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Effect of the Type of Molecular Nonplanar Structure on the Chemical Reactivity of NH Bonds in the Coordination Center of Porphyrin Molecule

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Abstract—Effect of out-of-plane screwing of the porphyrin macrocycle (H_2P) by means of tetra-*meso*-substitution and intracyclic N-substitution on the state of NH bonds in the molecule is explored. By applying ^1H NMR, kinetic and quantum-chemical criteria of evaluation of the macrocycle NH-reactivity is found that such type of H_2P screwing does not increase reactivity of the NH bonds. It is shown that increased chemical NH activity is observed only in the porphyrins undergoing at a significant conformational screwing possess the polarization of the molecular π-system.

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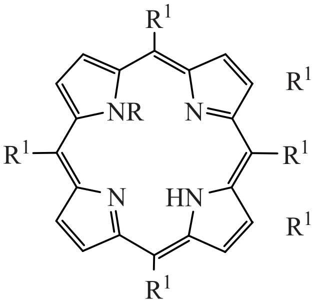
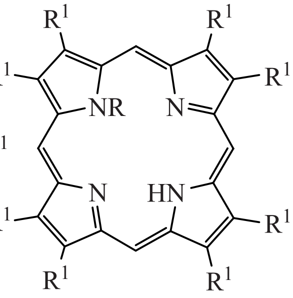
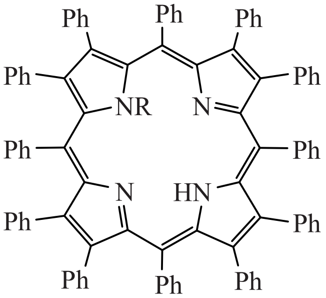
A large number of publications reports on the study of the effect of the out-of-plane screwing of macroring on the chemical properties and biological activity of porphyrins (compounds **I–XIII**) [1–4]. The porphyrins being derivatives of planar aromatic porphin (**I**) can become nonplanar owing to certain structural modifications [4, 5], including the following:

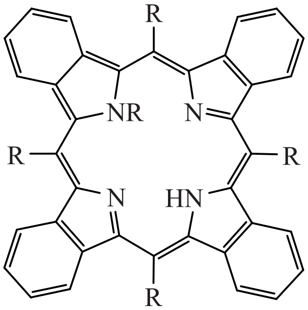
(1) Modification of H_2P molecule periphery by means of multiple (*nona-, deca-, undeca-* or *dodeca-*) substitution of exocyclic hydrogen atoms in the macrocycle β- and *meso*-positions simultaneously (e.g., compounds **XI** and **XIII**); introduction of bulky functional substituents to three or all four *meso*-positions [isopropyl (**VI**), *t*-butyl-, adamantoyl and others]; formation of overlapped monomeric or dimeric structures $H_4P_2(R)_n$ with short spacers R [6].

(2) Modification of the coordination center of H_2P, namely: substitution of H atoms of intracyclic NH groups (NR-substitution) as, e.g., in compounds **III, IV** and **X** [7]; protonation of tertiary nitrogen atoms with formation of H_2P mono- and dicationic forms H_3P^+ and H_4P^{2+} respectively [5, 8]; complexing with

