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Acid Properties of Porphyrins and Related Systems

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Abstract—Structural, energetic, and electronic aspects of a series of porphyrins and related compounds in their neutral, anion, and dianion electronic states have been studied by means of DFT calculations [B3LYP/6-31+G(d,p)]. Analysis of the electron density puts forward a number of different kinds of interactions between the inner atoms. Intramolecular correlations similar to those found in intermolecular N–H···N interactions have been found.

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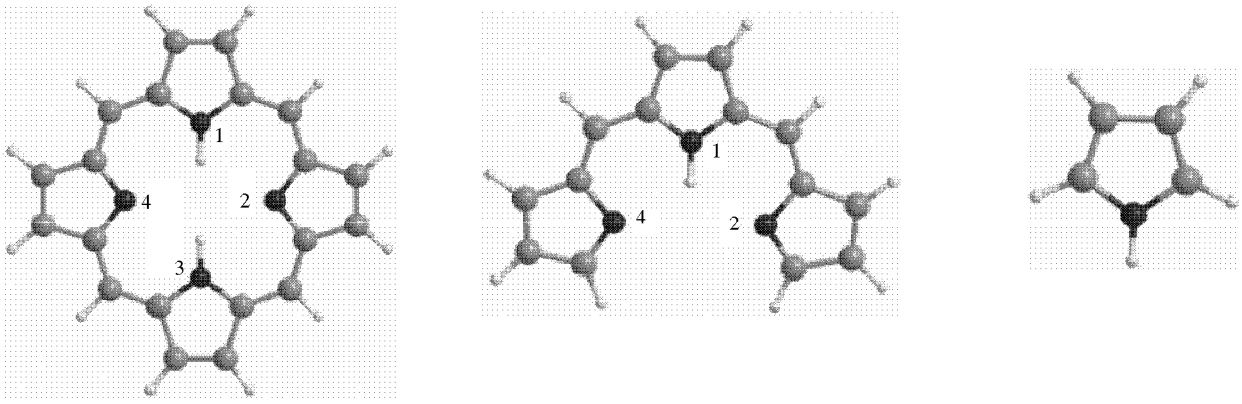
INTRODUCTION

The extraordinary importance of porphyrins and related systems (phthalocyanines, subsphthalocyanines, isocorroles, sapphyrins, porphycenes, subazaporphyrins, N-confused porphyrins, etc.) is never emphasized enough [1–5]. Porphyrins with both "pyridine-like" nitrogen atoms replaced by sulfur [6, 7], selenium [7], and tellurium atoms [8, 9] have received as much attention as porphycenes [10].

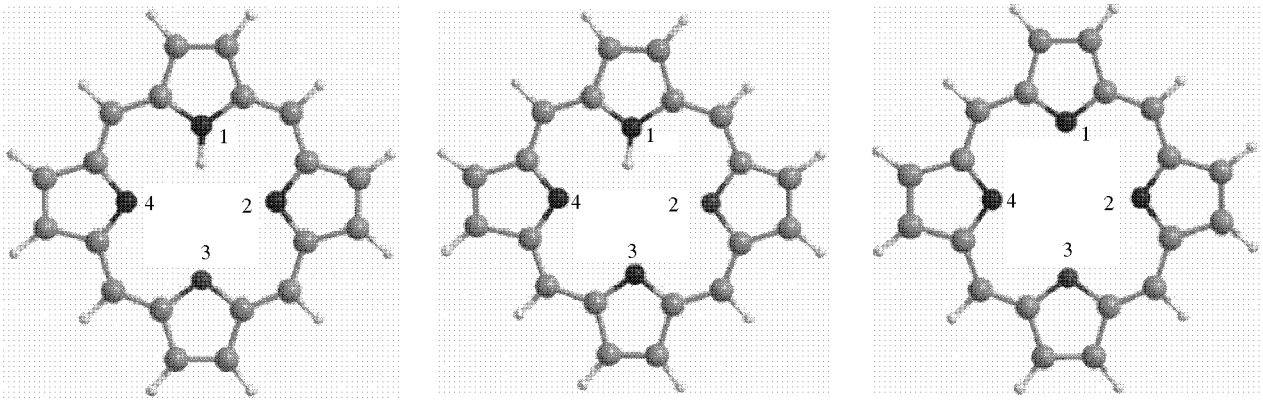
A number of experimental studies have been carried out to characterize the acid–base properties of these compounds. In general, most attention has been attached to mono- and diprotonation of these molecules [11–18]. In addition, the NH groups can be monodeprotonated in the presence of phosphazene bases [19–21] and dideprotonated with strong bases [22]. The physicochemical properties of these species has been characterized by NMR and visible spectroscopy [19, 22].

