

Interaction of Porphyrins and Porphyrin Analogs with Coordinating Organic Solvents

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Chemical interaction “porphyrin-solvent” between the reaction center of basic solvent and weakly acidic macrocyclic NH group is analyzed for different types of porphyrin ligands (H₂P). Planar and distorted ligands, common H₂P and porphyrin analogs are considered using spectrophotometric titration, kinetic measurements, ¹H NMR and fluorescent spectroscopy as well as quantum-chemical calculations. Reaction is usually reversible for non-planar compounds and proceeds in kinetic regime in the case of H₂P with more rigid aromatic structure like porphyrazines. Deepening of the saddle non-planar conformation favors formation of H-associates as compared to other distorted types of porphyrins (ruffle, wave, stepped, etc.) due to polarization of saddle structure. In dependence on the class of H₂P analogs they either, like corroles, repeat behavior of saddle non-planar common porphyrins, or undergo some kind of specific transformations like tautomerism of inverted H₂P analogs. Addition of a stronger base like diethylamine or piperidine to solution of H-associate in polar donating solvent usually results in formation of porphyrin monoanion.

Keywords: Porphyrins, porphyrin analogs, macrocyclic effect, acid-base H-associates, NH-reactivity criteria.

Introduction

Porphyrins and their analogs (H₂P, compounds I-XX) are known as highly aromatic and at the same time flexible macroheterocyclic ligands.^[1] On one hand their aromaticity is confirmed by theoretical calculations (Nuclear Independent Chemical Shifts, NICS, Harmonic Oscillator Model of Aromaticity, HOMA, and other quantitative criteria^[2]), high magnetic anisotropy^[3] and thermal stability,^[4] etc. Their ability to change structure and to adopt one of the typical non-planar conformations in both crystal and liquid phase^[1] can be used as a unique possibility to regulate reactivity of these compounds like it occurs in nature. Studies of last two-three decades show that namely conformational transformations of complex biomolecules including porphyrins *in vivo* are responsible for the exertion of their biological activity caused by structural and external changes of molecular environment.^[5]

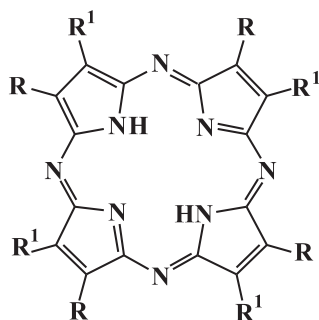
This paper is devoted to the investigation of the porphyrin interaction with electron-donating solvents in connection with some other aspects of their reactivity. This is a way to stress interrelation between spatial structure and chemical properties of porphyrin macromolecules.

Interaction of porphyrins with coordinating solvents is not a common property for all classes of tetrapyrrolic macrocycles. Porphyrinoid macrocycles can be classified for common porphyrins (I-XVI) and porphyrin analogs, for instance, XVII-XX.^[6,7] Porphyrin analogs differ from common porphyrins by the structure of coordination core dissimilar to H₂P (N₄H₂) and (or) different type of C_α-C_α bonding between pyrrolic or another aromatic units.^[7] Most typical classes of porphyrin-like analogs are N-substituted,^[8] expanded^[9] and heteroatom-substituted^[10] compounds, porphyrin isomers^[11] and carbaporphyrins^[12] including

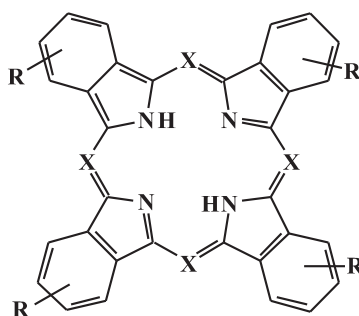
inverted porphyrin analogs (XVII-XVIII)^[13] as well as corroles (XIX-XX)^[14] and some other macrocycles. Their interaction with a solvent is mostly a subject of the further investigations, however some examples are known^[15-19] and will be discussed in this paper.

As for common porphyrins, they can be formally divided into three groups^[7,20] with characteristic basic structural features. Compounds of the first group are mainly planar β- and *meso*-substituted porphyrins and chlorins. The second group includes highly aromatic compounds, mainly porphine and porphyrazine derivatives with four β,β'-fused aromatic rings as well as porphyrazines themselves. The third group of compounds contains H₂P with a highly non-planar structure which nevertheless remains aromatic.^[5]

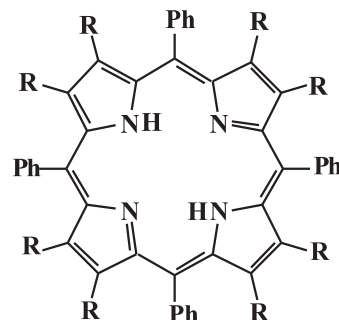
Highly distorted common porphyrins compose extended group of compounds.^[5,7] Within them macrocycles can be divided into several modifications which possess different types and degrees of non-planarity. Such a distorted structure can be reached with: 1) modification of the porphyrin periphery like simultaneous β- and *meso*-multisubstitution (IX, XI-XIII), tetra-*meso*-substitution with bulky groups (XIV-XVI), fitted with shortened spacers in the case of monomer or dimer formation, etc.; 2) modification of coordination core as in the case of substitution on inner-cyclic NH-groups,^[8] H₂P mono- and diacids formation, porphyrin complexation with metals with ionic radii higher or lower than the size of the N₄ coordination cavity, etc.; 3) ligand modification leading to decrease of its aromaticity, for instance, in the case of π-cation-radicals formation, or to diminishing of the π-system size due to β,β'-reduction in chlorins, etc.; 4) simultaneous effect of two or more above factors. In this paper only distortion effects of dodeca-, *meso*- and inner-cyclic N-substitution will be considered.