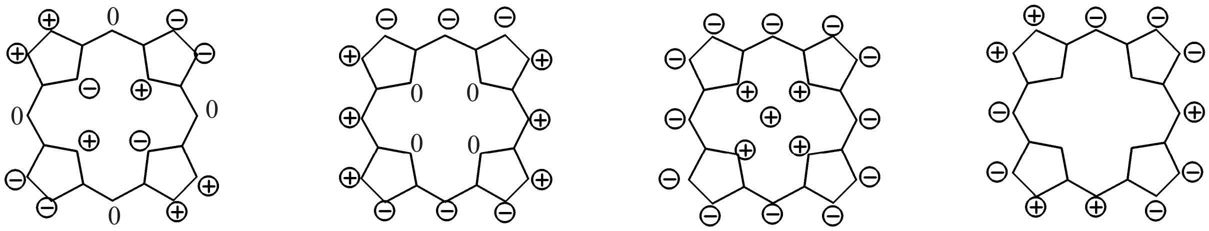

I–VIII


IX, X


XI


XII, XIII

R = R^1 = H (**I**); R = H, R^1 = Ph (**II**); R = Me, R^1 = Ph (**III**); R = R^1 = Ph (**IV**); R = H, R^1 = *p*-Pr (**V**); R = H, R^1 = *iso*-Pr (**VI**); R = H, R^1 = *cyclo*-Hex (**VII**); R = H, R^1 = *tert*-Bu (**VIII**); R = H, R^1 = Et (**IX**); R = Me, R^1 = Et (**X**); R = H (**XII**); R = Ph (**XIII**).



Saddle *Ruffle* *Dome* *Wave*

Fig. 1. Basic types of nonplanar conformations of H_2P and its complexes with metals. Signs "+" and "–" assume position of atoms over and below, respectively, of initial plane of macrocycle [4, 12].

metals with ionic radii much less or, on the contrary, much larger than the size of coordination cavity (r = 2.01 Å) as in the cases of Ni(II) or Zn(II), respectively;

(3) Changes in H_2P molecule leading to the loss of aromaticity [5], for example: formation of radical forms of porphyrins, of π-cation-radicals in particularicular; decrease in the size of π-chromophore by means of reduction of C_β–C_β bonds of pyrrole rings (chlorins, bacterio- and isobacteriochlorins, and other compounds).

(4) Combination of various factors (dodeca-substitution and protonation, etc.) [4].

The distortion of the planar structure of the porphyrin macrocycle commonly leads to an appearance of typical nonplanar conformations or combinations of such conformations that in a certain manner change the properties of the molecule. By extensive X-ray structural [4], spectral [1, 2, 9, 10], quantum-chemical [11], and other studies the molecular and ionic forms of H_2P and MP with nonplanar structure were classified according to the type of screwing as *saddle*, *ruffle*, *dome*, *wave*, *stepped*, *twisted*, *gable* etc. (Fig. 1) [12]. Among these conformation the most often in H_2P and their complexes with *d*-metals appear the *saddle* and *ruffle* conformations and their combinations.

As a measure of non-planarity of porphyrin molecules can serve not only the data of X-ray structural analysis [4, 12] reflecting structure of the macrocycles in solid phase but also the fluorescence data [2, 5], results of Raman spectra [10, 13] and in some cases NMR spectral characteristics [9] reflecting conformational state of compounds in solution.

The principal problem is whether a connection exists between nonplanar structure of the porphyrin macrocycle and chemical reactivity of NH bonds in its coordination center. If such connection really exists and hence simple change in the conformation of H_2P molecule can critically change its properties governing the state of NH bond in the macrocycle then it is prsumable that the mechanism with participation of these processes *in vivo* may be the same. In particular, the activation of chemical bonds in the reaction center of the porphyrin molecule leads to a spasmodic growth of their NH-acidity (by 10 and more orders of magnitude of pK_a value in DMSO [14]), to formation of stable H-associates of H_2P molecules and electron-donor solvents with incomplete proton transfer [15] and as a consequence to catalytic action of these solvents on the processes of capture of the atoms of *p*- and *d*-metals by porphyrin macrocycle [16].

Besides the dodeca-substitution, the most pronounced types of screwing of the planar structure of H_2P molecules can be induced by substitution at *meso* positions by bulky, most often alkyl, groups that leads to a *ruffle* conformation, and also the substitution of a hydrogen atom at one or more nitrogen atoms in the coordination center with the formation of N-substituted porphyrin analogs [7]. In the last case the *saddle* conformation of asymmetric type is typical for the molecules (Fig. 1). The present study is focused on the study of the relations between the structure and properties of *meso*-substituted H_2P with bulky groups (*ruffle*, compounds **VI–VIII**), as well as N-substituted (compounds **III, IV, X**) H_2P analogs (*saddle*).[1]

By their spectral characteristics, physicochemical properties, and reactivity both *meso*-substituted por-

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[1] The *ruffle* and *saddle* nonplanar conformations are characterized by the value (in Å) of average deviation of *meso* (ΔC_{meso}) and β (ΔC_β) carbon atoms from the parent macrocycle plane that can achieve 1.5 Å.