Previous, theoretical studies [23] have pointed out the importance of including electron correlation for adequate description of the geometry of porphyrin and related systems [24, 25]. A systematic study of



I **II** **III**

Fig. 1. Porphyrin (**I**) and its molecular fragments **II** and **III**.



IV (*1H*, 3*O*) **IV** (*1H*, 2*O*) **IV** (–)

Fig. 2. Porphyrin analogs **IV** with one nitrogen substituted by oxygen.

possible isomers of the porphyrin core has been carried out by several groups [26–29]. The mechanism of the *trans–trans* hydrogen transfer has been calculated to occur in a two-step process via a *cis* intermediate [30, 31].

METHODS

All the systems have been optimized with the Gaussian-98 and Gaussian-03 programs [32, 33] at the B3LYP/6-31+G(d,p) level [34–36]. Frequency calculations have been performed at the same computational level to confirm that the calculated geometries correspond to energy minima.

The electron density of the systems has been analyzed in terms of the Atoms in Molecules (AIM) methodology [37, 38] with the PROAIMV [39] and Morphy98 [40] programs.

RESULTS AND DISCUSSION

Porphyrin and Its Molecular Fragments

Initially, two isomers of the porphyrin core and their mono- and di-anions have been studied. In addition, two systems that can be considered as fragments of the porphyrin core, one with three pyrrole rings and the other pyrrole itself, have been considered in their neutral and anionic forms (Fig. 1).

The energy results for these systems are presented in Table 1. In agreement with previous studies [27, 29, 31, 41, 42], in **I** the 1H,3H tautomer is more stable than 1*H*,2*H* by 32 kJ mol^{-1} at the MP2 level, in good agreement with the results obtained here. In addition, the energies of the first and second deprotonation acts have been evaluated as the energy differences between the neutral molecule and the monoanion, in the first case, and between the monoanion and dianion, in the second case (Scheme 1).

Table 1. Energies of the neutral systems (Hartree), relative energy and deprotonation energies (kJ mol^{-1}) calculated at the B3LYP/6-31+G(d,p) computational level

System	E_{tot}	E_{rel}(1*H*,2*H*)	A_1	A_2
I	–989.611678[a]	35.1	1499.4	1867.5
II	–704.357737		1497.6	
III	–210.188173		1534.7	

[a] For (1*H*, 3*H*) tautomer.

Table 2. Interatomic distances (Å) between the inner nitrogen atoms in **I** and **II** and their derivatives

R	1 (1*H*,3*H*)	1 (1*H*,2*H*)	**I**(¯)	**I**(2¯)	**II**	**II**(¯)
N^1-N^2	2.938	3.215	2.911	2.956	2.873	3.285
N^1-N^3	4.237	4.178	4.129	4.181		
N^2-N^3	2.938	2.721	2.955	2.956		
N^2-N^4	4.073	4.178	4.167	4.181	3.947	5.137

Scheme 1.

$$MH_2 \xrightarrow{A_1} MH^- \xrightarrow{A_2} M^{2-}.$$

The experimental acidity of **III** has been found to be 1504.1±1.3 kJ mol^{-1}, which is well reproduced by the B3LYP/6-31+G** calculations including the ZPE correction (1496.1 kJ mol^{-1}).