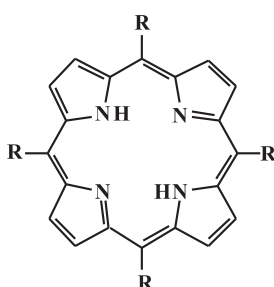
- I. $R = R^1 = H$;
 II. $R = R^1 = Ph$;
 III. $R = R^1 = (p\text{-}Br)Ph$;
 IV. $R = R^1 = (p\text{-}NO_2)Ph$;
 V. $R = Br$, $R^1 = H$;
 VI. $R = Cl$, $R^1 = H$



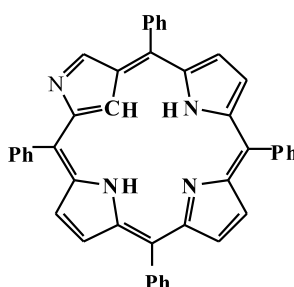
- VII. $X = N$, $R = \text{tert-Bu}$;
 VIII. $X = CH$, $R = H$;
 IX. $X = C\text{-}Ph$, $R = H$



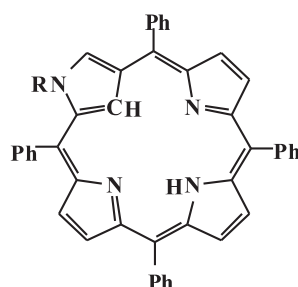
- X. $R = H$;
 XI. $R = Et$;
 XII. $R = Ph$;
 XIII. $R = Br$



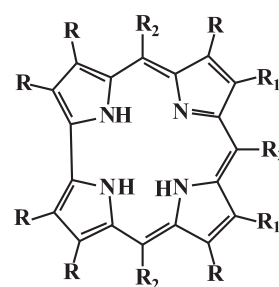
- XIV. $R = \text{iso-Pr}$;
 XV. $R = \text{cyclo-Hex}$;
 XVI. $R = \text{tert-Bu}$



XVIIa.

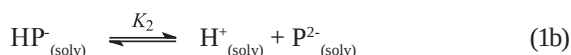
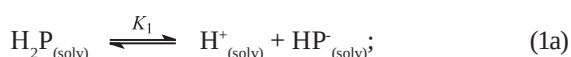


- XVIIb $R = H$;
 XVIII. $R = Me$

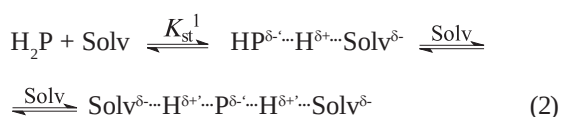


- XIX. $R = Me$, $R_1 = Et$, $R_2 = H$;
 XX. $R = R_1 = H$, $R_2 = Ph$

Acid-basic interaction is a complex process which consists of a number of steps with a variable degree of proton transfer from the acidic to basic reaction center, so called "protonation depth".^[21] For common porphyrin mono- and dianionic species are the final ones. In these species one or two of NH bonds respectively are broken and full proton transfer is realized (Equation 1).^[22]



In dependence on the acid and base strength several particles with an intermediate degree of porphyrin proton transfer can be formed. Porphyrin interaction with electron-donating solvent (Solv) such as dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), hexamethylphosphorotriamide (HMPTA), N,N-dimethylpropyleneurea (DMPU), pyridine (Py), piperidine (Pip), etc., is based on the formation of NH-associated molecular complexes like shown schematically by Equation (2). To react with porphyrin ligand the solvent has to combine high coordination and polarization abilities, expressed by donor number (DN) and dielectric constant (ϵ) characteristics, respectively. Usually donor numbers of the solvent molecules should not be exceeded by acceptor number (AN) values.^[7,17]



The strength and type of porphyrin-solvent interaction depend strongly on the flatness degree of macrocyclic ligand. Porphyrin compounds with mainly planar structure do not enter to the notable chemical interaction with coordinating solvents. Moreover, as was shown by calorimetric study of dissolution processes, even specific solvation of NH groups of H_2P coordination core is not very typical for these macrocycles.^[23] Such a conclusion was then confirmed by semiempirical calculations of deprotonation enthalpies for these molecules^[24] which have shown that their NH bonds are essentially covalent and not exposed to strong polarization or, moreover, to acid dissociation. Low reactivity of the coordination center of common porphyrins in solvation, acid-basic and complexation processes is easily explained from the point of view of macrocyclic effect (MCE) strategy,^[25,26] developed for porphyrins in the series of publications.^[23,27-29] MCE is a phenomenon of the spatial shielding of inner-cyclic reaction centers by their macrocyclic surrounding compared to non-macrocyclic one.^[25]

Macrocyclic effect often results in quite unusual reactivity changes of the macrocycle.^[26] In the case of porphyrin molecules where inner reaction center N_4H_2 is additionally protected by π -electronic cloud, MCE is especially complicated and consists of two components.^[29] The first, steric one, has a non-chemical nature which is realized in shielding of the coordination core by π -electrons and atoms of molecular surrounding (Figure 1). The second component of macrocyclic effect is π -electronic one acting through polarization or depolarization of the π -system as a result of changes of molecular symmetry, number and

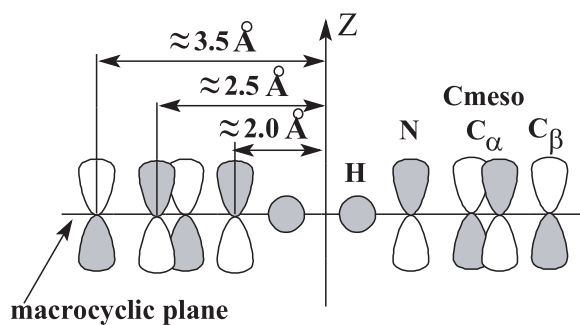


Figure 1. Coordination center shielding in porphyrin ligand.

nature of peripheral substituents, distortion or more serious modification of macrocycle. Under action of the same external factor steric and electronic components of MCE are changed asynchronously to each other causing sometimes unexpected reactivity.^[29]

Surprisingly, compounds of opposite structural type of porphyrins, *i.e.* aromatic and highly non-planar, are able to give spectrally resolved H-associated forms with donating organic solvents.^[30-36] In the case of highly aromatic H_2P the steric component of MCE seems to effectively provide spatial shielding of the coordination core preventing any types of interaction. However, another one, π -electronic component polarizes porphyrin molecules as in β, β' -fused or *meso*-azasubstituted ones and favors to interactions like (2).^[21,29]

Interaction with solvents of common porphyrins of the third group which are macrocycles with pronounced non-planar structure depends on the distortion degree and on the type of non-planar conformation of macrocycle. Therefore H-associates, formed according to Equation (2), are typical only for highly ($\Delta C_\beta \geq 1 \text{ \AA}$)* distorted H_2P of *saddle* shape (VII, XI-XIII, Figure 2,a).^[7,37]