Table 1. Electron absorption spectra of *meso*- and N-substituted porphyrins in organic solvents

Comp. no.	Solvent	λ_{Cope}, nm (log ε)	λ_{IV}, nm (log ε)	λ_{III}, nm (log ε)	λ_{II}, nm (log ε)	λ_{I}, nm (log ε)	$\Delta\lambda_1$, nm
IX	C_6H_6	395 (5.30)	497 (4.19)	530 (4.07)	567 (3.92) 596 (3.18)	621 (3.81)	–2
	DMF	387 (5.31)	495 (4.16)	528 (4.03)	565 (3.86) 592 (3.05)	619 (3.74)	
X	C_6H_6	412 (5.19)	506 (4.35)	536 (4.13)	586 (4.02) 615 (3.80)	643 (3.94)	–2
	DMF	409 (5.11)	504 (4.18)	533 (3.85)	585 (3.71) 618 (3.22)	641 (3.61)	
II	C_6H_6	418 (5.58)	514 (4.33)	548 (3.96)	591 (3.81)	647 (3.68)	–1
	DMF	416 (5.62)	513 (4.28)	548 (3.91)	590 (3.73)	646 (3.68)	
III	C_6H_6	426 (5.30)	499 (3.84) sh 521 (4.13)	572 (4.26)	614 (3.78)	677 (3.77)	–1
	DMF	425 (5.24)	498 (3.95) sh 532 (4.18)	564 (4.32)	614 (3.90)	676 (3.87)	
IV	C_6H_6	443	sh	592	sh	705	–1
	DMF	444	sh	595	sh	704	
VI	C_6H_6	417 (5.18)	521 (4.00)	559 (3.73)	603 (3.48)	661 (3.51)	–4
	DMF	415 (5.19)	518 (4.06)	533 (3.78)	599(3.53)	657 (3.54)	
VII	C_6H_6	420 (5.05)	526 (3.66)	561 (3.47)	606 (3.13)	663 (3.31)	–4
	DMF	420 (5.03)	524 (3.60)	560 (3.37)	601 (3.00)	659 (3.17)	

phyrins and N-substituted analogs of H_2P behave like compounds with a nonplanar structure. Thus, all the bands in the visible region of their electronic spectra suffer a red shift relatively to those in the spectra of predominantly planar H_2P (Table 1) that, however, is not a reliable criterion of nonplanarity of the molecules. The more convincing proofs are the photophysical characteristics describing properties of their excited states. As characteristics of nonplanar porphyrins significant Stock's shifts of neighboring bands in fluorescence spectra compared to the absorption bands ($\Delta\nu_I$), low fluorescence quantum yields (φ_{fl}), and transitions to the triplet state (φ_P) [2, 4, 5] are suggested. Besides, in vibration spectra of nonplanar porphyrins may occur typical frequency modes [10], and in ^{1}H NMR spectra are observed downfield shifts of NH proton signals at applying universal solvating solvents caused by deshielding of coordination center at the screwing of planar structure of the molecule.

Due to the activation of the out-of-plane vibrations, the porphyrins of these structural groups show enhanced solubility in organic solvents [17] and unusual for the predominantly planar H_2P redox properties [1]. The stability of the ligands and their complexes toward elevated temperature and the action of chemical reagents decreases [5, 18]. For example, the temperature of the start of the thermooxidative descomposition (t_{start}) of strongly nonplanar dodecaporphyrin (**XI**) and *N*-methyltetraphenylporphin (**III**) is lowered compared to almost planar compound (**II**) from 407 to 244°C and 260°C, respectively. Therewith it is established that aromaticity of strongly nonplanar porphyrins in its canonical understanding diminishes compared to planar molecules only by 3–5% [9].