Comparison of the resulting deprotonation energies indicates that open structure **II** is as acidic as **I**, and these structures are both more acidic than **III** in the gas phase. As expected, A_2 is much higher than A_1 due to the difficulties of generating a doubly charged species.

The interatomic distances between the inner atoms of the porphyrin core in **I** are listed in Table 2 together with data for 2. In the case of **I**, deprotonation only slightly affects the general molecular structure as indicated by the small variations in the interatomic distances (Table 2). In contrast, **II** expands to avoid repulsion of the naked nitrogen atoms in the deprotonated form. This process is hindered in the rigid porphyrin system. Among the variations observed, shortening of the N^1–N^2 and N^2–N^3 distances in the monoanion, which corresponds to strengthening of the hydrogen bond between these moieties, and lengthening of the N^2–N^3 and N^2–N^4 due to the increment of charge in these groups, deserve special mentioning. In the 1*H*,2*H* tautomer, the N^1–N^2 distance is clearly perturbed due to the presence of hydrogen atoms.

Porphyrin Analogs with a Heteroatom Other Than N

In the second part of the article, the porphyrin analogs where one of the nitrogen atoms has been substituted by oxygen, sulfur, or selenium have been studied (Fig. 2). The energy results for these compounds are presented in Table 3. The 1*H*,3*X* tautomer which can be considered as an analog to the 1*H*,3*H* tautomer of the porphyrin is the most stable, the energy gap increasing as the size of the X atom increases.

Regarding the acidity of the systems, an important increment is observed as the size of the X atom increases, so that the selenium derivative turns to be 68 kJ mol^{-1} more acidic than the oxygen one (note that this effect can be due either to stabilization of the anion or to destabilization of the neutral species). Comparison with the previous results indicates that the sulfur and selenium derivatives are stronger acids than porphyrin itself.

In order to gain insight in the stability of these compounds, the isodesmic reactions shown in Scheme 2 have been studied. Using the experimental heats of formation of pyrrole, furan, and thiophene (108.3, –34.7, and 115.0 kJ mol^{-1}, respectively) [43], the differences in the heats of formation of **IV–VI** vs. porphyrin **I**, neutral and deprotonated, have been calculated (Table 4).

The results show that the products of the isodesmic reaction (porphyrin and C_4H_4X) are preferred vs. the reactants (**IV–VI** and pyrrole), except for the anionic form of **VI**. In addition, the relative heat of formation of **IV**, **V** vs. **I** indicates that the former compounds have more negative heats of formation than **I**.

Table 3. Total energies (Hartree), relative energies and deprotonation energies (kJ mol^{-1}) of compounds **IV–VI**

X, system	Symmetry[a]	$E_{tot}(1H,3X)$	$E_{rel}(1H,2X)$[b]	A_1
O, **IV**	C_{2v}, C_s, C_{2v}	–1009.444407	20.6	1534.6
S, **V**	C_{2v}, C_s, C_{2v}	–1332.414824	35.6	1492.8
Se, **VI**	C_{2v}, C_s, C_{2v}	–3333.644887	38.5	1466.7

[a] Symmetry of the neutral molecules 1*H*,3*X* and 1*H*,2*X*, and the monoanion, respectively. [b] Relatively to the most stable 1*H*,3*X* isomer.

Scheme 2.

