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Reactivity of Tetraazaporphyrins in the Acid–Base Interactions with Nitrogen Bases

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Abstract—The review analyzes the data on the reactivity of β-substituted and β, β-tetrabenzofused tetraaza porphyrins in acid-base interactions in benzene and dimethylsulfoxide with cyclic and acyclic, in the latter case primary, secondary, and tertiary, nitrogen bases. Unusually low rate of the processes was established. The effect of the medium dielectric permittivity, the nature of the base and of the substituents in the tetraaza porphyrin macrocycle on the rate and activation parameters of acid-base interactions are demonstrated. The structure and stability of the tetraaza porphyrin complexes with the proton transfer are discussed.

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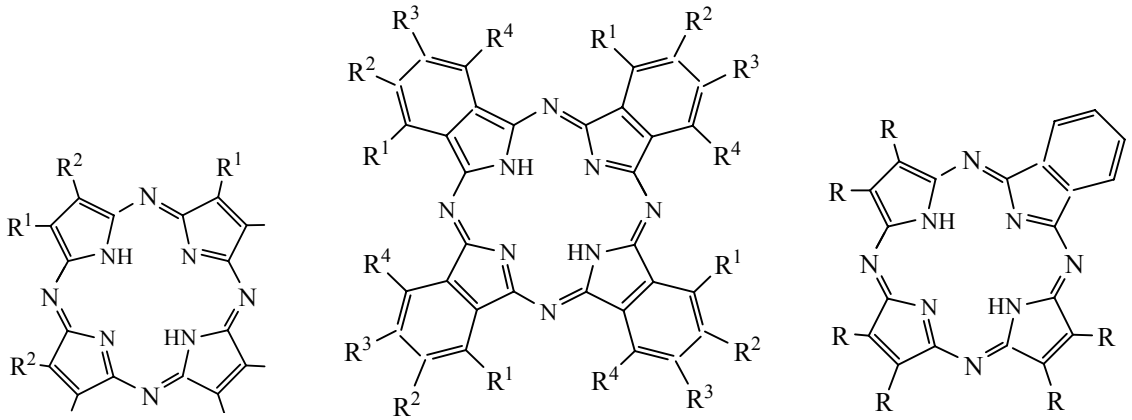
In the recent time a comprehensive study of the chemical properties of the macrocycles of porphyrin type became an object of increasing attention of researchers, not only because of their key role in a number of vital processes, but also due to their expanding practical applications in catalysis, biological and chemical monitoring, qualitative and quantitative analysis, and in various fields of medicine.

Among the structural diversity of porphyrins special place belongs to their tetraaza-substituted counterparts, the tetraaza porphyrins, which are classified as the aromatic multicenter ampholytes [1]. They have two NH- acid sites and six basic sites, two pyrrolenine intracyclic nitrogen atoms and four nitrogen *meso*-atoms in a closed π-conjugated system. As a consequence of the electron-withdrawing action of these nitrogen atoms the tetraaza porphyrins have strong acid properties. In inert solvents they enter into kinetically controlled interaction with the nitrogen-containing bases to form a proton-transfer complexes that are not typical for the porphyrins. These complexes have different stability in time.

The acid properties of tetraazaporphyrins. At the action of strong base in a non-aqueous solvent the tetraazaporphyrins undergo two-stage acid ionization at the intracyclic NH bonds, which results in the successive formation of the mono- and dianionic forms with similar values of the constants pK_{a1} and pK_{a2} [2–4]. The constant values are strongly dependent not only on the structural features of the macrocycle, but also on the solvation factors. The comparison of acidity of β-substituted tetraaza porphyrins [H_2TapR], [H_2Tap($C_6H_4CF_3$)$_6$(C_4N_4)], and β,β-tetrabenzofused tetraaza porphyrins [H_2PcR] in the gas phase excludes the medium effect and, therefore, the most reliably reflects the relationship between proton-donor ability of the tetraaza FORMULA

According to [5, 6], the presence of four nitrogen atoms in the tetraaza porphine (H_2Tap) compared with porphine (H_2P) leads to a redistribution of π-electron density of the whole molecule and increases the acid properties of the molecule by ten orders of magnitude compared to H_2P (pK_a 22.82). The introduction to the pyrrole rings of H_2Tap of electron-donor substituents results in an increase of covalency and strength of the NH bonds that hampers the process of acid ionization [6]. On the contrary, the expansion of π-conjugated system of the macrocycle at the condensation of four electron-acceptor benzene rings in tetraaza porphine promotes strong stabilization of mono- and dianions and increases the acidity of the molecule. So, the pK_{a1} value of phthalocyanine (H_2Pc) is lower than that of tetraaza porphine (Table 1). A similar but more powerful effect on the acidity of NH bonds has octaphenyl substitution in H_2Tap. The values of pK_{a1} of tetraaza porphine and octaphenyltetraaza porphine (H_2TapPh$_8$) differ by 2 units (Table 1). Further growth