Obviously partial localization of the π-electron density in the pyrrole rings of the macrocycles of types **III, IV, VI–VIII**, and **X** leads to an increase in basicity of the tertiary nitrogen atoms and in their ability to bind proton even in acids of a moderate strength [8]. Also, the ability of the studied nonplanar H_2P to complex formation in the medium of solvents with moderate donor–acceptor characteristics, e.g., in acetonitrile increases [19].

The problem whether the nonplanar *meso*- (**VI–VIII**) and N-substituted macrocycles (**III–IV, X**) belong to the group of the porphyrins with chemically

Table 2. Effect of solvent nature on the position of signals of NH protons ($\Delta\delta_{NH}$, ppm) in the ^{1}H NMR spectra of H_2P possessing chemically active or inert NH bonds

Porphyrin	Solvent	δ_{NH}, ppm	Solvent	δ_{NH}, ppm	$\Delta\delta_{NH}$, ppm
II	$CDCl_3$	–2.76	DMSO-d_6	–2.91	–0.15
VI	$CDCl_3$	–1.79	DMSO-d_6	–2.17	–0.38
VII	$CDCl_3$	–1.60	DMSO-d_6	–1.94	–0.34
XI[a]	$CDCl_3$	–0.90	Py-d_5	+1.00	+1.90

[a] Published data [9].

active NH bonds has never been discussed. To our best knowledge, to this moment there is no data on the acidity of NH bonds in the molecules of *meso*-substituted porphyrins with bulky *meso*-substituents. There are rather contradictory data [5,7] on the effect of intracyclic N-substitutents in H_2P molecule on its acid properties. Commonly, transfer of a porphyrin with chemically active NH bond from universally solvating medim to a polar electron-donor solvent is accompanied by change in the structure of the bands of its electronic spectrum [5,14,15]. From the data in Table 1 follows that positions of the bands of N- and *meso*-substituted compounds under study in benzene and DMF remain practically the same. Moreover, shift of the most low-frequency Q_x band in the electron absorption spectra of compounds **III, IV, VI** and **VII** at this replacement of the solvent, that is, solvatochromic effect of the macrocycles, under these conditions is not higher than 4 nm. However, the data of electron absorption spectra are not adequate for the conclusion about the state of NH bonds in these compounds [5].

For solving the problem of the nature of NH-reactivity of the porphyrins with nonplanar structure of their π-system it is reasonable to use ^{1}H NMR, kinetic, and quantum-chemical criteria of chemical reactivity of NH bonds in these molecules we have suggested previously [20]. Unfortunately, in most cases the signal of NH proton in ^{1}H NMR spectra of N-substituted porphyrins is not seen at all [7]. In contrast, the NH signals and their dependence on the nature of solvent are clearly seen in the spectra of nonplanar *meso*-substituted porphyrins (Table 2). Analysis of the data in Table 2 leads to a conclusion that δ_{NH} values of compounds **II, VI–VII** suffer an upfield shift at the replacement of the universally solvating chloroform by electron-donor DMSO, while for compound **XI** and the other NH-active macrocycles the typical situation is the opposite [20].

For confirming the fact of low chemical activity of NH bonds in nonplanar *ruffle* H_2P we will use two other criteria of NH-activity, the quantum-chemical and kinetic ones [20].

Table 3 contains for comparison the data of quantum-chemical calculations of enthalpy of formation of H_2P ligands, their mono- (HP^-, $\Delta H_{f(-1)}$, kcal mol^{-1}) and dianions (P^{2-}, $\Delta H_{f(-2)}$, kcal mol^{-1}), as well as the values of deprotonation heat of the ligands

Table 3. Enthalpy characteristics of deprotonation [$\Delta H_{f(-1)}$ and $\Delta H_{f(-2)}$, kcal mol^{-1}] and formation of mono- and dianionic forms $\Delta H_{(-1)}$ and $\Delta H_{(-2)}$, kcal mol^{-1} of the porphyrins with planar and nonplanar structures