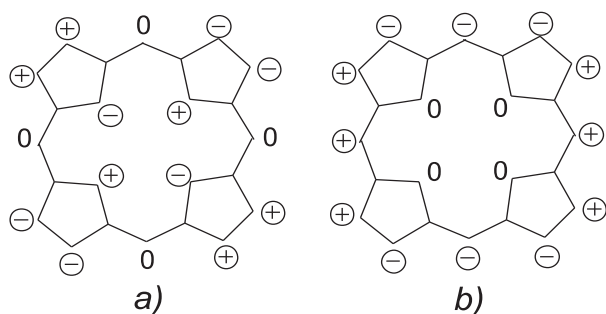


Figure 2. Idealized non-planar porphyrin conformations:^[5] a) saddle; b) ruffle

The first example of porphyrin H-associate was found by Whalley^[30] for porphyrine **I** and its β -alkyl- or benzoderivatives in pyridine solution. That time associates were called “pyridinium salts” which is not quite correct first of all because the proton transfer in them is not complete.^[21] Then studies of Luk’yanets^[31] have shown that similar solvent-associated structures are formed by substituted phthalocyanine **VII** in solution of aliphatic amines, however stability of H-associates and conditions in which they exist were not found. Later extended studies carried out by Petrov

* ΔC_β is a deviation of β -atoms from mean macrocyclic plane.

et al.^[33,38-40] have illustrated that stability of H-associates strongly depends on the NH-activity and macrocycle rigidity of porphyrine ligand as well as on the nature of base and solvent system. For example, the most of highly active porphyrine derivatives with electron-withdrawing acceptor groups (F, Cl, Br, NO_2 , SO_3H) in β -phenyl substituents or β -positions directly react with electron-donating solvents whatever their polarity and coordination ability is.^[33,40] So, ability of porphyrine derivatives to form H-associates (2) increases in a series of β -substituents: H- (**I**) < Ph- (**II**) < (*p*-Br)Ph- (**III**) < (*p*- NO_2)Ph- (**IV**) < Br- (**V**) $\approx$ Cl- (**VI**).^[40] Meantime, less polarized tetra-*tert*-butylphthalocyanine (**VII**)^[31,39] with four donating alkyl groups are able to form H-associates only in polar media ($\epsilon \geq 30$) such as DMF or DMSO in the presence of basic low-polar molecules with the higher donor numbers like Py (33.1) or DEA (50).^[41] Such a way, both factors as high polarity and donor strength have to be presented in solvent system to provide the formation of H-complexes (2). In the presence of organic base tetrabenzoporphyrin (**VIII**) and its planar derivatives, which are less aromatic compounds if compared to H_2TAP (**I**) but more aromatic if compared to common H_2P , give H-associates in very tiny amounts which are not registered in absorption spectra and are confirmed only by cross-methods, for instance, by kinetic measurements of complex formation, 1H NMR spectroscopy, quantum chemical calculations.^[7,42]

The main feature of the formation of porphyrine H-associates is an Equilibrium (2) shifted to the right. It is usually caused by low stability of the associated form with a partial proton transfer in electron-donating media.^[33,38] Therefore, many cases of destruction of the porphyrine H-associates are known especially in low-polar donating solvents for instance, aliphatic amines.^[38] The thermal stability of H-associate formed by β -octaphenylporphyrine (**II**) with pyridine [$H_2(\beta-Ph)_8TAP \cdot 2Py$] in a solid determined by derivatography method was found to be quite high. In the presence of the air above H-associate does not lose solvent molecule up to $150^\circ C$.^[43] The evaporation enthalpy of the solvent from it equals $41.2 \text{ kJ} \cdot \text{mol}^{-1}$. Reaction (2) for porphyrines can be followed by UV-vis spectroscopy and characterized by the rate constant. Graphic calculations of kinetic data usually show the first or second reaction order on the base concentration depending on the nature of porphyrine ligand.^[33,40]

The aim of this paper is to compare behavior of highly aromatic and distorted H_2P and their modified analogs in electron-donating media.

Experimental

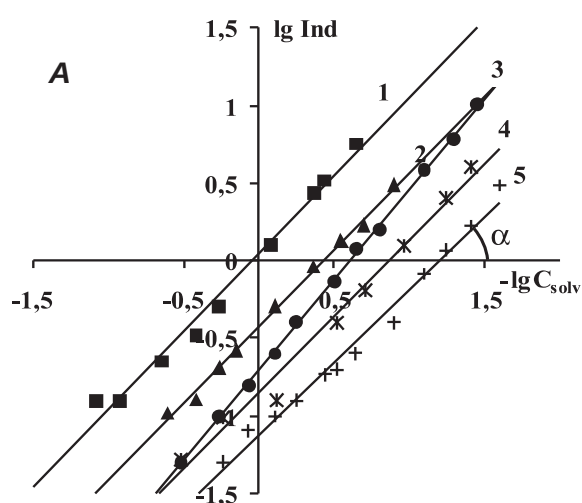
Porphyrinoid compounds (**VIII-IX**, **XI-XIII**, **XVII-XX**) have been obtained according to published synthetic methods.^[44-50] All solvents were commercial products and purified according to known procedures.^[51] Measurements of the electronic absorption spectra including spectrophotometric titration were done on Hitachi U2000 and Hitachi U2020 spectrophotometers. Processes of monoanions (1) or H-associates (2) formation were monitored by absorption spectra in benzene-DMF, benzene-DMSO, benzene-HMPTA, benzene-DMPU, benzene-pyridine (Py), benzene-piperidine (Pip), benzene-diethylamine (DEA) and DMF-DEA solvent systems. Corresponding equilibrium constants K_{st} were calculated using

Equation (3). Number of solvent molecules (n) participating in processes (1) or (2) was estimated by graphic method from the logarithmic dependence of the indicator ratio ($Ind = C_{H_2P \cdot Solv} / C_{H_2P}$) from the concentration of coordination solvent C_{solv} (Figure 3).

