d[MgTapHal_4]/d\tau = k[H_2TapHal_4{\cdot}2DMSO][Mg(OAc)_2]^n. \quad (4)$$

Here, k is the rate constant of a first-order reaction, n is the reaction order with respect to $Mg(OAc)_2$, which is close to zero.

The limiting stage of the process in this case is of unimolecular nature, and the introduction of Mg^{2+} ion in the coordination cavity of the macrocycle proceeds in two steps through dissociation of the complex with the proton transfer:

$$H_2TapHlg_4{\cdot}2DMSO \xrightarrow{k_1} [H_2TapHlg_4{\cdot}DMSO]^- + H^+ + DMSO,$$

$$[H_2TapHlg_4{\cdot}DMSO]^- + Mg^{2+} \xrightarrow{k_2} MgTapHlg_4 + H^+ + DMSO,$$

$$k_1 < k_2.$$

The dissociation, which leads to the formation of doubly charged anion $[TapHal_4]^{2-}$ is unlikely, since already the singly charged anion has the steric structure no less favorable for the coordination of Mg^{2+} [15]. A similar scheme of the mechanism occurs at the interaction of the proton transfer complex of octa(*p*-nitrophenyl)tetraazaporphin $H_2Tap(C_6H_4NO_2)_8{\cdot}2DMSO$ with $Mg(OAc)_2$ in dimethyl sulfoxide [4].

Table 2. The position of absorption bands (λmax, nm) in the electronic absorption spectra of metal complexes and proton-transfer complexes of tetraazporphyrins in dimethyl sulfoxide [4, 15, 16]

Compound	λ_{max}, nm
$H_2TapBr_4{\cdot}2DMSO$	620
$CuTapBr_4$	606
$NiTapBr_4$	606
$CoTapBr_4$	589
$ZnTapBr_4$	613
$H_2TapCl_4{\cdot}2DMSO$	618
$CuTapCl_4$	600
$NiTapCl_4$	604
$CoTapCl_4$	586
$ZnTapCl_4$	610
$H_2Tap(C_6H_4NO_2)_8{\cdot}2DMSO$	660
$CuTap(C_6H_4NO_2)_8$	636
$NiTap(C_6H_4NO_2)_8$	640
$CoTap(C_6H_4NO_2)_8$	630
$ZnTap(C_6H_4NO_2)_8$	648
$CdTap(C_6H_4NO_2)_8$	656

According to [16], the protons of NH groups in the proton transfer complexes of β-substituted tetraazaporphyrins can be more or less strongly displaced along the fourth order symmetry axis toward the proton-acceptor center of the DMSO molecules. This should affect the strength of the intermolecular hydrogen bond between the endocyclic nitrogen atoms and hydrogen atoms, and should be reflected in the kinetic parameters of the process. Indeed, in going from $H_2Tap(C_6H_4NO_2)_8{\cdot}2DMSO$ to $H_2TapCl_4{\cdot}2DMSO$ and $H_2TapBr_4{\cdot}2DMSO$, the rate of reaction with $Mg(OAc)_2$, judging from the values of k_{eff}, increases by more than an order of magnitude, while the E_a and $\Delta S^{\neq}$ of the process significantly decreased (Table 3).

The state of the proton transfer tetraazaporphyrine complexes in the strong basic media. As mentioned earlier, the proton transfer complexes $H_2TapR{\cdot}2DMSO$, $H_2Tap(Pyz)_4R{\cdot}2DMSO$ and $H_2Rs(NO_2)_4(t\text{-}Bu)_4{\cdot}2DMSO$ in the DMSO medium possess a sufficiently high kinetic stablity. The same is observed when rather weak nitrogen bases (pyridine, 2-methylpyridine) are introduced in the dimethylsulfoxide solution. In contrast, adding stronger bases [morpholine (Mor), butylamine ($BuNH_2$), piperidine (Pipy), diethylamine (Et_2NH)] leads to the destabilization of the proton transfer complexes. Regardless of the nature of the nitrogen-containing base, a

Table 3. Kinetic parameters of the reaction of proton-transfer complexes of tetraazaporphyrins with magnesium acetate in dimethyl sulfoxide [16][a]

Complex	T, K	$k_{ef}\times10^5$, s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
$MgTapBr_4$	298	1.33[b]	50	179
	308	2.55		
	318	4.55		
	328	8.50		
$MgTapCl_4$	298	0.94[b]	45	198
	308	1.70		
	318	2.97		
	328	5.03		
$MgTap(C_6H_4NO_2)_8$	298	0.09[b]	83	90
	308	0.28		
	318	0.74		
	328	2.03		

[a] $[H_2TapBr_4\cdot2DMSO] = [H_2TapCl_4\cdot2DMSO] = 0.5\times10^{-5}$ M, $[H_2Tap(C_6H_4NO_2)_8\cdot2DMSO] = 0.3\times10^{-5}$ M, $[Mg(OAc)_2] = 1.8\times10^{-4}$ M. [b] k_{ef} calculated by the Arrhenius equation.