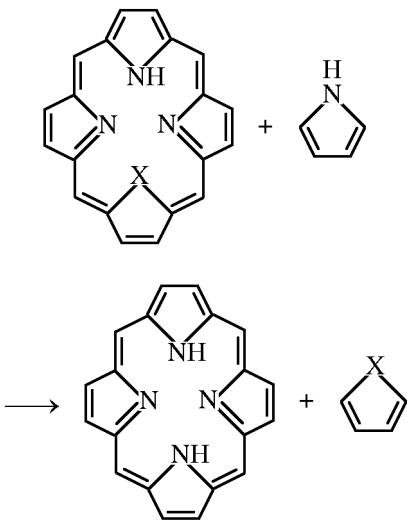


Table 4. Energies of isodesmic reactions and relative heats of formation of **IV–VI** vs. **I** (kJ mol^{-1})

X, system	Energy of isodermic rection		Heat of formation **IV–VI** vs. **I**	
	neutral form	anionic form	neutral form	anionic form
O, **IV**	–45.46	–80.74	–97.5	–62.3
S, **V**	–70.00	–63.49	–63.3	–56.8
Se, **VI**	–16.70	15.98		

Table 5. Interatomic distances between the inner atoms in **IV–VI** and their derivatives

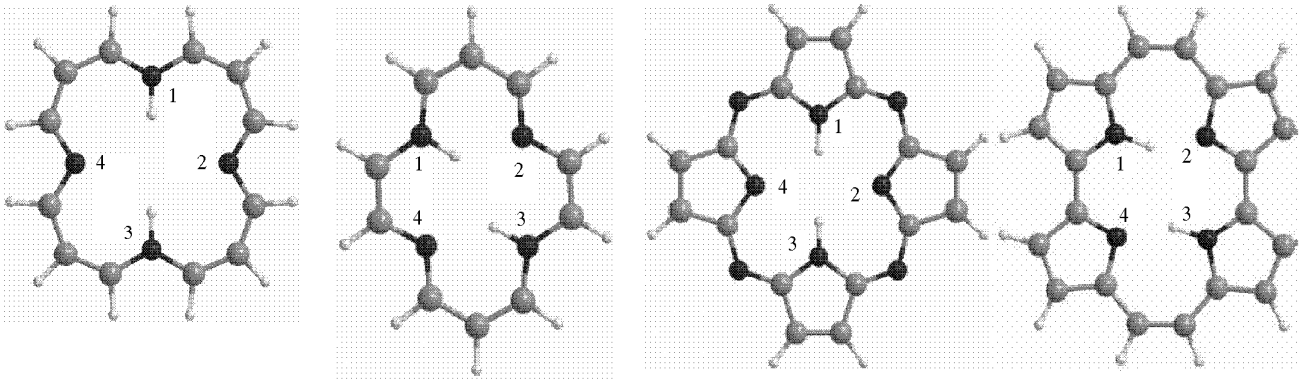
R	**IV** (1*H*,3X)	**IV** ($^-$)	**V** (1*H*,3X)	**V** ($^-$)	**VI** (1*H*,3X)	**VI** ($^-$)
N^1–N^2	2.898	2.933	3.020	3.036	3.065	3.059
N^1–X^3	4.203	4.211	3.561	3.483	3.387	3.245
N^2–X^3	2.955	2.945	2.702	2.671	2.629	2.588
N^2–N^4	4.074	4.102	4.461	4.495	4.539	4.574

The geometric parameters of **IV** in its neutral and anionic forms are very similar to those obtained for **I**. In contrast, the inclusion of sulfur and selenium (systems **V** and **VI**) produce an essential distortion of the system, which is reflected by the elongation of the N^1–N^2 and, especially, N^2–N^4 distances. Upon deprotonation a significant shortening of the N^1–X^3 distance is observed in the sulfur and selenium derivatives, implying chalcogen interaction between these moieties [44, 45].

Cyclic Systems Related to Porphyrins

In the third part of this article, four cyclic compounds and their mono and dideprotonated anions have been studied. The chosen systems were porphyrin model **VII**, dibenzotetraaza[14]annulene **VIII**, phthalocyanine **IX**, and porphycene **X** (Fig. 3).

The energy results for these molecules are presented in Table 6. Two of the systems considered here, **VII** and **IX**, with an inner ring similar to **I,** are more



VII **VIII** **IX** **X**

Fig. 3. Porphyrin-related neutral systems studied.

