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Kinetics of Acid–Base Interaction of Octaphenyl-Substituted Tetraazaporphyrins with Nitrogen-Containing Bases in a System Benzene–Dimethylsulfoxide

O. A. Petrov[a], N. V. Chizhova[b], and G. V. Osipova[a]

[a] *Ivanovo State Chemical Technological University, pr. Engel'sa 7, Ivanovo, 153000 Russia*
e-mail: poa@isuct.ru

[b] *Institute of the Chemistry of Solutions, Russian Academy of Sciences, Ivanovo, Russia*

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Abstract—Effect of dimethylsulfoxide additives on the kinetics of acid–base interaction of octaphenyl-substituted tetraazaporphyrins with nitrogen-containing bases in benzene is studied. A strong effect of the solvent on the process rate and activation parameters is revealed. The relation of the molecular structure of the interacting molecules to their reactivity is demonstrated.

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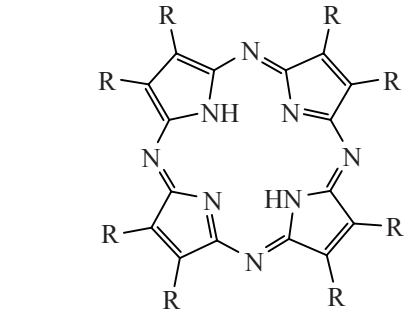
Acid–base interactions with participation of tetrapyrrole macrocycles are of great interest because natural porphyrins are present in many biochemical systems and play a key role in many vital processes. As model compounds for the study of acid–base interaction can be used tetraazaporphyrins, the structural analogs of bio-porphyrins. Due to electron-acceptor effect of their nitrogen *meso* atoms and electronic effect of substituents in the macrocycle pyrrole rings the tetraazaporphyrins possess a pronounced acidity of intracyclic NH bonds [1, 2] that exhibits in the interactions with nitrogen-containing bases. Quantitative data for these reaction are scarce. The most complete information was obtained only for tetrahalotetraazaporphyrins ($H_2TapHal_4$, Hal = Br and Cl) [3–6]. It has been found that $H_2TapHal_4$ in reactions with bases behave like dihydric NH-acids and form complexes with proton transfer. Therewith, the electronic effects of halogen atoms transmitted to the macrocycle reaction center from the semi-isolated $C_\beta{=}C_\beta$ bonds do not affect the process of the acid–base interaction, and the proton transfer from NH-groups of $H_2TapHal_4$ to the base proceeds 10^8–10^{11} times more slowly than from relatively simple proton-donor molecules [7, 8]. Besides, it has been found [4, 6] that formation of the complexes with the proton transfer from $H_2TapHal_4$ is a process of a complicated mechanism, and the kinetic parameters of the acid–base interaction depending significantly not only the properties of the environment and the pK_a value of the nitrogen-containing base but also on the steric shielding of the proton-acceptor center. In contrast to $H_2TapHal_4$, the data on the acid–base interaction of octaphenyl-substituted tetraazaporphyrins is much poorer [3, 9, 10].

Therefore in the present work we investigated the effect of dimethylsulfoxide (DMSO) additives on the process of the acid–base interaction of octa(*p*-nitrophenyl)tetraazaporphin [$H_2Tap(C_6H_4NO_2\text{-}p)_8$] and octa(*p*-bromophenyl)tetraazaporphin [$H_2Tap(C_6H_4Br\text{-}p)_8$] with nitrogen-containing bases (B) in benzene. As bases B we used butylamine ($BuNH_2$), morpholine (Mor), benzylamine ($BzNH_2$), diethylamine (Et_2NH) and triethylamine (Et_3N).

In preliminary experiments it was established that changes in the spectra of reaction mixture in the process of reaction of $H_2Tap(C_6H_4NO_2\text{-}p)_8$ with $BuNH_2$ in the system benzene–DMSO containing up to 1.25% of DMSO were identical with the same in benzene [9]. In the electron absorption spectrum (EAS) of $H_2Tap(C_6H_4NO_2\text{-}p)_8$ (λ_I 670, λ_{II} 602 nm) the intensity of the band at λ 650 nm grows in time and simultaneously diminish the bands λ_I and λ_{II} (Fig. 1). Similar pattern was observed in the reaction of $H_2Tap(C_6H_4Br\text{-}p)_8$ with $BuNH_2$ in benzene containing up to



R = Br [$H_2Tap(C_6H_4Br)_8$],

R = NO_2 [$H_2Tap(C_6H_4NO_2)_8$].