Emission spectra were measured on the spectrofluorimeter CM 2203. Stokes shifts are calculated according to Equation (4) where ν_i^{fl} and λ_i^{fl} are, respectively, wave number (cm^{-1}) and wavelength (nm) of the first (adjacent) bands in fluorescence spectra; λ_i^{abs} ν_i^{abs} are wave number and wavelength of the first bands in absorption spectra. 1H NMR measurements were done using Bruker 200 spectrometer. Formation enthalpies of porphyrins and electric dipole moments were estimated from semi-empirical quantum-chemical calculations using AM1 and PM3 methods within Hyperchem 5.0 package.

$$pK_{st} = n \lg C_{solv} - \lg (Ind) \quad (3)$$

$$\Delta\nu_i = \nu_i^{fl} - \nu_i^{abs} = 10^7(\lambda_i^{fl} - \lambda_i^{abs}) / \lambda_i^{fl} \lambda_i^{abs} \quad (4)$$



nature is applicable just for comparative studies. It varies from 0.025 for Py to 13.8 for HMPTA or about $5 \cdot 10^2$ times. The number of NH protons transferred to the solvent molecule in the case of **XIII** equals one (Figure 3, A).^[36] Data obtained by us appeared to be very close to that found for benzene media.^[36]

There is a strong dependence of the pK_{st} values on the characteristics of donating solvent. However this dependence is quite complicated. The constant of H-associate stability depends on the solvent polarity (ϵ or μ values) favoring to charges separation during acid-basic process, as well as on the coordination ability (for instance, DN value) showing how strong the base is. Stability of H-associate is determined also by molar volume of the base molecule (V_M) as a characteristic of steric hindrances of its reaction center. Therefore there is no clear linearity between pK_{st}^1 value and individual solvent characteristics (Figure 3, B).

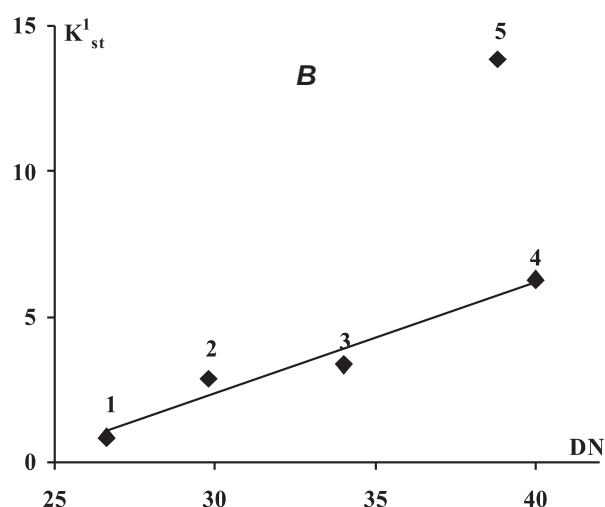


Figure 3. Graphic determination of a number of solvent molecules (n), forming H-associate with **XIII** according to Equation 2 (A) and dependence of these H-associates $HP \cdot H \cdot Solv$ stability constants K_{st}^1 on the donor number of basic solvent (B). Solvent - DMF (1), DMSO (2), DMPU (3), Pip (4), HMPTA (5).

Results and Discussions

Ability of non-planar dodecasubstituted porphyrins to form acid-basic associates with an incomplete proton transfer was found first for dodecaphenylporphyrin (**XII**)^[34] and its functional derivatives.^[35] About thirty five solvents of different donor-acceptor nature were taken under investigation and typical absorption spectra changes were discussed although nothing about H-associates structure was written.

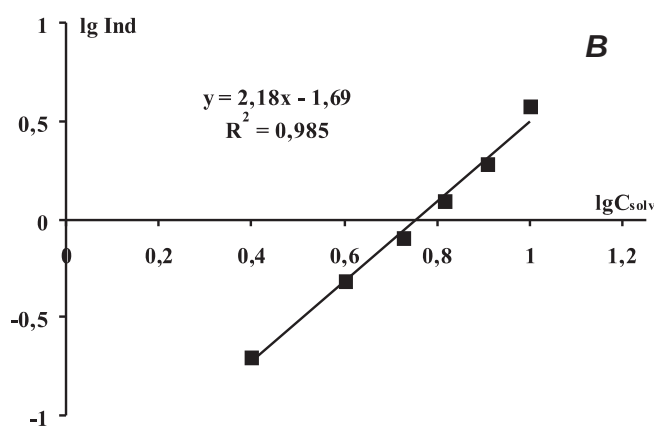
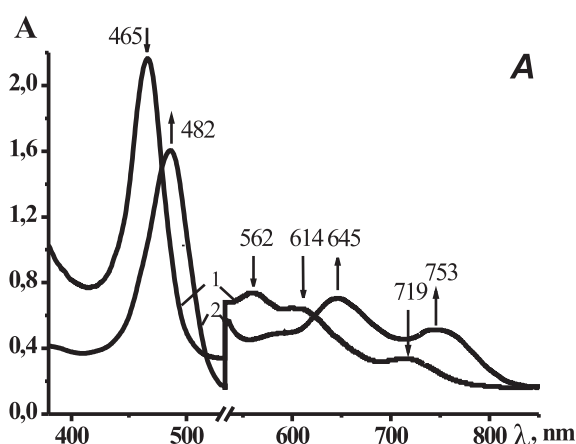
There is only one paper devoted to the stability of H-associates $H_2P \cdot Solv$ with non-planar β -octabromo-*meso*-tetraphenylporphyrin (**XIII**) where solvents were Pip, Py, DMF and DMSO in toluene media.^[36] In contrast to the reaction (2) of porphyrazines^[21,33] this one is characterized by equilibrium constant K_{st} and formed H-associates are relatively stable in solution. In our work we have broaden the number of basic solvents (Figure 3) and found that conclusions made in^[36] are correct. Within studied bases the equilibrium constant K_{st}^1 measured according to^[36] in "benzene - Solv" system because of its non-thermodynamic

β -Octabromo-*meso*-tetraphenylporphyrin (**XIII**) is one of the typical porphyrins with an expressed non-planar saddle-shaped structure combined with a small ruffling (Figure 2, b).^[5,45] Moreover, NH-bonds in this molecule are additionally polarized by eight bromine atoms, located in β -positions. These are two main reasons for the most effective interaction of this H_2P with coordinating solvents including low-donating ones like acetone (DN = 17.0) as compared to other dodecasubstituted porphyrins studied. According to our spectral data H-associates stability decreases in a series of compounds: $H_2(\beta-Br)_8TPP$ (**XIII**, $\Delta C_\beta = 1.26$; $\Delta C_{\beta}^{meso} = 0.32$)^{*} > $H_2(\beta-Ph)_8TPP$ (**XII**, 1.28) > $H_2(\beta-Et)_8TPP$ (**XI**, 1.17) >> H_2TPTBP (**IX**, 0.77), which corresponds to the lowering to the macrocycle non-planarity determined by X-ray crystallography data^[5] and data of fluorescence spectra as an indicator of conformation of the porphyrin molecule in solution.^[7,52] In the case of with compounds distortion of the molecular structure in crystal state can be easily characterized by ΔC_β parameter (in Å) of β -atoms deviation from mean

^{*} ΔC_β parameter is not available for the ligand and is presented for zinc complex.