H_2TapR H_2PcR $[H_2Tap(C_6H_4CF_3)_6(C_4H_4)]$

$R^1 = R^2 = H$ (H_2Tap); $R^1 = H$, $R^2 = Br$ (H_2TapBr_4); $R^1 = H$, $R^2 = Cl$ (H_2TapCl_4); $R^1 = R^2 = Ph$ (H_2TapPh_8); $R^1 = R^2 = p$-NO_2-Ph [$H_2Tap(C_6H_4NO_2)_8$]; $R^1 = R^2 = p$-Br-Ph [$H_2Tap(C_6H_4Br)_8$]; $R^1 = R^2 = m$-CF_3-Ph [$H_2Tap(C_6H_4CF_3)_8$]; $R^1 = R^2 = R^3 = R^4 = H$ (H_2Pc); $R^1 = R^3 = R^4 = H$, $R^2 = t$-Bu [$H_2Pc(t\text{-Bu})_4$]; $R^1 = NO_2$, $R^2 = R^4 = H$, $R^3 = t$-Bu [$H_2Pc(NO_2)_4(t\text{-Bu})_4$]; R = *m*-$CF_3$-Ph [$H_2Tap(C_6H_4CF_3)_6(C_6H_4)$].

of proton-donor ability is observed in going from tetraaza porphine to terabromotetraaza porphine (H_2TapBr_4) and tetrachlorotetraaza porphine (H_2TapCl_4). In this case, the nature of the Hlgogen atom has no significant effect on the ability to deprotonation of H_2TapCl_4 and H_2TapBr_4 (Table 1).

There is no information so far on the thermodynamic acidity of octa(*p*-nitrophenyl)tetraaza porphine [$H_2Tap(C_6H_4NO_2)_8$], octa(*p*-bromophenyl)tetraaza porphine [$H_2Tap(C_6H_4Br)_8$], octa(*m*-trifluoromethylphenyl)tetraaza porphine [$H_2Tap(C_6H_4CF_3)_8$], hexa(*m*-trifluoromethylphenyl)benzotetraaza porphine [$H_2Tap(C_6H_4CF_3)_6(C_4N_4)$], tetra(4-*tert*-butyl)phthalocyanine [$H_2Pc(t\text{-Bu})_4$] and tetra(3-nitro-5-*tert*-butyl)phthalocyanine [$H_2Pc(NO_2)_4(t\text{-Bu})_4$]. Data on the proton-donor ability of these tetraaza porphyrins were obtained by studying their reactivity in the acid–base interactions.

Spectral pattern of the acid–base interactions of tetraazaporphyrins. Structure and stability of the proton transfer complexes. Acid–base interactions of tetraaza porphyrins with nitrogenous bases (B) in benzene (dimethylsulfoxide) occur only at a significant excess of the base [7–15]. The spectral changes during the reaction are independent of the nature of substituents in the macrocycle, as well as of the nature of the base (Figs. 1–3). They indicate an increase in the effective symmetry of the π-chromophore molecules from D_{2h} to D_{4h} as a result of changes in the energy of π-orbitals [1] and show that the β-substituted and β,β-tetrabenzofused tetraaza porphyrins exhibit the properties of dibasic NH-acids in the presence of bases and form the proton transfer complexes $H_2TapR{\cdot}2B$, $H_2PcR{\cdot}2B$, and $H_2Tap(C_6H_4CF_3)_6(C_4N_4){\cdot}2B$, where B is pyridine (Py), 2-methylpyridine (MePy), morpholine (MorPh), benzylamine ($BzNH_2$), piperidine (Pipy), *n*-butylamine ($BuNH_2$), *tert*-butylamine (t-$BuNH_2$), diethylamine (Et_2NH), triethylamine (Et_3N), tri-*n*-butylamine (Bu_3N).

In these complexes the hydrogen atoms bound to the base molecules and to the intracyclic nitrogen atoms [16] are located axially above and below the plane of the macrocycle, on the four order symmetry axis, which is a necessary condition of the high symmetry of the charge distribution [17]. The degree of proton transfer from the NH-acid to the acceptor site of the base depends on the electronic and geometric structure of the interacting molecules, that is, on their strength and steric features, as well as on the medium dielectric permittivity. In H_2TapR, H_2PcR and $H_2Tap{\cdot}(C_6H_4CF_3)_6(C_4N_4)$ the complete transfer of protons

Table 1. First stage acid ionization constants of tetraaza porphyrins in the gas phase [6]

Tetraaza porphine	pK_{a1}
Tetraaza porphine	12.36
Octaphenyltetraaza porphine	10.36
Tetrachlorotetraaza porphine	9.09
Tetrabromotetraaza porphine	8.45
Phthalocyanine	11.23