Table 6. Energy characteristics systems **VII–X**

System	Symmetry[a]	E_{tot}	A_1	A_2
VII	D_{2h}. C_{2v}. D_{4h}	–684.675105	1464.8	1828.8
VIII	C_{2h}. C_s. D_{2h}	–607.276409	1541.4	1930.1
IX	D_{2h}. C_{2v}. D_{4h}	–1053.761962	1438.6	1833.1
X	C_{2h}. C_s. C_{2h}	–989.611816	1520.5	1876.1

[a] Symmetry of the neutral molecules, monoanion, and dianion, respectively.

acidic than the latter, whereas **VIII** and **X** that present a smaller ring or a different distribution of the pyrrole rings are less acidic than **I**. Thus, ring size and shape seem to be important as modulators of this property.

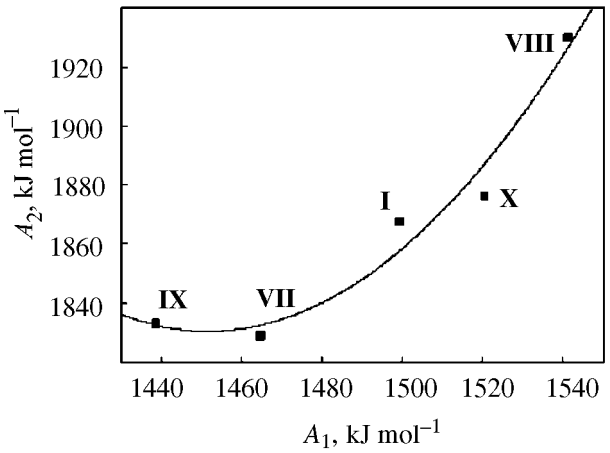


Fig. 4. A_1 vs. A_2 (kJ mol–1) for porphyrin **I** and its related compounds **VII–X**. Second-order polynomial curve fit, R = 0.96.

Regarding the second deprotonation energies of these molecules, they seem to be related to the first ones (Fig. 4). However, in the case of **IX**, the presence of four additional nitrogen atoms seems to be a factor to provide extra stabilization of the dianion. The A_1 and A_2 values have been correlated with a second-order polynomial equation (Fig. 4).

A selection of the interatomic distances of the compounds studied in this section is presented in Table 7. Comparison of the inner distances in **VII** and **I** clearly indicates that the absence of pyrrole rings in the former case allows expansion of the system, which is impossible in the rigid porphyrin core. The opposite effect is observed on the introduction of the new four nitrogen atoms in **IX**, which produce a considerable contraction of the ring in the latter compared to **I**. The first and second deprotonation produces, in the four systems considered here, an initial shortening of the N^1–N^3 distance and lengthening in the second step. In the same way, the N^2–N^4 distance increases from the neutral form to monoanion, in all the cases, and even more in the dianions of **VII** and **X**.

Electron density analysis provides information on interatomic interactions in a system. Some of them correspond to the classical view of a bond, while others correspond to weak interactions, such as hydrogen bonds and van der Waals contacts. The character of the interaction can be found out based on the value of the Laplacian (negative or positive) at the bond critical point. In the present study, in addition to the expected bond critical points for the covalent bonds, a number of weak interatomic interactions in the central part of the ring were found (Table 8).

Table 7. Interatomic distances (Å) between the inner atoms in **VII–X** and their derivatives

R	**VII**	**VII** ($^-$)	**VII** ($^{2-}$)	**VIII**	**VIII** ($^-$)	**VIII** ($^{2-}$)
N^1–N^2	3.211	3.195	3.266	2.715	2.774	2.829
N^1–N^3	4.655	4.519	4.619	3.964	3.798	3.955
N^2–N^3	3.211	3.232	3.266	2.749	2.728	2.765
N^2–N^4	4.424	4.569	4.619	3.761	3.957	3.955
R	**IX**	**IX** ($^-$)	**IX**($^{2-}$)	**X**	**X** ($^-$)	**X**($^{2-}$)
N^1–N^2	2.768	2.736	2.763	2.664	2.746	2.816
N^1–N^3	3.992	3.866	3.908	3.966	3.897	4.018
N^2–N^3	2.768	2.763	2.763	2.839	2.791	2.865
N^2–N^4	3.832	3.912	3.908	3.819	3.927	4.018