Table 1. Formation of H-associates by dodecasubstituted porphyrins and spectral shifts of bands $Q_x(0-0)$ in their electronic absorption spectra in basic solvents ($\Delta\lambda_{Q_x}$, nm) in dependence on the Solv characteristics,^[41] C_6H_6 is a standart solvent.

Solvent	Solv characteristics		Porphyrin		
	ε	DN	$H_2(\beta-Et)_8TPP$, XI	$H_2(\beta-Ph)_8TPP$, XII	$H_2(\beta-Br)_8TPP$, XIII
Tol	≈ 2	≈ 0	no formation (-7)	no formation (+2)	no formation (-5)
Pip	4.3	40	no formation (+9)	no formation (+2)	stable (+32)
DEA	3.6	50	no formation	no formation	stable
DMSO + 5% DEA	-	-	monoanion	monoanion	monoanion
Py	12.3	33.2	weak interaction (+2)	weak interaction (+19)	stable (+17)
DMF	36.7	26.6	formation (+30)	formation (+27)	stable (+41)
DMSO	46.7	29.8	formation (+15)	formation (+31)	stable (+51)
DMPU	36.1	34	no formation (+9)	no formation (-8)	stable (+31)
HMPTA	30	38.8	no formation (+4)	no formation (-3)	stable (+28)

**Figure 4.** UV-vis spectral changes (A) and graphic determination of donating solvent reaction order ($\lg \alpha = 2$) (B) for **XII** H-associate formation in C_6H_6 -DMSO system, 298 K: 1- molecular form of H_2P in C_6H_6 ; 2 – H-associate $H_2P \cdot 2Solv$ in DMSO.

macrocyclic plane which is given in parentheses. Presumably an increase of NH-acidity and ability of non-planar ligand to form H-associates (2) is caused by dipole moments inherent for this kind of distorted conformation. Semi-empirical calculations by AM1 or PM3 methods show significant μ -values within 1.0 – 2.9 D even for symmetrically substituted *saddle* porphyrins,^[7,53] although for relatively planar H_2TPP dipole moment equals zero. Even highly non-planar *ruffle* porphyrin conformations characterized by C_{meso} -atoms deviation (ΔC_{meso} , Å) from mean H_2P plane do not favor polarization of NH bonds and H-associates formation. For example, dipole moments of ruffled tetra-*meso*-substituted H_2P like tetra-*iso*-propylporphyrin (**XIV**; $\Delta C_{meso} = 0.67 \text{ Å}$), tetra-*cyclo*-hexylporphyrin (**XV**; 0.77 Å) or tetra-*tert*-butylporphyrin (**XVI**; $\approx 0.90 \text{ Å}$) are close to zero (< 0.1 D by AM1 method), presumably, because of the high-symmetrical distorted structure with acidic NH-groups situated in the macrocycle plane and additionally protected by macrocyclic effect (Figure 2,b).^[29] Quantum-chemical calculations of deprotonation enthalpies also point out rather low NH-acidity of these compounds.^[7]

The formation of H-associate by non-planar common H_2P is accompanied by typical spectral changes in the ab-

* ΔC_{meso} values not available for the ligand are presented for nickel complex, Å.

sorption spectra (Figure 4,A; Table 1). So, the long-wave $Q_x(0-0)$ band as well as Soret or B-band undergo further red shift and poorness of the spectra due to Q-bands degeneration and an increase of molecular symmetry. H-Associates of dodecasubstituted H_2P in basic solvents can be called relatively stable only when spectral shifts ($\Delta\lambda_{Q_x}$) of the Q_x band are higher than 15 nm (Table 1) and are not formed at all if one of two conditions – high donor strength and polarity of the solvent – is not fulfilled.

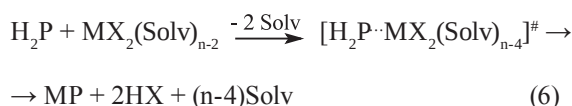
Less non-planar dodecasubstituted compounds, for instance, **XI**, form weaker H-associates with two or even more solvent molecules in dependence on the media coordination properties. So, dodecaphenylporphyrin (**XII**) form H-complexes of 1:1 and 1:2 composition in DMSO (Figure 4) with a $pK_{st}^{1,2}$ value 0.78 ± 0.01 . Already in a little weaker basic media (DMF) a number of solvent molecules which are in interaction with porphyrin increases up to 15. According to our unpublished results this behavior is normally reproduced in all systems where porphyrin and solvent are, relatively, too weak acid and base to form 1:1 or 1:2 stable complexes. Such a surprising number of solvent molecules found from graphic indicator dependences (Figure 4,B, see also **XIX-XX** H-associate formation) is explained by the situation when independent proton transfer is not justified

thermodynamically and takes place only under formation of some kind of channels for proton transfer constructed from specially arranged solvent molecules. Analogous cases of transfer channels formation seem to be found earlier for different types of proton transfer.^[54,55] The higher number of molecules participating in the interaction with porphyrin NH-protons corresponds to less stable H-associates.