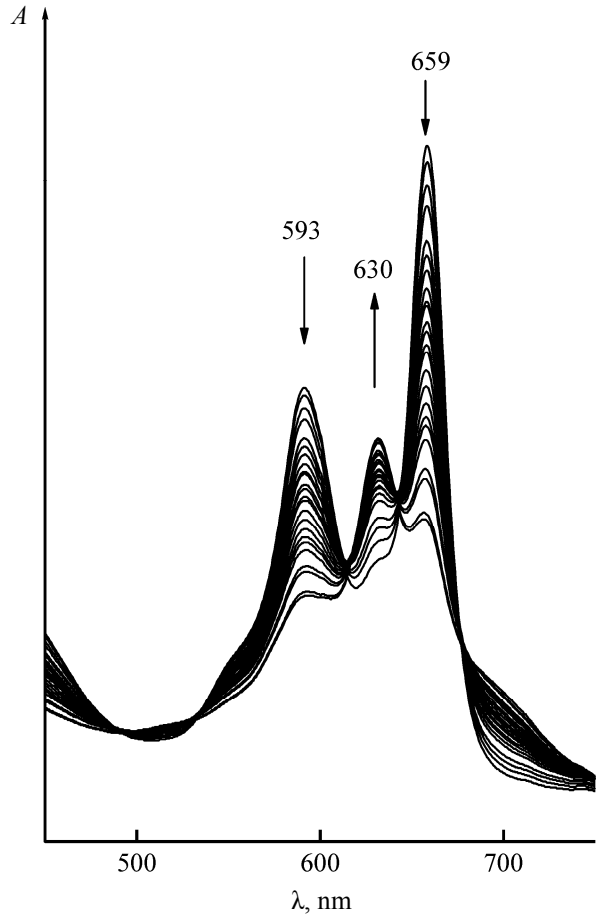


Fig. 1. Change in the electron absorption spectrum of the $H_2Tap(C_6H_4CF_3)_8$ in benzene in the presence of *n*-butylamine in the course of 60 min at $c(BuNH_2)$ = 6.5 M and T = 348 K [15].

from the NH-groups to the substrate leading to the formation of solvent-separated ion pairs and their subsequent dissociation does not occur [18]. The acid-base interaction is limited either to the stage of the formation of H-complex (H-associate **I**), or ion complex (ion-ion associate), which is H-bonded ion pair **II.**

Gradual varying proton-donor and proton-acceptor properties of the partner molecules the acid-base equilibrium (1) can be shifted toward the formation of more or less polar structure.

According to [7–15, 19], the complexes $H_2TapR\cdot 2B$, $H_2PcR\cdot 2B$ and $H_2Tap(C_6H_4CF_3)_6(C_4N_4)\cdot 2B$ in the system of nitrogen base–benzene are extremely unstable and decompose in time. The exceptions are complexes $H_2Tap(C_6H_4Br)_8\cdot 2BuNH_2$ in the system of *n*-butylamine–benzene and $H_2Pc(t\text{-}Bu)_4\cdot 2B$ (B is

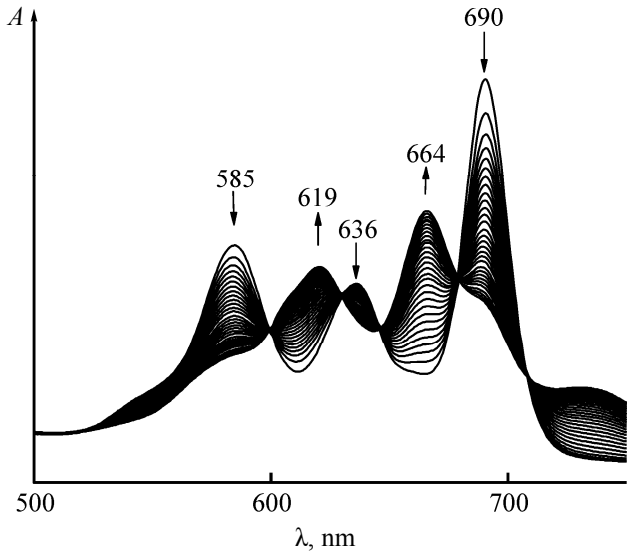


Fig. 2. Change in the electron absorption spectrum of the $H_2Tap(C_6H_4CF_3)_6(C_4N_4)$ in benzene in the presence of *n*-butylamine in the course of 90 min at $c(BuNH_2)$ = 2.53 M and T = 338 K [12].

$BuNH_2$, *t*-$BuNH_2$, Et_2NH, Pipy) in dimethylsulfoxide, which have sufficiently high kinetic stability .

The decomposition of the complexes $H_2Tap\cdot(C_6H_4NO_2)_8\cdot 2B$ system of nitrogen base–benzene is described by the second order kinetic equation, the first order with respect to the proton transfer complex and the first order with respect to the base [19]. For the proton transfer complexes of β-tetrahalo-substituted

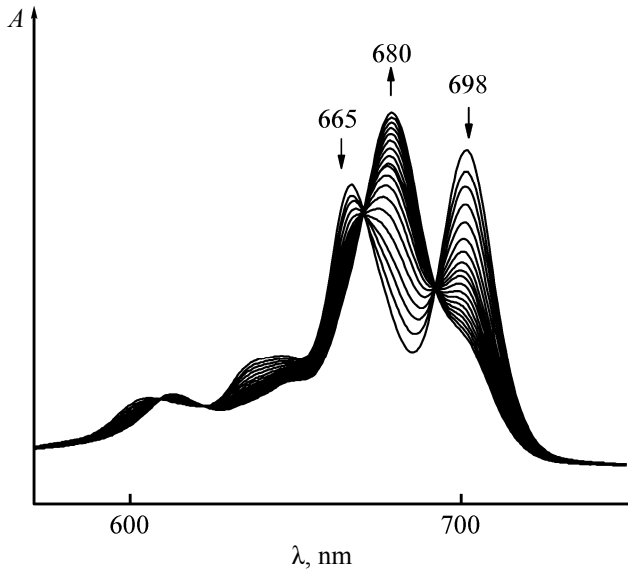
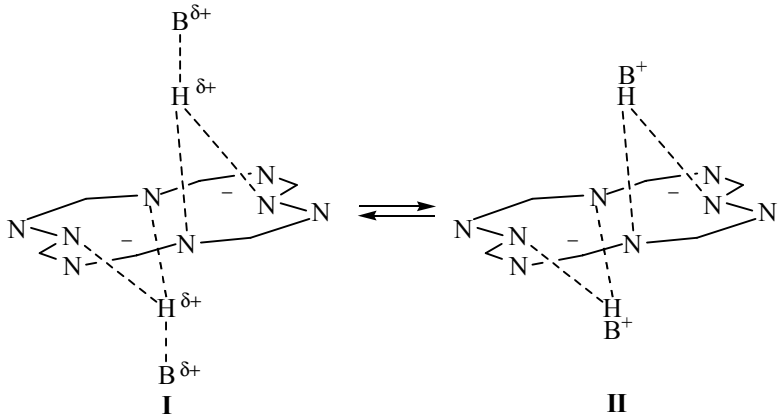