40% of DMSO [10]. According to [1], in the acid–base interaction involving tetraazaporphyrin the energy of the lowest unoccupied molecular orbital (LUMO) π_1^* and of highest occupied molecular orbital (HOMO) π_1 grow, while the energy of HOMO π_2 and LUMO π_2^* remain practically the same. Decrease in the energy difference between two HOMOs π_1 and π_2 as well as degeneration of two LUMOs $\pi_{1,2}^*$ (Fig. 2) leads to increase in symmetry of the molecule π-chromophore from D_{2h} to D_{4h} (Fig. 1). This indicates that $H_2Tap(C_6H_4NO_2\text{-}p)_8$ in the presence of $BuNH_2$ behaves as dihydric NH-acid.

More detailed study showed that interaction of $H_2Tap(C_6H_4NO_2\text{-}p)_8$ with $BuNH_2$ in the system benzene–DMSO was described by the equation of the first order with respect to NH-acid (Fig. 3):

$$-d[H_2Tap(C_6H_4NO_2\text{-}n)_8]/d\tau = k_{eff}[H_2Tap(C_6H_4NO_2\text{-}n)_8], \quad (1)$$

where k_{eff} is the effective reaction rate constant.

The reaction order on $BuNH_2$ found graphically as the slope of the straigth lines in Fig. 4 is close to unity. In this case relations (2) and (3) are fulfilled

$$k_{eff} = k[BuNH_2], \quad (2)$$

$$-d[H_2Tap(C_6H_4NO_2\text{-}n)_8]/d\tau = k[H_2Tap(C_6H_4NO_2\text{-}n)_8][BuNH_2]. \quad (3)$$

These data suggest that the acid–base interaction proceeds in two steps:

$$H_2Tap(C_6H_4NO_2\text{-}n)_8 + BuNH_2 \xrightarrow{k_1} H_2Tap(C_6H_4NO_2\text{-}n)\cdot BuNH_2, \quad (4)$$

$$H_2Tap(C_6H_4NO_2\text{-}n)BuNH_2 + BuNH_2 \xrightarrow{k_2} H_2Tap(C_6H_4NO_2\text{-}n)\cdot 2BuNH_2. \quad (5)$$

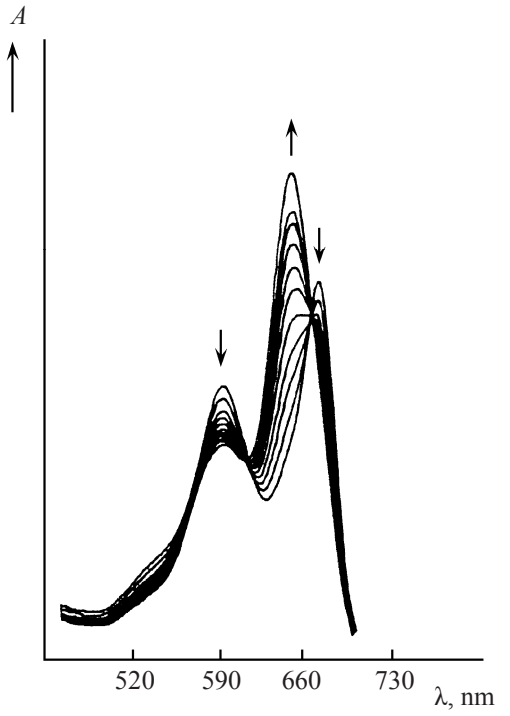


Fig. 1. Change in time of the electron absorption spectrum of $H_2Tap(C_6H_4NO_2\text{-}p)_8$ in the presence of $BuNH_2$ in the system benzene–0.5% DMSO at 318 K.