To estimate the NH-reactivity of common porphyrins the series of quantitative criteria as ¹H NMR-spectral, kinetic and quantum-chemical calculations was suggested.^[7,20,37] The first is based on the shift of NH-proton signal in ¹H NMR-spectrum under changing a solvent from universally solvating (US) to basic electron-donating one (BS) providing H-associate formation (5). The value is positive, if H-associates are formed and increases with NH-acidity of the porphyrin (Table 2).^[37]

$$\Delta\delta_{\text{NH}} = \delta_{\text{BS}} - \delta_{\text{US}} \quad (5)$$

According to the kinetic criteria the formation of H-complex with coordinating solvent H₂P·nSolv is possible when the complexation reaction (6) of porphyrin ligand with a solvato complex of d-metal salt MX₂(Solv)_{n-2} in coordinating solvents is higher (BS = DMSO, DMF, Py) than in moderately proton-donating media (for instance, AS = AcOH) at the same conditions (Equation 7, Table 3).



$$k_{\text{v}}^{\text{BS}} > k_{\text{v}}^{\text{AS}} \quad (7)$$

$$\delta\Delta H_{\text{f}(0-2)} = \Delta H_{\text{f}(0)} - \Delta H_{\text{f}(-2)} \quad (8)$$

Values of $\delta\Delta H_{\text{f}(0-2)}$ (8) on the formation enthalpy of porphyrin ligands H₂P ($\Delta H_{\text{f}(0)}$) and dianions P²⁻ ($\Delta H_{\text{f}(-2)}$) in vacuum were calculated from semi-empirical quantum-chemical data to characterize the relative stability of dianions.^[24] They are more positive for NH-active H₂P (**I**, **V**, **IX**, **XI-XIII**) comparing to common classic ligands (**X**). If the chemical activity of NH bonds is high, the value $\delta\Delta H_{\text{f}(0-2)}$ is usually positive (Figure 5). The macrocycle is NH-active, if at least two of three above criteria are realized.^[20]

These criteria are applicable for any structural group of common H₂P,^[20] however not proved to be appropriate in the case of porphyrin analogs yet excepting N-substituted ones.^[7] Reactivity of NH bonds in molecules of N-substituted porphyrin analogs is quite low as an application of quantitative criteria shows. To our knowledge at the moment only compounds from two classes of porphyrin analogs, namely, inverted porphyrins, for instance, **XVII**^[15-17] and corroles (**XIX-XX**)^[18,19] are able to interact with electron-donating solvents. However the result of such interaction is principally different for these two kinds of analogs.

Corroles are found to be more NH-active comparing to porphyrins of similar structure. If H₂(β-Alk)₈P and H₂TPP (**X**) are inert in relation to coordinating solvents and even do not exposed to specific solvation in their media,^[23] corresponding corroles H₃(β-Alk)₈Cor (**XIX**) and

Table 2. Solvent influence on the position of signals NH (δ_{NH} , ppm) in ¹H NMR spectra of porphyrins.

Porphyrin	Solvent (US)	δ_{NH}	Solvent (BS)	δ_{NH}	$\Delta\delta_{\text{NH}}$, ppm
H ₂ TAP (I) ^[20]	CD ₂ Cl ₂	-2.07	Py-d ₅	-0.97	+1.10
H ₂ TPP (X)	CDCl ₃	-2.76	DMSO-d ₆	-2.91	-0.15
H ₂ TPTBP (IX)	CDCl ₃	-1.16	DMSO-d ₆	-1.10	+0.06
H ₂ (β-Et) ₈ TPP (XI) ^[20]	CDCl ₃	-2.00	DMSO-d ₆	not found	-
H ₂ (β-Ph) ₈ TPP (XII) ^[20]	CDCl ₃	-0.90	DMSO-d ₆	+1.00	+1.90
H ₂ T(β-Br) ₈ TPP (XIII)	CDCl ₃	-1.65	DMSO-d ₆	+0.52	+2.10

Table 3. Dependence of the rate of reaction (6), k_{v} , l·mol⁻¹·s⁻¹, between porphyrins and Zn^{II} and Cu^{II} acetates from donor-acceptor properties of the solvent.^[20]

Porphyrin	$C_{\text{M(OAc)}_2} \cdot 10^3$, mol·l ⁻¹	k_{v} and rate increase direction		
		AcOH	Py	
H ₂ (β-Br) ₄ TAP (V) ^[20]	M=Zn, (0.3)	0.007±0.0003	930±140	→
H ₂ TAP (I)	M = Zn, (0.3)	0.0087±0.0003	5.79±0.04	→
H ₂ TBP (VIII)	M = Zn, (2.6)	slow	0.0069±0.0018	→
H ₂ (β-Et) ₈ P ^[20]	M = Zn, (5.0)	3.67±0.05	slow	←
H ₂ TPP (X) ^[20]	M = Zn, (0.48)	38.6±0.90	slow	←
H ₂ TPTBP (IX)	M = Zn, (2.6)	slow	0.100±0.001	→
H ₂ (β-Et) ₈ TPP (XI) ^[20]	M = Cu(II), (0.05)	0.00065±0.00004	1230±40	→
H ₂ (β-Ph) ₈ TPP (XII) ^[20]	M = Cu(II), (0.005)	slow	754±20	→
H ₂ (β-Br) ₈ TPP (XIII)	M = Zn(II), (0.22)	slow	fast	→

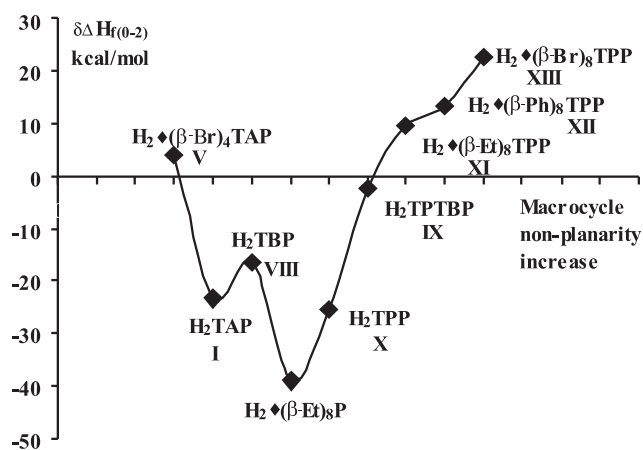


Figure 5. The relative stability of dianionic species P^{2-} , $\Delta\Delta H_{f(0-2)}$ (8), kcal·mol⁻¹, in vacuum (data from [24] are used).