Fig. 3. Change in the electron absorption spectrum of H_2Pc (*t*-Bu)$_4$ in DMSO in the presence of diethylamine in the course of 80 min at $c(BuNH_2)$ = 2.41 M and T = 318 K [13].



I II (1)

tetraaza porphyrins $H_2TapHlg_4 \cdot 2B$ (Hlg = Br or Cl) the equation is as follows:

$$-d[H_2TapHlg_4 \cdot 2B]/d\tau = k\,[H_2TapHlg_4 \cdot 2B][B]^n,$$

where k is the decomposition rate constant, n is the reaction order with respect to the base. In the cases when B is Py, MePy, MorPh, Et_3N, Bu_3N, or Pipy the n value is close to unity, and when B is $BzNH_2$, $BuNH_2$, t-$BuNH_2$, or Et_2NH, it is close to two.

Judging from the values of k^{298} (Table 2), in going from $H_2Tap(C_6H_4NO_2)_8 \cdot 2B$ to $H_2TapCl_4 \cdot 2B$ and $H_2TapBr_4 \cdot 2B$ the kinetic stability of the tetraaza porphyrin complexes with the proton transfer decreases, in agreement with an increase in the macrocycle acidity. With increase in the NH-acidity the equilibrium (1) is shifted to a more polar structure, which, at a large excess of base enters more easily into the competition for the proton that leads to the formation of the doubly charged anion [19]. In the medium of mild solvating ability and due to the lack of compensation of the excess negative charge in the macrocycle, the tetraaza porphyrin dianion spontaneously decomposes to colorless low molecular weight products.

According to the data in Table 2, the rate of decomposition of the complexes depends on the strength and steric features of nitrogen bases. In the series Py → MorPh → Pipy, an increase in pK_a by 6 orders of magnitude leads to ~6000 and ~16500 times increase in the values of k^{298} for $H_2TapBr_4 \cdot 2B$ and $H_2TapCl_4 \cdot 2B$ respectively. A similar but less pronounced effect is observed in the case of $H_2Tap(C_6H_4NO_2)_8 \cdot 2B$.

With increasing steric screening of the nitrogen atom in the proton-acceptor molecule the opposite effect is observed. When replacing the pyridine (pK_a 5.23 [20]) by close by basicity 2-methylpyridine (pK_a 5.97 [20]), or n-butylamine (pK_a 10.60 [20]) by diethylamine (pK_a 10.93 [20]), or triethylamine (pK_a 10.87 [20]) by tri-n-butylamine (pK_a 10.89 [20]), the stability of the proton-transfer complexes increases (Table 2).

Kinetic pattern of acid–base interactions of β-substituted tetraaza porphyrins. The reaction of the

Table 2. Decomposition rate constants of the proton transfer complexes of tetraaza porphyrins in the system of nitrogen bases–benzene [19] [$H_2TapBr_4 \cdot 2B$] = [$H_2TapCl_4 \cdot 2B$] = 0.4×10^{-5} M; [$H_2Tap(C_6H_4NO_2)_8 \cdot 2B$] = 0.5×10^{-5} M

Tetraaza porphyrin proton-transfer complex	$k^{298}\times10^2$, l^n mol^{-n} s^{-1}
$H_2TapBr_4 \cdot 2Py$	1.14[a]
$H_2TapBr_4 \cdot 2MePy$	0.087[a]
$H_2TapBr_4 \cdot 2MorPh$	0.12
$H_2TapBr_4 \cdot 2Et_3N$	1.66[a]
$H_2TapBr_4 \cdot 2Bu_3N$	0.066[a]
$H_2TapBr_4 \cdot 2Pipy$	6.93
$H_2TapBr_4 \cdot 2BzNH_2$	0.29
$H_2TapBr_4 \cdot 2BuNH_2$	3.30
$H_2TapBr_4 \cdot 2(t\text{-}BuNH_2)$	23.12[a]
$H_2TapBr_4 \cdot 2Et_2NH$	1.08
$H_2TapCl_4 \cdot 2Py$	0.82[a]
$H_2TapCl_4 \cdot 2MePy$	0.12[a]
$H_2TapCl_4 \cdot 2MorPh$	0.14
$H_2TapCl_4 \cdot 2Et_3N$	2.97[a]
$H_2TapCl_4 \cdot 2Bu_3N$	0.38[a]
$H_2TapCl_4 \cdot 2Pipy$	13.49
$H_2TapCl_4 \cdot 2BzNH_2$	0.28
$H_2TapCl_4 \cdot 2BuNH_2$	0.76
$H_2TapCl_4 \cdot 2(t\text{-}BuNH_2)$	20.55[a]
$H_2TapCl_4 \cdot 2Et_2NH$	0.33
$[H_2Tap(C_6H_4NO_2)_8] \cdot 2MorPh$	0.12[b]
$[H_2Tap(C_6H_4NO_2)_8] \cdot 2BzNH_2$	0.59[b]
$[H_2Tap(C_6H_4NO_2)_8] \cdot 2BuNH_2$	2.82[b]
$[H_2Tap(C_6H_4NO_2)_8] \cdot 2(t\text{-}BuNH_2)$	1.37[b]
$[H_2Tap(C_6H_4NO_2)_8] \cdot 2Pipy$	2.36[b]