Table 8. Electron densities ρ in the critical points of bonds between the inner atoms in **I, II**, and **IV–X** (only unique interactions are shown)

System	*r*	$\nabla^2\rho$	Interacting atoms	Interatomic distance, Å
I (1*H*,3*H*)	0.0148	0.0486	H· · ·N	2.316
I (1*H*,2*H*)	0.0313	0.0863	H· · ·N	1.942
I (1*H*,2*H*)	0.0076	0.0240	N· · ·N	3.126
I (1*H*,2*H*)	0.0069	0.0329	H· · ·H	2.070
I($^-$)	0.0147	0.0503	H· · ·N	2.315
I ($^-$)	0.0101	0.0337	N· · ·N	2.956
I ($^{2-}$)	0.0099	0.0338	N· · ·N	2.956
II	0.0169	0.0558	H· · ·N	2.242
IV (1*H*,3O)	0.0155	0.0521	H· · ·N	2.287
IV (1*H*,3O)	0.0086	0.0309	O· · ·N	2.955
IV (1*H*,2O)	0.0209	0.0649	H· · ·N	2.137
IV (1*H*,2O)	0.0095	0.0310	N· · ·N	2.993
IV (1*H*,2O)	0.0076	0.0330	O· · ·H	2.541
IV (1*H*,2O)	0.0100	0.0353	O· · ·N	2.887
IV ($^-$)	0.0103	0.0354	N· · ·N	2.933
IV ($^-$)	0.0086	0.0315	O· · ·N	2.945
V (1*H*,3S)	0.0113	0.0405	H· · ·N	2.453
V (1*H*,3S)	0.0104	0.0383	S· · ·H	2.545
V (1*H*,3S)	0.0240	0.0768	S· · ·N	2.702
V (1*H*,2S)	0.0243	0.0697	H· · ·N	2.053
V (1*H*,2S)	0.0064	0.0226	N· · ·N	3.193
V (1*H*,2S)	0.0221	0.0709	S· · ·H	2.269
V (1*H*,2S)	0.0316	0.0955	S· · ·N	2.558
V ($^-$)	0.0086	0.0288	N· · ·N	3.036
V ($^-$)	0.0251	0.0803	S· · ·N	2.671
V($^-$)	0.0054	0.0211	S· · ·N	3.483
VI (1*H*,3Se)	0.0106	0.0387	H· · ·N	2.499
VI (1*H*,3Se)	0.0176	0.0502	Se· · ·H	2.374
VI (1*H*,3Se)	0.0309	0.0920	Se· · ·N	2.629
VI (1*H*,2Se)	0.0255	0.0727	H· · ·N	2.031
VI (1*H*,2Se)	0.0057	0.0200	N· · ·N	3.266
VI (1*H*,2Se)	0.0274	0.0746	Se· · ·H	2.215
VI (1*H*,2Se)	0.0480	0.1233	Se· · ·N	2.409
VI ($^-$)	0.0084	0.0279	N· · ·N	3.059
VI($^-$)	0.0331	0.0966	Se· · ·N	2.589
VI ($^-$)	0.0096	0.0318	Se· · ·N	3.245
VII	0.0088	0.0291	H· · ·N	2.570
VII ($^-$)	0.0085	0.0292	H· · ·N	2.584
VIII	0.0365	0.0982	H· · ·N	1.883
VIII ($^-$)	0.0262	0.0778	H· · ·N	2.038
VIII ($^-$)	0.0153	0.0517	N· · ·N	2.780
VIII ($^{2-}$)	0.0137	0.0460	N· · ·N	2.829
IX	0.0210	0.0692	H· · ·N	2.154
IX ($^-$)	0.0208	0.0728	H· · ·N	2.147
IX ($^-$)	0.0144	0.0533	N· · ·N	2.763
IX ($^{2-}$)	0.0141	0.0537	N· · ·N	2.763
X	0.0547	0.1219	H· · ·N	1.691
X ($^-$)	0.0393	0.0983	H· · ·N	1.831
X ($^-$)	0.0161	0.0556	N· · ·N	2.761
X ($^{2-}$)	0.0131	0.0420	N· · ·N	2.866