$H_3(ms-Ph)_3Cor$ (XX) are able to form H-associated or even monoanionic species.^[18,19]

NH-Activity of *meso*-substituted molecule is higher as compared to β -octaalkylsubstituted one, presumably, because of substituents effect and different non-planarity pattern. Accordingly, $H_2(\beta-Et)_8P$ is about 500 times weaker acid in NR_4OH -MeCN solvent system comparing to H_2TPP (see pK_1 values in [56]). Presumably the same regularity is common for substituted corroles. So, H-associates are formed already at $H_3(ms-Ph)_3Cor$ (XX) dissolution in polar coordinating solvent like DMF or HMPTA (Figure 6, A). This behavior of *meso*-substituted corrole, NH-activity of which is not very high is comparable to common dodecasubstituted porphyrins of medium non-planarity and polarity (XI). More than two donating solvent molecules form H-associates with *meso*-phenylsubstituted corrole XX. The slope of the logarithmic dependence of Ind from C_{solv} for titration of $H_3(ms-Ph)_3Cor$ in benzene with HMPTA and DMF equals 6 and 11, respectively (see Figure 6, B). Possible reasons are discussed earlier.

Usually non-planarity of porphyrins in solution can be roughly characterized by the Stokes shifts of the neighbouring

bands of fluorescence and absorption spectra $\Delta\nu_1$ (Table 4, Equation 4). In the case of corroles fluorescent data do not let us to make certain conclusion about non-planarity degree of the molecule because the values of Stokes shifts (Table 4) are also determined by molecule polarization. Even according to the quite rough semi-empirical calculations electric dipole moments of β - and *meso*-substituted corroles XIX-XX are about 1-2 D. Presumably macrocycle polarization is a key reason drawing solvent interactions of porphyrinoid macrocycles.

Addition of about 50% of stronger base (DEA) to DMF solution causes formation of the corrole monoanion $H_2(ms-Ph)_3Cor^-$ accompanied by minor changes of the absorption bands structure. The same spectral picture is observed in strongly basic 0.01M NR_4OH solution in DMF (Figure 6, C). As known from literature,^[14] corrole monoanion formation makes molecule more planar and more aromatic, therefore deeper deprotonation level is not considered.

Interaction of less acidic β -alkylsubstituted corrole (XIX) with coordinating solvents does not proceed only in presence of polar weakly basic molecules like DMF (Figure 7, A) and takes place just after addition of organic N-base as Pip or DEA. According to the spectral changes monoanionic species are directly formed in this solvent system. The slope of the indicator dependence (Figure 7, B) is close to one.

In opposite to corroles the interaction of inverted porphyrin analogs and dipolar aprotic solvents usually results in porphyrinoid tautomeric transformation.^[15-17,57,58] This type of solvent dependent tautomerism $a \rightleftharpoons b$ was discovered by Furuta [15] and more precisely studied by Ziegler.^[16] Later the same two tautomeric forms were found for inverted analogs with different substitution pattern.^[57,58] In our last work^[17] we have extensively studied the influence of solvent nature and found limitations for tautomer *b* formation, which are $\epsilon \geq 30$; $\mu > 3.5D$; $DN > 25 > AN$. Standard tautomeric mechanism procedure which is independent on the basic solvent nature within above limits is suggested.^[17]

Tautomer *b* of the inverted porphyrin analogs represents some kind of special H-associate with participation of the external NH-group in the position 2 of the macrocycle

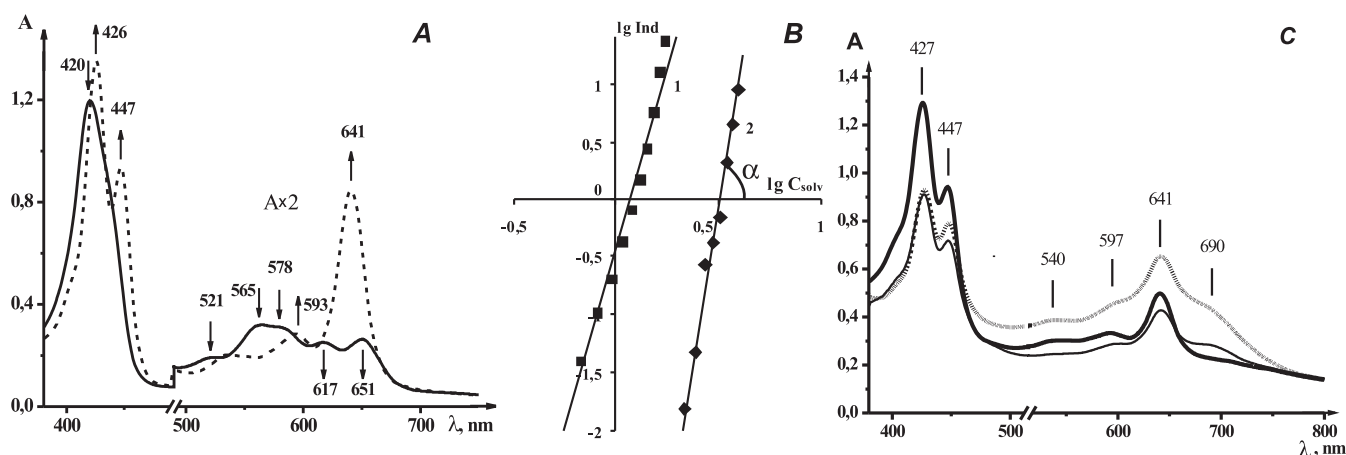


Figure 6. UV-vis spectral changes during H-associate formation (dotted line) with $H_3(ms-Ph)_3Cor$ (XX) in C_6H_6 -DMF system, 298 K $C_{H_3Cor} = 1.9 \cdot 10^{-5}$ mol·l⁻¹ (A), graphical determination of donating solvent order in reaction (2) ($\lg \alpha \sim 6$ for HMPTA (1) and 11 for DMF (2)) (B) and absorption spectra of XX at monoanion formation in basic media: DMF (thick solid line); 4.67 M DEA in DMF (thin solid line); 0.01 M $[NBu_4]OH$ in DMF (dashed line) (C).

Table 4. Characteristics of the absorption and fluorescence spectra of β - and *meso*-substituted porphyrins and corroles.