[a] $k^{298}\times10^5$. [b] $k^{298}\times10^7$, n is the reaction order with respect to the base.

acid-base interaction of β-tetrahalo-substituted tetraaza porphyrins H_2apHlg$_4$ (Hlg = Br and Cl) with a nitrogen bases in benzene

$$H_2TapHlg_4 + 2B \rightarrow H_2TapHlg_4 \cdot 2B \quad (2)$$

is described by the kinetic equation (3):

$$-d[H_2TapHlg_4]/d\tau = k\,[H_2TapHlg_4][B]^n. \quad (3)$$

Here, k is the rate constant, n is the reaction order with respect to the base.

In the reactions of $H_2TapHlg_4$ with cyclic (pyridine, 2-methylpyridine, morpholine, piperidine) and acyclic tertiary amines (triethylamine, tri-*n*-butylamine) the n value is close to unity. Limiting step of the process in this case is of bimolecular nature ($k_1 < k_2$), and the intermolecular proton transfer from the NH-groups to $H_2TapHlg_4$ occurs in two stages [7, 9]:

$$H_2TapHlg_4 + B \; H_2TapHlg_4 \cdot B, \quad (4)$$

$$H_2TapHlg_4 \cdot B + B \; H_2TapHlg_4 \cdot 2B. \quad (5)$$

A similar two-step process occurs at the interaction of $H_2Tap(C_6H_4NO_2)_8$ [7, 10, 11], $H_2Tap(C_6H_4CF_3)_8$ [11, 15], $H_2Tap(C_6H_4Br)_8$ [8] and the $H_2Tap(C_6H_4CF_3)_6 \cdot (C_4N_4)$ [12] with cyclic and acyclic primary amines.

On the contrary, at the interaction of $H_2TapHlg_4$ with primary and secondary acyclic amines (benzylamine, *n*-butylamine, *tert*-butylamine, diethylamine) the reaction order of with respect to the base is close to two. In this case, the rate-limiting step is not a trimolecular process, but a bimolecular reaction between $H_2TapHlg_4$ and H-bonded dimeric molecules of the bases. This does not exclude the possibility of the two-stage process, according to Eqs. (4) and (5), with $k_1 \approx k_2$ [7, 9].

The interaction of β-substituted tetraaza porphyrins with bases in benzene is characterized by unusually low values of the rate constants (Table 3) due to the action of the macrocyclic effect, which includes both steric and electronic (polarization) components [21]. The latter is determined by the efficiency of the transmission of electronic effects of the peripheral substituents on the reaction center of the molecule. Thus, tetra-substitution in the porphine molecule followed by introduction of electron-withdrawing substituents to the pyrrole rings increases significantly the polarity of NH bonds (Table 1). As a result, favorable conditions appear for proton transfer from the acid to the base. On the other hand, the continuous π,π-overlaping in the 16-membered macrocycle (C_8N_8), the inclusion of *n*-electron pairs of endocyclic nitrogen atoms in the *n*π-conjugation, and the increase in the number of π-electrons in the conjugated system due to the *meso*-nitrogen atoms favor the growth of the aromaticity and the conformational rigidity of the molecule. Relatively high rigidity of the flat conformation of tetraaza porphyrin macrocycle [21] as well as the presence of substituents at its pyrrole rings causes an increase in the steric component, which characterizes the screening of intracyclic NH-group protons by atoms and π-electrons. It hampers the most favorable contact between the reaction sites of the partner molecules and introduces the major contribution to the kinetics of the interaction H_2TapR and $H_2Tap(C_6H_4CF_3)_6(C_4N_4)$ with bases.