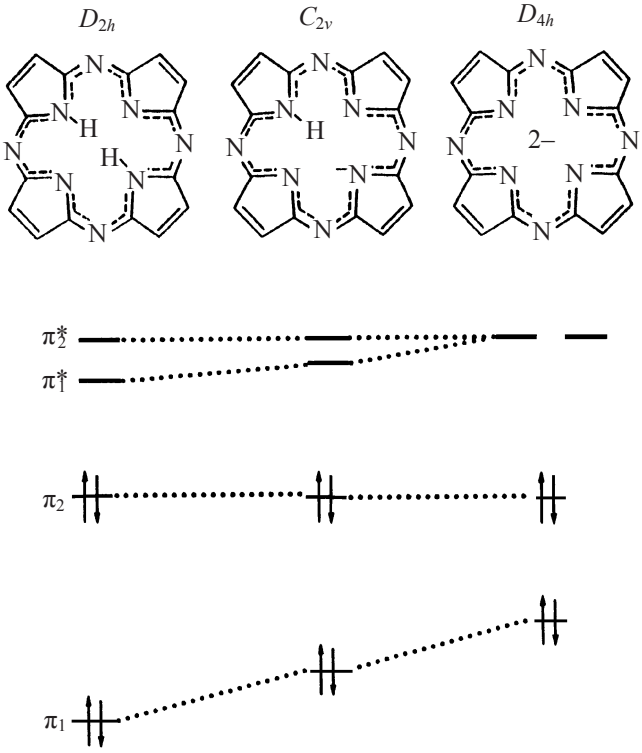


Fig. 2. Change in the energy of HOMO and LUMO in the process of acid ionization of tetraazaporphyrin macrocycle.

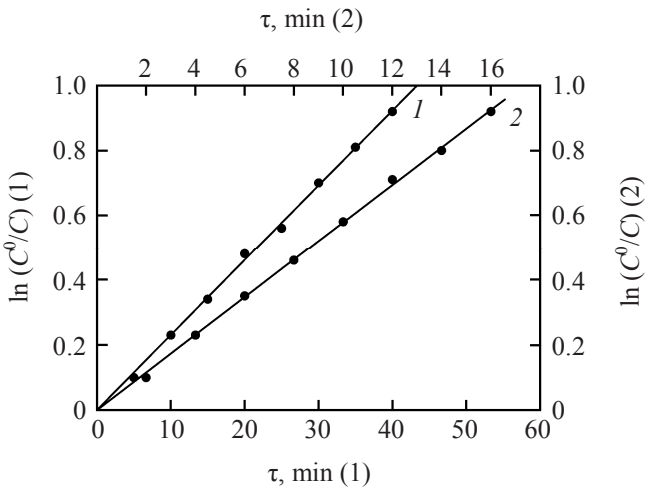


Fig. 3. Plots ln(C^o/C) vs. reaction duration of H_2Tap·$(C_6H_4NO_2$-$p)_8$ with butylamine at the concentrations (mol l^{-1}): [$BuNH_2$] = (*1*) 3.04 and (*2*) 0.025 in the system benzene–DMSO with DMSO content (*1*) 0.5% and (*2*) 1.25 % at 298 K.

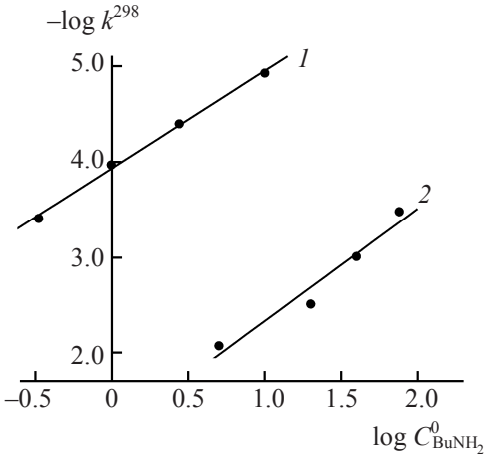
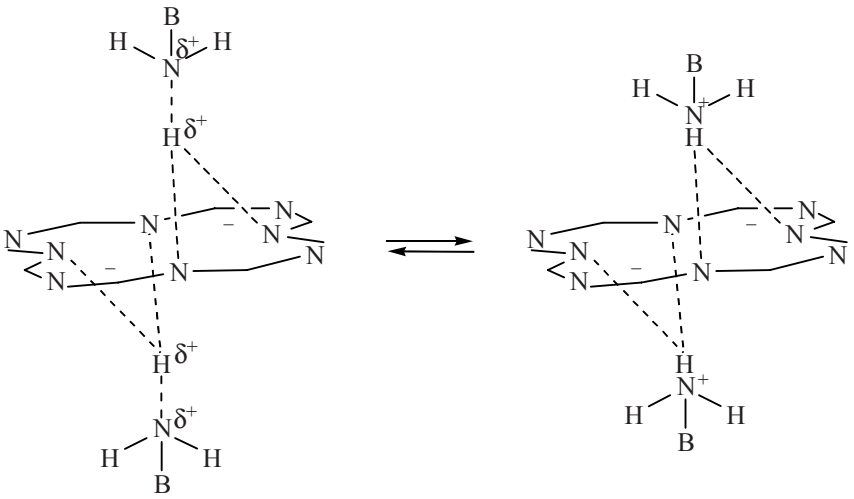