decrease in time occurs of unsplit *Q*-bands with λ 620, 618, 660, 643, 643, 662, and 677 nm for $H_2TapBr_4\cdot$2DMSO, $H_2TapCl_4\cdot$2DMSO, $H_2Tap(C_6H_4NO_2)_8\cdot$2DMSO, $H_2Tap(Pyz\text{-}t\text{-}Bu)_4\cdot$2DMSO, $H_2Tap(PyzEt_2)_4\cdot$2DMSO, $H_2Tap(PyzPh_2)_4\cdot$2DMSO, and $H_2Pc(NO_2)_4\cdot(t\text{-}Bu)_4\cdot$2DMSO, respectively (Fig. 3). Despite the high basicity and dielectric constant of the medium, among all the studied proton transfer complexes only the complex $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot$2DMSO does not decompose in the presence of morpholine and diethylamine [5], and the $H_2Tap(PyzEt_2)_4\cdot$2DMSO and $H_2Tap\cdot(Pyz\text{-}t\text{-}Bu)_4\cdot$2DMSO in the presence of diethylamine [7].

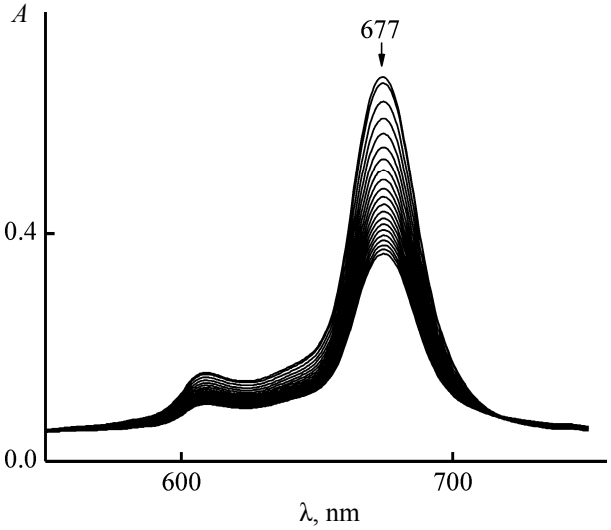


Fig. 3. Changes in the electron absorption spectrum of $H_2Rs(NO_2)_4(t\text{-}Bu)_4\cdot$2DMSO in the system *n*-butylamine–DMSO within 45 min at $[BuNH_2]$ 5.05 M and T = 338 K.

The decomposition of the complexes $H_2Tap\cdot(C_6H_4NO_2)_8\cdot$2DMSO, $H_2Tap(Pyz\text{-}t\text{-}Bu)_4\cdot$2DMSO, $H_2Tap\cdot(PyzEt_2)_4\cdot$2DMSO, and $H_2Tap\ (PyzPh2)_4\cdot$2DMSO in the DMSO – morpholine (*n*-butylamine, piperidine) can be described by a kinetic equation of the second order, the first with respect to the proton transfer complex and the first with respect to the base [6, 7, 16]. For the complexes $H_2TapHal_4\cdot$2DMSO the equation is:

$$-d[H_2TapHal_4\cdot2DMSO]/d\tau = k[H_2TapHal_4\cdot2DMSO][B]^2.$$

Here, k is the third order rate constant of decomposition, B = $BuNH_2$, Et_2NH.

The instability of the tetraazaporphyrin proton transfer complexes in strongly basic media with a high dielectric permeability of the medium is associated with the occurrence of competition for the proton, which leads to the formation of doubly charged anion [16]. Due to the lack of compensation for the excess charge in the macrocycle it undergoes spontaneous decomposition with the formation of low molecular weight colorless products.

Judging from the values of k^{298} (Table 4), the maximum rate of decomposition of the complexes $H_2Tap(Pyz)_4R\cdot$2DMSO is observed in the presence of *n*-butylamine (pK_a = 10.60 [17]) and piperidine (pK_a = 11.23 [17]), which possess a sufficiently high proton-acceptor power greatly facilitating the competitive reaction for the proton that leads to the decay of the macrocycle π-chromophore [16]. Judging from the k^{298} values replacing *n*-butylamine by the less basic morpholine (pK_a 8.70 [17]) reduces the rate of destruction on the background of growing E_a of the process (Table 4).

Among all the studied tetraazaporphyrin proton transfer complexes the complex $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot$2DMSO has the maximum stability over time, which has the minimum values of the decomposition constants k^{298} in the presence of *n*-butylamine or piperidine (Table 4).