Comp. no.	$\Delta H_{f(0)}$, kcal mol^{-1}	$\Delta H_{f(-1)}$, kcal mol^{-1}	$\Delta H_{f(-2)}$, kcal mol^{-1}	$\delta\Delta H_{f(0-1)}$, kcal mol^{-1}	$\delta\Delta H_{f(0-2)}$, kcal mol^{-1}	$\Delta H_{(-1)}$, kcal mol^{-1}	$\Delta H_{(-2)}$, kcal mol^{-1}
I	221.00	200.81	264.09	*20.19*	*–43.09*	347.01	777.49
IX[a]					*–39.01*		
II[a]					*–25.64*		
V	151.91	132.54	192.37	*19.37*	*–40.46*	347.83	774.86
VI	178.54	160.12	217.27	*18.42*	*–38.73*	348.78	773.13
VII	131.62	111.92	167.04	*19.70*	*–35.42*	347.50	769.82
VIII	195.96	176.05	231.19	*19.91*	*–35.23*	347.29	769.63
X	129.24	113.26	–	*15.98*	–	351.22	–
III	352.27	329.70	–	*22.57*	–	344.63	–
IV	392.90	372.72	–	*20.18*	–	347.02	–
XII	265.25	237.53	281.80	*27.72*	*–16.55*	339.48	750.95
XIII	401.29	371.91	403.63	*29.38*	*–2.34*	337.82	736.74
XI	587.56	554.62	574.27	*32.94*	*13.29*	334.26	721.11

[a] Published data [21].

(ΔH_{-i}) into mono- and dianions in a vacuum for basically flat not NH-active porphyrins **I–II, V, IX**, and of nonplanar *meso*-substituted porphyrins **VI–VII** and N-substituted H_2P analogs **III–IV, X**. The accepted as estimates $\delta\Delta H_{f(0-2)}$ values (Table 3) show that unlike the dodeca-substitution of H_2P (compound **XI**), the *meso*- or N- substitution in the macrocylcle does not lead to the chemical activation of the NH bonds (Fig. 2). The $\delta\Delta H_{f(0-2)}$ values only slightly tend to shift to the positive side (by 5–8 units only), while even in the compounds with weak NH-activity like H_2TBP (**XII**) and H_2TPTBP (**XIII**) this shift attains 26.5 and 23.3 units respectively (Table 3). Inasmuch as the N-substituted porphyrins are monohydric acids, analysis of their quantum-chemical data can be based on the $\delta\Delta H_{f(0-1)}$ values. It follows from the data in Table 3 and in Fig. 2 that this value also, compared to the NH-active compounds **XII** and **XIII**, practically does not grow relatively to unsubstituted porphin (**I**). Thus, quantum-chemical calculations confirm the conclusion on the absence of a noticeable chemical activity of NH bonds in nonplanar *meso*-substituted H_2P and N-substituted porphyrin analogs.

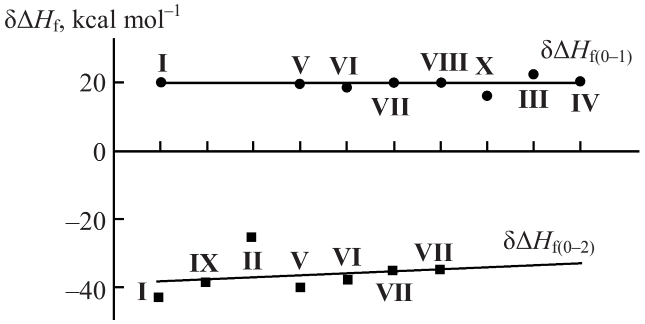

Fig. 2. Plots of characteristics of relative stability of the H_2P mono- and dianions ($\delta\Delta H_{f(0-1)}$ and $\delta\Delta H_{f(0-2)}$, kcal mol^{-1}) with chemically inactive NH bond against molecular structure (data of [21]).