Fig. 4. The plots of log k_{eff} vs. log [$BuNH_2$] for the reaction of $H_2Tap(C_6H_4NO_2$-$p)_8$ with butylamine in the medium of benzene–DMSO with DMSO content (*1*) 0.5% and (*2*) 1.25 % at 298 K.

Judging from the results of quantum-chemical calculations [1], the first step of the acid–base interaction proceeds with decrease in the symmetry of the tetraazaporphyrin macrocycle from D_{2h} to C_{2v}, therefore in the electronic spectra should occur a blue shift of the longwave component Q_x leading to a diminished splitting of the *Q*-band. However, under the conditions of considerable excess of $BuNH_2$ such spectral changes do not occur. Decrease in the H_2Tap·$(C_6H_4NO_2$-$p)_8$ concentration in the system benzene–DMSO proceeds with the retention of clear isobestic points without appearance in the reacting system of intermediate spectral form, namely, $H_2Tap(C_6H_4NO_2$-$p)$·$BuNH_2$ (Fig. 1). This fact suggests that $k_1 < k_2$. Note that similar two-step process of the acid–base interaction probably occurs also in the case of formation of $H_2Tap(C_6H_4Br$-$p)_8$·$2BuNH_2$ [9].

It was reported earlier [11] that in the products of the acid–base interaction of tetraazaporphyrin with nitrogen-containing bases the intracyclyc hydrogen atoms connected with the molecules B were located over and under the macrocycle plane that provided a high symmetry of the charge distribution [12]. Therewith, in the low-polar benzene whose solvating ability is poor the complete transfer of NH groups protons from the acid to the base does not occur which would lead to the formation of solvent-separated ion pairs followed by dissociation. The acid–base interaction is restricted basically to the step of formation of H-complex (**I**) [11]. When H_2Tap $(C_6H_4NO_2$-$p)$ is taken instead of $H_2Tap(C_6H_4Br$-$p)_8$, and also when benzene–DMSO solvent with higher polarity is applied instead of benzene, a shift of acid–base equilibrium to the formation of ionic complex, the H-bound ion pair **II**, is expectable.

Analysis of the kinetic data (Tables 1 and 2) leads to a conclusion that the acid–base interaction of H_2Tap $(C_6H_4Br$-$p)_8$ and $H_2Tap(C_6H_4NO_2$-$p)_8$ with $BuNH_2$ in benzene is characterized by extremely low rates and unusually high E_a and $\Delta S^{\neq}$ characteristics of the process due to the steric component of the effect of the macrocycle. Thus, the continuous π,π-overlapping over 16-membered macrocycle (C_8N_8), the inclusion into the *n*π-conjugation of *n*-electron pairs of intracyclic nitrogen atoms, and the increase in the number of π-electrons in the conjugated system in account of nitrogen *meso* atoms favors decrease in the conformational flexibility of $H_2Tap(C_6H_4Br$-$p)_8$ and $H_2Tap(C_6H_4NO_2$-$p)_8$ molecules. The relatively high rigidity of planar conformation of the tetraazaporphyrin macrocycle [13] as well as the existence of eight *p*-nitrophenyl (*p*-bromophenyl) substituents in its pyrrole rings defines steric shielding of NH groups protons by atoms and π-electrons. Therefore the most favorable contact of reaction centers of molecules of the partners is restricted as reflected in the kinetic parameters of the process. Noteworthy that further inhibition of acid–base interaction occurs when not only the proton-