Despite the structural similarity of the complexes $H_2Tap(Pyz)_4R\cdot$2DMSO, in the system of DMSO–$BuNH_2$ (Pipy, Mor) the complexes $H_2Tap\ (Pyz\text{-}t\text{-}Bu)_4\cdot$2DMSO and $H_2Tap\ (PyzEt_2)_4\cdot$2DMSO have higher kinetic stability than $H_2Tap\ (PyzPh2)_4\cdot$2DMSO . Thus, in going from the close by stability $H_2Tap\ (Pyz\text{-}t\text{-}Bu)_4\cdot$

Table 4. Kinetic parameters of decomposition of the proton-transfer complexes of tetraazaporphyrins with dimethylsulfoxide in the nitrogen-containing base-dimethyl sulfoxide [3, 5, 7][a]

Complex	Base	$k^{298}\times10^6$, l^n mol^{-n} s^{-1}	E_a, kJ mol^{-1}
H_2TapBr_4·2DMSO	*n*-Butylamine	7.2[b]	10
	Diethylamine	1.04[b]	28
H_2TapCl_4·2DMSO	*n*-Butylamine	10.5[b]	10
	Diethylamine	1.15[b]	27
$H_2Tap(C_6H_4NO_2)_8$·2DMSO	*n*-Butylamine	2.12[b]	29
	Diethylamine	0.073[b]	51
$H_2Tap(Pyz$-*t*-$Bu)_4$·2DMSO	Morpholine	30	94
	n-Butylamine	90	64
	Piperidine	65	76
$H_2Tap(PyzEt_2)_4$·2DMSO	Morpholine	40	85
	n-Butylamine	80	68
	Piperidine	100	62
$H_2Tap(PyzPh_2)_4$·2DMSO	Morpholine	75	47
	n-Butylamine	248	28
	Diethylamine	75	47
	Piperidine	232	44
$H_2Pc(NO_2)_4$(*t*-Bu)$_4$·2DMSO	*n*-Butylamine	0.18	60
	Piperidine	0.4	69

[a] $[H_2TapBr_4$·2DMSO] = $[H_2TapCl_4$·2DMSO] = $[H_2Tap(PyzPh2)_4$·2DMSO] = 1.2×5.10 M; $[H_2Tap$ (Pyz-*t*-Bu)$_4$·2DMSO] = 1.18×10^{-5} M; $[H_2Tap(PyzEt_2)_4$·2DMSO] = 1.24×10^{-5} M $[H_2Rs(NO_2)_4$(*t*-Bu)$_4$·2DMSO] = 1.15×10^{-5} M. [b] $k^{298}\times10^3$, *n* is the order of reaction with respect to the base.

2DMSO, and H_2Tap $(PyzEt_2)_4$·2DMSO to the H_2Tap·$(PyzPh2)_4$·2DMSO the k^{298} values grow, and E_a of the process is significantly reduced (Table 4). Further increase in the stability of π-chromophore complex system H_2Tap $(PyzPh2)_4$·2DMSO is observed in dimethylsulfoxide solution with the addition of diethylamine. The decreased reactivity of Et_2NH (pK_a = 10.93 [17]), as compared with the close in basicity $BuNH_2$ is caused by the effect of the stronger steric shielding of the nitrogen unshared electron pair by bulky alkyl substituents, and the interaction between the $H_2Tap(PyzPh2)_4$·2DMSO and Et_2NH leading to the formation of kinetically unstable dianion $[Tap(PyzPh_2)_4]_2$ is hampered, and the stability of the proton-transfer complex H_2Tap $(PyzPh2)_4$·2DMSO increases (Table 4).

Similarly the complex $H_2Tap(C_6H_4NO_2)_8$·2DMSO in the system of DMSO–$BuNH_2$ (Et_2NH) is stable in time (Table 4).

These data indicate that the increase in the rate of decomposition of the proton transfer complexes in strongly basic media in a series of $H_2Pc(NO_2)_4$(*t*-Bu)$_4$·DMSO → H_2Tap (Pyz-*t*-Bu)$_4$·2DMSO ≈ H_2Tap·$(PyzEt_2)_4$·2DMSO → H_2Tap $(PyzPh2)_4$·2DMSO ≈ $H_2Tap(C_6H_4NO_2)_8$·2DMSO is associated with an increase in the acidity of the macrocycle [18] forming the complex.

In the case of complexes H_2TapBr_4·2DMSO and H_2TapCl_4·2DMSO the process of degradation does not depend on the nature of the base and the halogen atom in the tetraazaporphyrin macrocycle (Table 4). Since the loss of kinetic stability of these complexes obeys a complex kinetic law [16], comparing the values of k^{298} and E_a with those for the complexes H_2Tap·$(C_6H_4NO_2)_8$·2DMSO, $H_2Pc(NO_2)_4$(*t*-Bu)$_4$·2DMSO, and $H_2Tap(Pyz)_4R$·2DMSO is senseless.

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