Table 3 shows that the rate and activation parameters of the acid-base interactions involving $H_2TapHlg_4$ quite strongly depend on the nature of the proton acceptors. Thus, with increasing pK_a of the base the rate of intermolecular proton transfer from the NH groups of $H_2TapHlg_4$ increases, and E_a of the process decreases. Therewith, there is a linear relationship between log k^{298} and pK_a (Fig. 4), and the E_a and $\Delta S^{\neq}$ values change in parallel, indicating the presence of the kinetic compensation effect [18]. Among all studied cyclic basis, the maximum reactivity in the interaction with $H_2TapHlg_4$ shows piperidine, which has a sterically accessible nitrogen atom in the molecule [22] and is a rather strong proton acceptor (pK_a 11.23 [20]). The introduction of oxygen atom in the piperidine molecule does not affect the spatial structure of the base [22], but leads to a decrease in the pK_a by ~2.5 orders of magnitude, and, as a result, reduces the rate of acid-base interactions. In the case of pyridine (pK_a 5.23 [20]), there is a further inhibition of the process, which is primarily due to the low proton-acceptor ability of this base compared to piperidine and morpholine. The minimum rate and maximum energy barrier occur in the interaction of $H_2TapHlg_4$ with 2-methylpyridine (pK_a 5.97 [20]), which completely fall out of correlation log $k^{298} = f$(pK_a) (Fig. 4), due to a stronger than in pyridine steric shielding of the lone electron pair of the nitrogen atom. A similar contribution of steric factors to the proton transfer from a NH-acid to a base is observed at replacing $BuNH_2$ (pK_a 10.60 [20]) by Et_2NH (pK_a 10.93 [20]), and Et_3N (pK_a 10.87 [20]) by Bu3N (pK_a 10.89 [20]) (Table 3). Along with the increase in the number and length of the alkyl substituents, the optimal spatial orientation of the acid-base centers is hampered by the

Table 3. Kinetic parameters of acid-base interactions of tetraaza porphyrins with nitrogen bases in benzene [7–12, 15] $[H_2TapR] = (0.4–0.8)\times10^{-5}$ M, $[H_2Tap(C_6H_4CF_3)_6(C_4N_4)] = 0.82\times10^{-5}$ M

Tetraaza porphyrin	Base	$k^{298}\times10^6$, l^n mol^{-n} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
H_2TapBr_4	Pyridine	23	69	92
	2-Methylpyrididine	1.50	87	54
	Morpholine	0.72[a]	26	224
	Benzylamine	0.78[a]	29	226
	Piperidine	28.30[a]	20	237
	n-Butylamine	6.60[a]	11	270
	tert-Butylamine	0.076[a]	18	283
	Diethylamine	4.00[a]	15	261
	Triethylamine	24	46	165
	Tri-*n*-butylamine	8.60	26	262
H_2TapCl_4	Pyridine	36	40	188
	2-Methylpyrididine	4.00	49	174
	Morpholine	0.80[a]	28	220
	Benzylamine	0.65[a]	31	223
	Piperidine	22.80[a]	23	229
	n-Butylamine	3.80[a]	23	235
	tert-Butylamine	0.09[a]	28	251
	Diethylamine	1.10[a]	30	218
	Triethylamine	110	30	214
	Tri-*n*-butylamine	23	24	260
$H_2Tap(C_6H_4NO_2)_8$	Morpholine	0.04	94	60
	Benzylamine	0.045	85	78
	Piperidine	1.20	78	99
	n-Butylamine	1.80	86	75
	tert-Butylamine	0.80	94	47
$H_2Tap(C_6H_4Br)_8$	*n*-Butylamine	0.16	92	63
$H_2Tap(C_6H_4CF_3)_8$	Morpholine	0.11	55	181
	Benzylamine	0.23	56	180
	Piperidine	6.15	32	238
	n-Butylamine	4.20	32	255
	tert-Butylamine	0.43	50	186
$H_2Tap(C_6H_4CF_3)_6(C_4H_4)$	Piperidine	0.55	64	150
	n-Butylamine	0.60	61	154

[a] $k^{298}\times10^{-2}$, *n* is the reaction order with respect to the base.

branching of the hydrocarbon chain of the amine. Thus, the rate of proton transfer from the NH-groups of $BuNH_2$ and *t*-$BuNH_2$ (pK_a 10.45 [20]) differ ~90 and 40 times for H_2TapBr_4 and H_2TapCl_4 respectively (Table 3).

In going from β-tetrahalo-substituted to β-phenyl-substituted tetraaza orphyrins the macrocycle deprotonation becomes more difficult. Thus, $H_2Tap(C_6H_4CF_3)_8$ [11], $H_2Tap(C_6H_4NO_2)_8$ [7], $H_2Tap(C_6H_4Br)_8$ [8, 10], and the $H_2Tap(C_6H_4CF_3)_6(C_4N_4)$ [12] are inactive in the reaction with the bases having mild proton-acceptor ability (pyridine, 2-methylpyridine), as well as with the bases having strongly sterically shielded nitrogen atom (diethylamine, triethylamine, tri-*n*-butylamine). However, despite the structural similarity of β-phenyl-substituted tetraaza porphyrins, $H_2Tap(C_6H_4CF_3)_8$, in contrast to $H_2Tap(C_6H_4NO_2)_8$, enters more easily into the acid–base interaction with morpholine, benzylamine, piperidine,