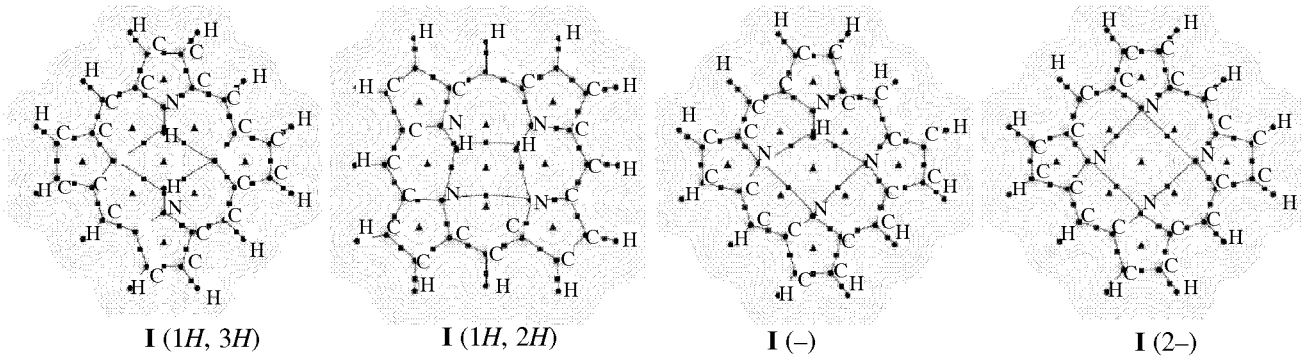


Fig. 5. Electron density map in the molecular plane of the four derivatives of **I**. The positions of nuclei and bond and ring critical points are indicated by circles, squares, and triangles, respectively. In addition, bond paths are shown.

In the neutral systems with alternating NH and N moieties, the interactions found corresponds to N–H···N hydrogen bonds. Interestingly, in most of the cations, removal of hydrogen atoms does not lead to disappearance of bonding interactions, since now they correspond to N···N interactions. As an illustrative example, Fig. 5 depicts the maps of electron density in the molecular plane of the four derivatives of **I**. Interactions between heteroatoms (N···N, O···N, S···N, and Se···N) are also found in some of the neutral molecules. It can be argued that these interactions are present due to the congestion in the central part of the