I **II**

Table 1. Kinetic parameters of acid–base interaction of octa(*p*-nitrophenyl)tetraazaporphin with butylamine in benzene [9] and in benzene–DMSO medium [$H_2Tap(C_6H_4NO_2$-*p*$)_8$] 0.45×10^{-5} mol l^{-1}

Medium	$C^0_{BuNH_2}$, mol l^{-1}	T, K	$k_{eff}\times10^5$, s^{-1}	$k\cdot10^4$, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
Benzene	1.01	298	0.18	0.018	86	75
Benzene–0.5% DMSO	0.1	298	1.18±0.02	1.10±0.03	41±5	210±16
		308	1.80±0.06	1.65±0.08		
		318	3.35±0.16	3.13±0.17		
	0.36	298	4.06±0.21	1.25±0.06	34±5	223±15
		308	5.52±0.26	1.70±0.08		
		318	9.75±0.45	3.00±0.15		
	1.01	298	10.60±0.45	1.05±0.05	40±5	195±15
		308	18.45±0.80	1.83±0.09		
		318	29.25±1.16	2.90±0.12		
	3.04	298	38.40±1.55	1.20±0.05	37±4	194±13
		308	64.05±2.25	2.00±0.08		
		318	97.70±3.70	3.05±0.13		
Benzene–1.25% DMSO[a]	0.013	298	3.27±0.15	5.27±0.27	22±3	204±11
		308	4.40±0.19	7.10±0.33		
		318	5.75±0.25	9.25±0.43		
	0.025	298	9.60±0.36	5.55±0.23	25±6	189±20
		308	13.40±0.57	7.76±0.38		
		318	18.25±0.84	10.55±0.55		
	0.05	298	30.80±1.27	5.15±0.22	26±7	214±21
		308	41.90±1.70	7.00±0.30		
		318	59.55±3.00	9.95±0.50		
	0.2	298	84.80±3.60	5.40±0.27	21±3	224±11
		308	107.55±5.15	6.85±0.35		
		318	146.00±7.00	9.30±0.50		

[a] In the medium of benzene–1.25% DMSO the values are scaled: $k_{eff}\times10^4$, $k\times10^2$.

Table 2. Kinetical parameters of acid–base interaction of octa(*p*-bromophenyl)tetraazaporphin with nitrogen-containing bases in benzene [5] and in benzene–DMSO medium [10], $[H_2Tap(C_6H_4Br\text{-}p)_8]$ 0.53×10^{-5} mol l^{-1}

Medium	Base (B)	C_B^0, mol l^{-1}	$k_{eff}\times10^6$, s^{-1}	$k^{298}\times10^6$, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
Benzene	Butylamine	3.04	0.61	0.16	92	63
Benzene–2.5% DMSO	Butylamine	3.04	1.80	0.63	82	97
Benzene–7.5% DMSO	Butylamine	2.42	7.00	3.16	80	90
Benzene–20% DMSO	Butylamine	0.76	63.65	87.20	60	130
Benzene–30% DMSO[a]	Butylamine	0.05	0.12	3.16	28	207
Benzene–40% DMSO[a]	Butylamine	0.05	3.70	99.00	29	175
Benzene–50% DMSO	Morpholine	0.28	2.00	6.00	24	272
Benzene–50% DMSO	Benzylamine	0.23	2.50	15.30	35	228
Benzene–50% DMSO	Diethylamine	0.24	51.00	185.00	19	260
Benzene–50% DMSO	Triethylamine	0.24	3.70	18.90	32	236

[a] In benzene–30% DMSO and benzene–40% DMSO media $k_{eff}\times10^3$, $k\times10^3$.

donor, but also proton-acceptor center is sterically shielded. In benzene medium no inter-action occurs between $H_2Tap(C_6H_4NO_2\text{-}p)_8$ [9] or $H_2Tap(C_6H_4Br\text{-}p)_8$ [5] with Et_2NH or Et_3N, unlike the case of $BuNH_2$ which is close to them by basicity.