Now let us consider the data that form the basis of the kinetic criterion of NH-reactivity. From the experimental values obtained for the reaction of complex formation (1) of the ligands **III** and **X** follows (Table 4) that the rates of complex formation of N-substituted compounds fall with the increase in the electron-donor property of solvent: propanol-1 > DMF > DMSO > Py [22], that corresponds to the behavior of porphyrins whose NH bond is localized, i.e., chemically inert. Moreover, in pyridine that activates NH bonds the rate of reaction of nonplanar H(N–Me)TPP (**III**) with zinc acetate not only grows relatively to the media with lower coordinating activity, but at attaining certain concentration of the product an equilibrium is established [23].

$$\xrightarrow{-2\,\mathrm{Solv}} \mathrm{H(NR)P} + \mathrm{MX_2(Solv)}_{n-2}$$
$$[\mathrm{H(NR)P}\cdots\mathrm{MX_2(Solv)}_{n-4}]^{\#}$$
$$\rightarrow \mathrm{(X)M(NR)P} + \mathrm{HX} + (n-4)\mathrm{Solv}. \qquad (1)$$

An additional argument in favor of the absence of NH–activity in N-substituted porphyrins is the negative activation entropy in the reactions of their coordination with *d*-metal salts. On the contrary, positive $\Delta S^{\#} = S^{\#} - S^{\mathrm{init}}$ in NH–reactive H_2P we attribute to a substantial solvation of the initial state on the reaction coordinate (Table 4) [5].

Data on the kinetics of complex formation of nonplanar porphyrins in a *ruffle* conformation are practically absent. Our study on an example of H_2T(*i*-Pr)P (**VI**) and H_2T(*cyclo*-Hex)P (**VII**) (ΔC_{meso} for their complexes with Ni(II) are respectively 0.74 and 0.77 Å [4]) showed that rates of this reactions with copper, zinc and cadmium acetate in electron-donor

Table 4. Kinetic parameters of reaction (1) of N-substituted porphyrins with $Zn(OAc)_2$ in organic solvents

Comp. no.	$C_{\mathrm{salt}} \times 10^3$ mol l^{-1}	Solvent	k_v^{298}, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
X	2.6	Py	0.014	77.0±1.4	–30±2
	2.0	DMSO	5.20	52.8±2.8	–56±3
	2.0	DMF	fast	–	–
	0.2		131.4	7.1±0.1	–189±15
	0.2	PrOH-1	fast	–	–
III	2.6	Py	slow	–	–
	2.0	DMSO	6.14	34.1±2.8	–124±7
	2.0	DMF	fast	–	–
	0.2		18.8	32.8±2.0	–119±9
	0.2	PrOH-1	fast	–	–

solvents (DMF, DMSO) for which is expected formation of H-associates with active NH bonds are very low and the respective metallocomplexes do not form practically in the temperature range 298–338 K. This fact evidences significantly in favor of localized NH bond in the *meso*–substituted porphyrin molecules.

It can be noted also that *meso*-substituted H_2P with bulky substituents as a rule do not enter in the reaction of complex formation with *d*-metal salts in acetic acid and other solvents with expressed proton-donor function. Distortion of the macrocycle planar structure leads to a partial localization of π-electron density in pyrrole rings and to increased basicity of the molecule. Since the porphyrin protonated forms (H_3P^+ and H_4P^{2+}) forming in proton-donor media are inactive in the reaction (1), this rule is fulfilled also for other nonplanar H_2P such as N- (**III–IV, X**) or dodeca-substituted (**XI, XIII**) molecules. Some of the dodeca-substituted compounds still enter in the reaction (1) in AcOH but with a very low rate [24]. The best medium for the synthesis of MP with nonplanar *meso*-substituted porphyrins is a polar solvent with moderate donor–acceptor properties, e.g., acetonitrile. The reaction (1) with more screwed H_2T(*cyclo*-Hex)P (**VII**) proceeds in this solvent very rapidly, while with H_2T(*iso*-Pr)P (**VI**) with $k_v \sim 10\ \mathrm{l\ mol^{-1}\ s^{-1}}$ at 298 K.