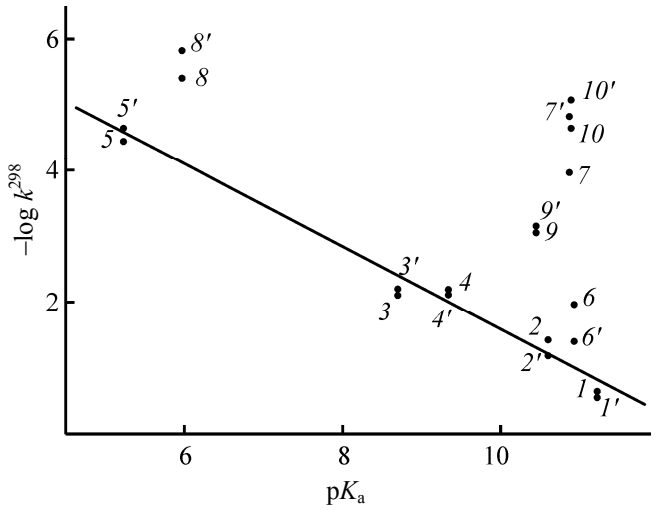


Fig. 4. Dependence of log k^{298} on pK_a for the reactions H_2TapCl_4 (1–10) and H_2TapBr_4 (*1*'–*10*') with piperidine (*1, 1*'), *n*-butylamine (*2, 2* '), morpholine (*3, 3*'), benzylamine (*4, 4*'), pyridine (*5, 5*'), diethylamine (*6, 6*'), triethylamine (*7, 7*'), 2-methylpyridine (*8, 8*'), *tert*-butylamine (*9, 9*'), and tri-*n*-butylamine (*10, 10*') in benzene. (–log k^{298} = 7.86 – 0.62pK_a, linear correlation coefficient is –0.98427).

n-butylamine, and *tert*-butylamine in benzene (Table 3). Octa(*p*-bromophenyl)tetraaza porphine is less active than the $H_2Tap(C_6H_4CF_3)_8$ and $H_2Tap(C_6H_4NO_2)_8$ in the reactions with bases. Of all studied bases, it interacts only with *n*-butylamine, the rate of transfer of the NH-groups protons of $H_2Tap(C_6H_4Br)_8$ and $H_2Tap{\cdot}(C_6H_4CF_3)_8$ to $BuNH_2$, judging from the values of k^{298}, differs about 26 times, and in the case of the $H_2Tap(C_6H_4NO_2)_8$, ~10 times (Table 3). By its reactivity $H_2Tap(C_6H_4CF_3)_6(C_4N_4)$ occupies an intermediate position between the $H_2Tap(C_6H_4NO_2)_8$ and $H_2Tap{\cdot}(C_6H_4Br)_8$. Thus, in going from $H_2Tap(C_6H_4NO_2)_8$ to $H_2Tap(C_6H_4CF_3)_6(C_4N_4)$ and from $H_2Tap(C_6H_4CF_3)_6(C_4N_4)$ to $H_2Tap(C_6H_4Br)_8$, the rate of acid-base interactions with *n*-butylamine in benzene, according to the values of k^{298}, is reduced 3 and ~ 4 times, respectively (Table 3). Consequently, with increasing spatial shielding of the macrocycle reaction site and/or with decreasing acidity of tetraazaporphyrins in the series $H_2TapBr_4 \approx H_2TapCl_4 \rightarrow H_2Tap(C_6H_4CF_3)_8 \rightarrow H_2Tap(C_6H_4NO_2)_8 \rightarrow H_2Tap(C_6H_4CF_3)_6(C_4N_4) \rightarrow H_2Tap(C_6H_4Br)_8$ the interaction of the macrocycles with the nitrogen bases in benzene becomes more difficult.

Besides the proton-donor and proton-acceptor ability of partner molecules, the acid-base interactions involving tetraazaporphyrins depend on the medium dielectric permittivity. Thus, at the replacement of benzene (ε 2.27 [23]) by chlorobenzene (ε 5.61 [23]) the values of k^{298}, E_a, and $\Delta S^{\neq}$ do not undergo significant changes [7, 9, 24]. The situation is different in the mixed solvent benzene–dimethyl sulfoxide, whose dielectric permittivity is higher [25]. It follows from Tables 3 and 4 that in the system of benzene–DMSO the acid-base interactions of $H_2Tap(C_6H_4NO_2)_8$ and $H_2Tap(C_6H_4Br)_8$ with $BuNH_2$ proceed much easier compared to benzene. At a concentration of DMSO more than 1.25% the reaction between the $H_2Tap{\cdot}(C_6H_4NO_2)_8$ and $BuNH_2$ occurs almost instantly at the rate immeasurable by usual kinetic methods. A similar situation is observed in the interaction of $H_2Tap(C_6H_4Br)_8$ with $BuNH_2$ in the system of benzene–50% DMSO. The strong dependence of the reaction rate on the percentage of DMSO in benzene due to the change of the medium dielectric permittivity, which affects directly the polarity of the transition state and, as a consequence, the rate of acid-base interactions.

It is important to note that while in the system of benzene–50% DMSO the reaction between $H_2Tap(C_6H_4Br)_8$ and $BuNH_2$ (pK_a 10.60 [20]) is extremely fast, in the case of MorPh (pK_a 8.70 [20]) and $BzNH_2$ (pK_a 9.34 [20]) it is characterized by relatively low rate constants due to reduced proton-acceptor ability of these bases (Table 4). On the contrary, an increase in pK_a of base by ~ 2 orders of magnitude in the series MorPh → $BzNH_2$ → Et_3N has no significant effect on the rate and activation parameters of the process. However, the replacement of Et_3N (pK_a 10.87 [20]) by Et_2NH with the close basicity (pK_a 10.93 [20]) leads to a significant increase in the k^{298} and decrease in E_a of the process, due to the most favorable steric accessibility of the lone electron pair of the nitrogen atom in these bases.