Compound	Solvent	Absorption, λ_i^{abs} , nm	Fluorescence, λ_i^{fl} , nm	Stoks shifts $\Delta\nu_i$, cm^{-1} ($\Delta\lambda_i$, nm)
$\text{H}_2(\beta\text{-Et})_8\text{P}$	C_6H_6	623	624	26 (1)
$\text{H}_2\text{TPP (X)}$	C_6H_6	645	651	146 (6)
$\text{H}_3(\beta\text{-Me}_6\text{Et}_2)\text{Cor (XIX)}$	C_6H_6	596	600	112 (4)
$\text{H}_3(\text{ms-Ph})_3\text{Cor (XX)}$	C_6H_6	650	670	459 (20)
	DMF	640	654	335 (14)

(**XVIIb**). The localized molecule of donor solvent in this case stabilizes the form **b**.^[15,17] Addition of tiny amount of stronger base (DEA) which is comparable to the porphyrinoid concentration to the solution of tautomer **b** causes immediate deprotonation of the external NH-group. Dissociation of this H-associate is confirmed by spectrophotometric titration (Figure 8) as well as by disappearing of NH-signal at +12.81 ppm in ^1H NMR-spectra after addition of $1 \cdot 10^{-6}$ M DEA to DMSO d_6 solution of **b**. Deprotonation process is characterized by dissociation constant which equals $1.82 \cdot 10^{-7}$ in DMF. Tautomeric process and further deprotonation in

DMF-DEA media are not common for **XVIII** which does not possess free external NH group.

Conclusions

To form H-associates with electron-donating organic solvents which are characterized by incomplete proton transfer, porphyrins and their analogs have to possess some kind of specific structural features. The macrocyclic structure should be polarized owing either to non-planar, usually *saddle*, conformation or rigid π -system (porphyrazines)

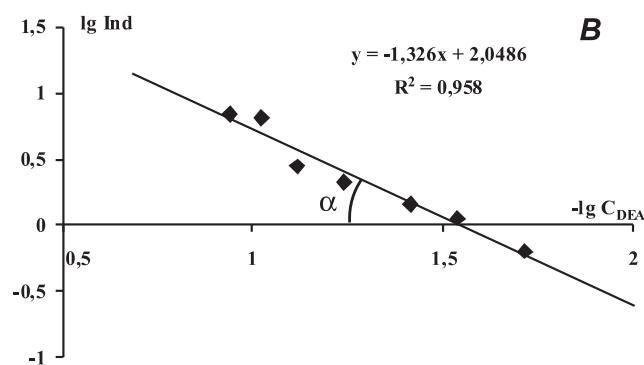
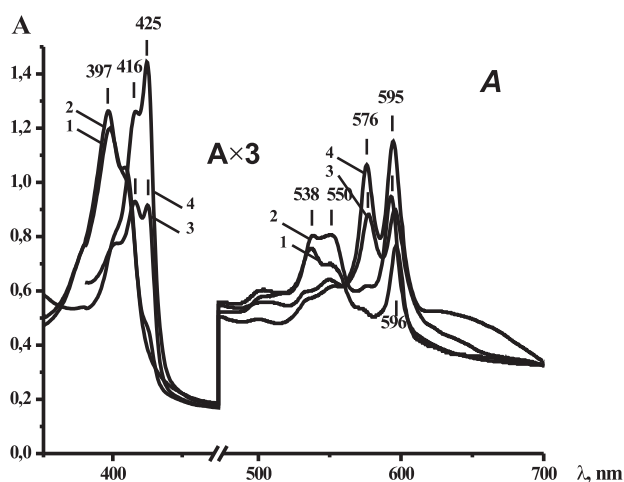


Figure 7. Absorption spectra of **XIX** ($C_{\text{H}_3\text{Cor}} = 1.9 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$) in C_6H_6 (1), DMF (2), 0.13 M DEA in DMF (3) and 0.01 M $[\text{NBu}_4]\text{OH}$ in DMF (4) (A); indicator dependence $\lg(\text{Ind}) = \lg C_{\text{DEA}}$ for **XIX** titration with DEA in DMF media (B).

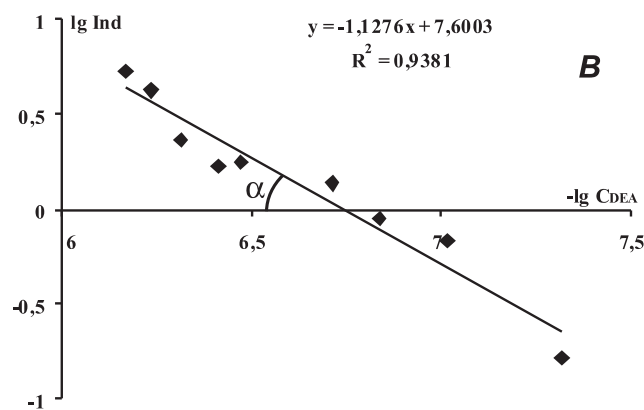
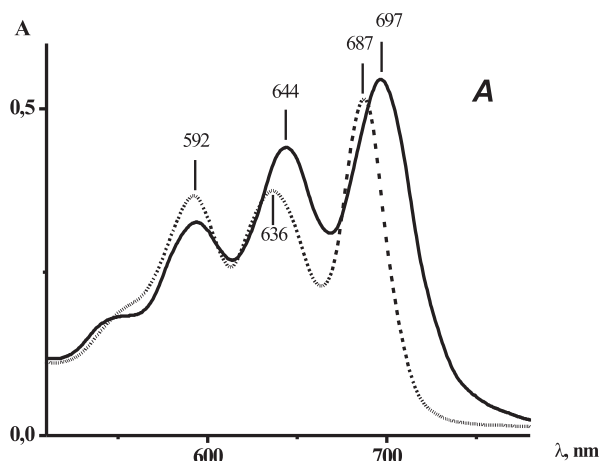


Figure 8. Absorption spectra of inverted porphyrin analog **XVII** in DMF (solid line, tautomer **b**) and $2 \cdot 10^{-6}$ M DEA in DMF (dashed line, monoanion) (A) and graphic determination of a number of NH protons splitted off ($\text{tg } \alpha \approx 1.1$) from the molecule **XVIII** in DMF-DEA solvent system (B).

or specific constitution of modified macrocycle (corroles). Combination of both high polarization and characteristics of donor solvent strongly favors the formation of H-associated acid-basic particles.

Acknowledgements. This work was carried out under financial support of Russian Foundation for Basic Research (project № 06-03-96327) and Russian Science Support Foundation. Authors are kindly appreciated to Prof. A.S. Semeykin and Dr. P.A. Shatunov.

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Received 4.06.2008

Accepted 5.11.2008

First publish on the web 14.03.2009