Thus, all three quantitative criteria confirm the absence of chemical activity of NH bonds in both *meso*-substituted porphyrins with bulky functional groups leading to formation of *ruffle* conformation [4] and with N-substituted compounds with low symmetrical moderately *saddle*-like conformation. Thus, according to quantum-chemical calculations of geometry, the ΔC_β values for compounds **X** and **III** are approximately equal to 0.1 and 0.5 Å, respectively [25]. The data obtained allow to conclude that the chemical activity of NH bonds in H_2P molecules does not appear at any screwing planar structure of the molecule but specifically depends on the type of conformation of the screwed macrocycle. Only the pronounced symmetrically screwed saddle conformation of H_2P possessing high orthogonal dipole moment [26] leads to the appearance of NH-activity in properly nonplanar H_2P. The nonplanar H_2P with ruffle conformation in crystalline state and in solutions [4] are low polar and do not display chemical activity of NH bonds. Another reason for the absence of activity of the NH protons of the coordination center in ruffle porphyrins follows from the structure of the ruffle conformation (Fig. 1). As seen, in the saddle conformation the protons are deviated from the initial macrocycle plane while in the ruffle conformation the planar structure of N_4H_2 coordination center is not distorted.

EXPERIMENTAL

Porphyrins **II–IV, VI, VII, IX,** and **X** were prepared, purified and identified along the described procedures [7,19,27,28]. Solvents were dried and purified by commonly used methods described in [29].

Electron adsorption spectra of the explored compounds were registered on a Hitachi U 2020 spectrophotometer, the ^{1}H NMR spectra on a Bruker spectrometer with operating frequency 200 MHz at 303 K. Progress of reaction (1) was followed spectrophotometrically according to the procedure described in [19,23]. The change in enthalpy at the formation of neutral and deprotonated forms of the porphyrins was estimated using quantum-chemical calculations by semiempirical AM1 method (Hyperchem 5.0 program package) with the formulas (2, 3) taking enthalpy of proton formation in gas phase $\Delta H_f(H^+) = 367.2$ kcal mol^{-1}.

$$\Delta H_{(-i)} = i\Delta H_f(H^+) + \Delta H_{f(-i)} - \Delta H_{f(0)}, \qquad (2)$$

$$\Delta H_{f(0-i)} = \Delta H_{f(0)} - \Delta H_{f(-i)}. \qquad (3)$$

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REFERENCES

1. Barkigia, K.M., Chantranpong, L., Smith, K.M., and Fajer, J., *J. Am. Chem. Soc.*, 1988, vol. 110, p. 7566.
2. Gentemann, S., Nelson, N.J., Jaquinod, L., Nurco, D.J., Leung, S.H., Medforth, C.J., Smith, K.M., Fajer, J., and Holten, D., *J. Phys. Chem., B*, 1997, vol. 101, no. 7, p. 1247.
3. Shelnutt, J.A. Song, X.-Z., Ma, J.-G., Jia, S.L., Jentzen, W., and Medforth, C.J., *J. Chem. Soc. Reviews*, 1998, vol. 27, p. 31.
4. Senge, M., O., *Chem. Commun*., 2006, p. 243.