Despite the structural similarity of octaphenyl-substituted tetraazaporphyrins, $H_2Tap(C_6H_4Br\text{-}p)_8$ is less active in the reaction with B than $H_2Tap\cdot(C_6H_4NO_2\text{-}p)_8$. In benzene medium it does not enter into the reaction with morpholine and benzylamine [5]. In the case of butylamine the rates of the acid–base interaction of $H_2Tap(C_6H_4NO_2\text{-}p)_8$ and $H_2Tap(C_6H_4Br\text{-}p)_8$ differ by a factor of ~10 (Tables 1 and 2). Hence, the replacement of eight *p*-nitrophenyl substituents by *p*-bromophenyl ones increases covalence and strength of intracyclic NH bonds and diminishes proton-donor ability of $H_2Tap(C_6H_4Br\text{-}p)_8$.

It was shown earlier [11] that the values k, E_a, and $\Delta S^{\neq}$ characterizing the acid–base interactions involving tetraazaporphyrin do not undergo considerable changes at the replacement of chlorobenzene by benzene because in the studied range of dielectric permeability of the media the electrostatic effects of solvent are not crucial. Another situation occurs when mixed solvent with higher polarity and solvating strength is applied. From the data of Table 1it is seen that in the system benzene–DMSO the acid–base interaction of $H_2Tap(C_6H_4NO_2\text{-}p)_8$ with $BuNH_2$ is facilitated considerably as compared with benzene. At the addition of 0.5% of DMSO the reaction rate grows approximately 60-fold, the increase in DMSO concentration from 0.5% to 1.25% increases k^{298} ~500 times on the background of decrease in E_a and $\Delta S^{\neq}$ values. At the DMSO concentration over 1.25% the reaction between $H_2Tap\cdot(C_6H_4NO_2\text{-}p)_8$ and $BuNH_2$ proceeds practically instantly. Similar changes in *k*, E_a and $\Delta S^{\neq}$ occur in the reaction of $H_2Tap(C_6H_4Br\text{-}p)_8$ with $BuNH_2$ (Table 2). Small additives (2.5–7.5%) of the polar component affect the acid–base interaction less than the presence of 20% and higher of DMSO. In the mixed solvent the value of reaction rate constant grows sharply only when 50% of DMSO is added, and her the rate cannot be measured by ordinary kinetic methods of. The data obtained suggest that the strong dependence of the reaction rate constant and activation parameters of the process on the content of DMSO in benzene first of all is connected with the change in the dielectric permeability of the medium that affects directly the polarity of the forming transition state and consequently the rate of the acid–base interaction.

It is important to note that while in the system benzene–50% DMSO the reaction between $H_2Tap\cdot(C_6H_4Br\text{-}p)_8$ and $BuNH_2$ (pK_a = 10.60 [14]) is extremely fast, in the case of Mor (pK_a = 8.70 [14]) and $BzNH_2$ (pK_a = 9.34 [14]) it is characterized by rather low values of rate constants due to diminished proton-acceptor ability (Table 2). On the contrary, the increase in pK_a of nitrogen-containing bases by two orders of magnitude in the series Mor → $BzNH_2$ → Et_3N does not affect substantially the process rate and activation parameters. However, the replacement of Et_3N (pK_a = 10.87 [14]) by Et_2NH with similar basicity

(pK_a = 10.93 [14]) leads to a significant increase in k^{298} and a decrease in E_a of the process, that is defined by favorable steric accessibility of lone electron pair of the nitrogen atom.

EXPERIMENTAL

Octaphenyl-substituted tetraazaporphyrins were synthesized along the procedures in [15, 16]. Benzene, DMSO, and nitrogen-containing bases were twice purified according to [17, 18]. Kinetic measurements were carried out on a Lambda-20 spectrophotometer. To the thermostated cell were charged freshly prepared solutions of octaphenyl-substituted tetraazaporphyrin with a constant concentration and of nitrogen-containing base with varied concentration, in benzene–DMSO as a solvent. The reaction rate of the acid–base interaction was derived from the decrease in the optical density of the solution at the wavelength λ_{II} = 602 nm. The calculation of kinetic parameters of the acid–base interaction was carried out by the procedure described by us earlier [5].

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