Kinetic pattern of the acid–base interactions of β,β-tetrabensofused tetraaza porphyrins (phthalocyanines). The acid–base interaction of $H_2Pc(NO_2)_4{\cdot}(t\text{-}Bu)_4$ with nitrogen bases in benzene

$$H_2Pc(NO_2)_4(t\text{-}Bu)_4 + 2B \rightarrow H_2Pc(NO_2)_4(t\text{-}Bu)_4{\cdot}2B \quad (6)$$

is described by the kinetic equation:

$$-d[H_2Pc(NO_2)_4(t\text{-}Bu)_4]/d\tau = k\,[H_2Pc(NO_2)_4(t\text{-}Bu)_4][B]^n. \quad (7)$$

Here, k is the rate constant, n is the reaction order with respect to the base.

In the interaction of $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ with morpholine and benzylamine the n value is close to unity, and with *tert*-butylamine and diethylamine, to

Table 4. Kinetic parameters of acid-base interactions of tetraazaporphyrins with the nitrogen bases in benzene–DMSO [25] $[H_2Tap(C_6H_4Br)_8] = 0.53\times10^{-5}$ M, $[H_2Tap(C_6H_4NO_2)_8] = 0.45\times10^{-5}$ M

Tetraaza porphyrin	Base	x, %	$k^{298}\times10^3$, l^n mol^{-n} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
$H_2Tap(C_6H_4NO_2)_8$	*n*-Butylamine	0.5	0.11	41	210
		1.25	54.00	21	224
$H_2Tap(C_6H_4Br)_8$	*n*-Butylamine	2.5	0.63[a]	82	97
		7.5	3.16[a]	80	90
		20	87.20[a]	60	130
		30	3.16	28	207
		40	99.00	29	175
	Morpholine	50	6.00[a]	24	272
	Benzylamine	50	15.30[a]	35	228
	Diethylamine	50	185.00[a]	19	260
	Triethylamine	50	18.90[a]	32	236

[a] $k^{298}\times10^6$.

Table 5. Kinetic parameters of acid–base interactions of phthalocyanines with nitrogen bases in benzene [14] and dimethyl sulfoxide [13] $[H_2Pc(NO_2)_4(t\text{-}Bu)_4] = 0.9\times10^{-5}$ M, $[H_2Pc(t\text{-}Bu)_4] = 0.23\times10^{-5}$ M

Phthalocyanine	Base	$k^{298}\times10^4$, l^n mol^{-n} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
$H_2Pc(NO_2)_4(t\text{-}Bu)_4$[a]	Morpholine	0.025	45	356
	Benzylamine	0.69	30	328
	tert-Butylamine	0.08	30	245
	Diethylamine	0.37	11	328
$H_2Pc(t\text{-}Bu)_4$[b]	*tert*-Butylamine	0.002	70	142
	Diethylamine	0.019	64	148

[a] Benzene medium. [b] DMSO medium, n is the reaction order with respect to the base.

two. Therefore, depending on the nature of the base, the intermolecular proton transfer from the NH-groups of $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ to a base occurs either in two stages with the constants $k_1 < k_2$, or in one step [14], as in the case of β-tetrahalo-substituted tetraaza porphyrins [7, 9]. A similar one-step process occurs in the interaction of $H_2Pc(t\text{-}Bu)_4$ with diethylamine and *tert*-butylamine in DMSO [13].

According to [13, 14], tetra(3-nitro-5-*tert*-butyl)-phthalocyanine in benzene and tetra(4-*tert*-butyl)-phthalocyanine in DMSO do not react with pyridine and 2-methylpyridine. However, under the influence of more basic morpholine and benzylamine the separation of protons from NH-groups of $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ in benzene becomes significantly easier. The replacement of MorPh (pK_a 8.70 [20]) by $BzNH_2$ (pK_a 9.34 [20]) leads to a significant increase in the values of k^{298}, while the E_a of the process falls (Table 5). Piperidine and *n*-butylamine react with $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ in benzene and $H_2Pc(t\text{-}Bu)_4$ in DMSO extremely fast immediately after mixing the freshly prepared solutions [13, 14].

As might be expected, the increase in the number of alkyl substituents in the amine or branching of the hydrocarbon chain of nitrogen base prevents favorable contact of the reaction sites of the interacting molecules and impairs transport of protons from the NH-groups of $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ and $H_2Pc(t\text{-}Bu)_4$. Thus, the replacement of $BuNH_2$ by close in basicity Et_2NH or t-$BuNH_2$ leads to a significant decrease in the rate of acid-base interaction (Table 5).

It is important to note that at the replacement of dimethyl sulphoxide by benzene, $H_2Pc(t\text{-}Bu)_4$ became unreactive even in the presence of sufficiently strong nitrogen bases (piperidine, *n*-butylamine). This fact indicates that among all studied β-substituted and β,β-

tetrabenzofused tetraaza porphyrins, the $H_2Pc(t\text{-}Bu)_4$ behaves as a very weak dibasic NH-acid. Judging from the data in Tables 3 and 5, $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ has more pronounced acid properties than $H_2Tap(C_6H_4CF_3)_8$, but is inferior by the proton-donor ability to H_2TapBr_4 and H_2TapCl_4.

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