5. Berezin, D.B., *Doctorate Sci. (Chem.) Dissertation*, Ivanovo, 2007.
6. Koifman, O.I. and Mamardashvili, N.Zh., and Antipin, I.S., *Sinteticheskie retseptory na osnove porfirinov i ikh kon'yugatov s kaliks arenami* (Synthetic Receptors Based on Porphyrins and Their Conjugates with Calixarenes), Moscow: Nauka, 2006.
7. Lavallee, D.K., *The Chemistry and Biochemistry of N-Substituted Porphyrins*, New York: VCH Publishers, 1987.
8. Andrianov, V.G., Berezin, D.B., and Malkova, O.V., in: *Uspekhi khimii porfirinov* (Advances in Porphyrine Chemistry), Golubchikov, O.A., Ed., St. Petersburg: Sankt-Petersburg. Gos. Univ., 2001, vol. 3, p. 107.
9. Medforth, C.J., in: *The Porphyrin Handbook*, Kadish, K.M., Smith, K.V., and Guilard, R., Eds., vol. 5, p. 3, New York: Acad Press, 2000.
10. Shelnutt, J.A., Medforth, C.J., Berber, M.D., Barkigia, K.M., and Smith, K.M., *J. Am. Chem. Soc*., 1991, vol. 113, no. 11, p. 4077.
11. Ghosh, A., in: *The Porphyrin Handbook*, Kadish, K.M., Smith, K.V., and Guilard, R., Eds., New York: Acad. Press, 2000, vol. 7, p. 1.
12. Scheidt, W.R. and Lee, Y.-J., *Struct. Bonding (Berlin)*. 1987, vol. 64, p. 1.
13. Ghosh, A., Wasbotten, I.H., and Conradie, J., *J. Phys. Chem*., 2003, vol. 107, no. 15, p. 3613.
14. Berezin, D.B., Ivanova, Yu.B., and Sheinin, V.B., *Zh. Fiz. Khim*., 2007, vol. 81, no. 12, p. 2205.
15. Berezin, D.B. and Karimov, D.R., *Macroheterocycles*, 2008, vol. 1, no. 2.
16. Berezin, D.B., Toldina, O.V., and Kumeev, R.S., *Zh. Fiz. Khim*. 2004, vol. 78, no. 8, p. 1427.
17. Mamardashvili, G.M. and Berezin, B.D., in: *Uspekhi khimii porfirinov* (Advances in Porphyrine Chemistry), Golubchikov, O.A., Ed., St. Petersburg: Sankt-Petersburg. Gos. Univ., 2001, vol. 3, p. 130.
18. Berezin, D.B., Mis'ko, E.N., Antina, E.V., and Berezin, M.B., *Zh. Obshch. Khim*., 2006, vol. 76, no. 3, p. 506.
19. Berezin, D.B., Bazlova, I.Yu, Malkova, O.V., and Andrianov, V.G., *Koord. Khim*., 2000, vol. 26, no. 4, p. 315.
20. Berezin, D.B., *Koord. Khim*., 2007, vol. 33, no. 6, p. 476.
21. Stuzhin, P.A., *J. Porph. Phthaloc*., 2003, vol. 7, no. 12, p. 813.
22. Mis'ko, E.N., *Candidate Sci. (Chem.) Dissertation*, Ivanovo, 2005.
23. Berezin, D.B. and Toldina, O.V., *Zh. Neorg. Khim*., 2002, vol. 47, no. 12, p. 2075.
24. Golubchikov, O.A., Vlasova, E.K., Syrbu, S.A., and Kuvshinova, E.M., *Izvestiya VUZov. Khimiya i Khim. Tekhnol*., 2000, vol. 43, no. 6, p. 36.
25. Sazanovich, I.V., Van Hoek, A., Panarin, A.Yu., Bolotin, V.L., Semeykin, A.S., Berezin, D.B., and Chirvony, V.S., *J. Porph. Phthaloc*., 2005, vol. 9, no. 1, p. 59.
26. Chirvony, V.S., Sazanovich, I.V., Galievsky, V.A., Van Hoek, A., Schaafsma, T.J., Malinovskii, V.L., and Holten, D., *J. Phys. Chem*., 2001, vol. 105, no. 32, p. 7818.
27. Senge, M.O., Bischoff, I., Nelson, N.Y., and Smith, K.M., *J. Porph. Phthaloc*., 1999, vol. 3, no. 2, p. 99.
28. Veyrat, M., Ramasseul, R., Turowska-Tyrk, I., Scheidt, W.R., Autret, M., Kadish, K.M., and Marchon, J.-C., *Inorg. Chem*., 1999, vol. 38, no. 8, p. 1772.
29. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.