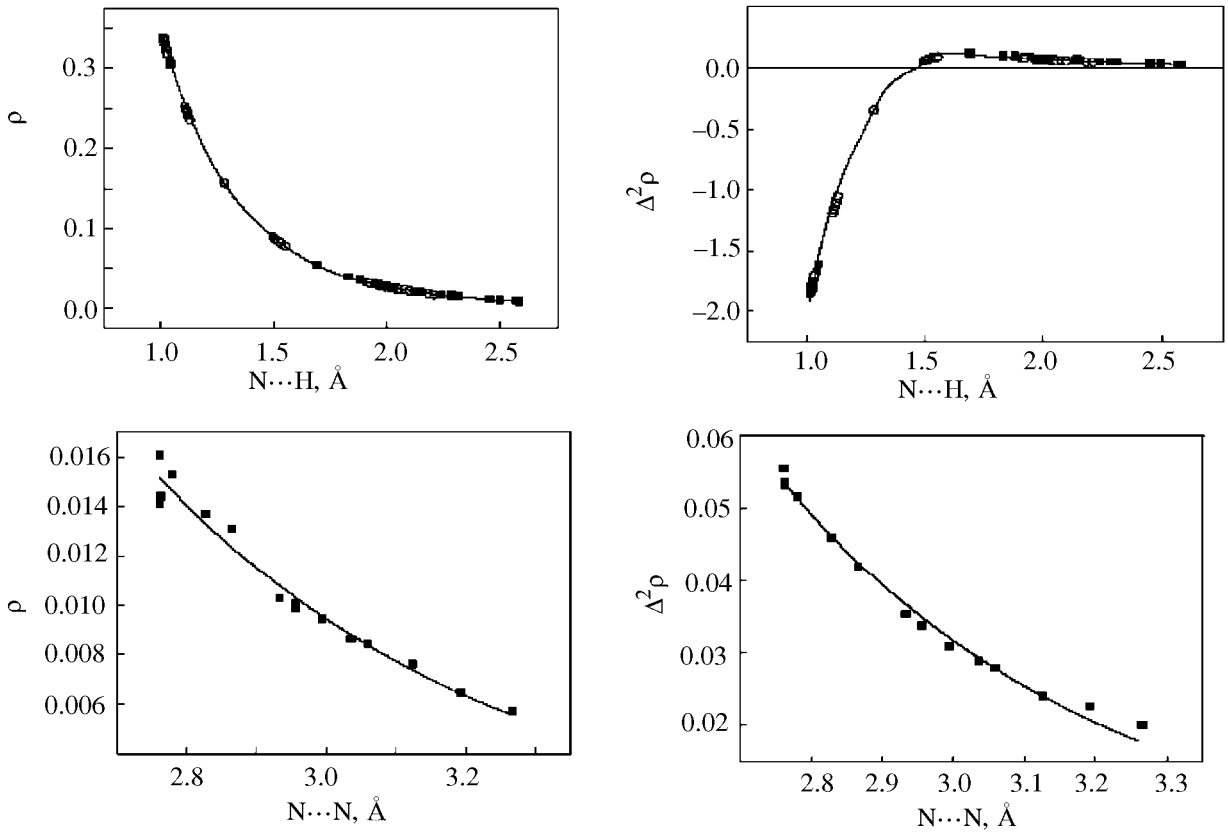


Fig. 6. Electron density and Laplacian (au) vs. interatomic distance (Å). The fitted curves for the N···H data corresponds to a joint function as described in [47]. The fitted curves for the N···N interactions correspond to simple exponential relationships. Black squares correspond to the data obtained in the present article and circles, to those taken from [46].

molecules, and, therefore, such interactions were not revealed in molecules **II** and **VII** whose rings are able to expand in their anionic form. In order to confirm this hypothesis, structure **VII** has been reoptimized with D_{4h} symmetry at different distances of the nitrogens to the molecular center. Analysis of the electron density distribution showed that bond critical point already appeared at N^1–N^2 distances shorter than 3.17 Å.

The properties of N···N and N···H interactions at the bond critical point have been analyzed vs. interatomic distances (Fig. 6). In order to check if the properties of the bond critical point obtained in the present case are similar to other intermolecular interactions, the N···H results have been plotted together with those previously reported for a larger set of hydrogen-bonded dimers and proton-transfer transition state structures [46], obtained at the same computational level (Fig. 6). The figures clearly show that the two sets of data, intramolecular and intermolecular, follow identical tendencies and can be considered together.

The relationship of the electron density and the Laplacian at the bond critical point vs. interatomic distance can be fitted with two exponential relationships, one for open-shell interactions (negative Laplacian values and large electron densities) and the other for pure closed-shell interactions (positive and low Laplacian values and low electron densities). These two exponential relationships can be considered together using a joint function that, in addition, will fit the intermediate values. In the case of the N···N interaction, only the closed-shell interaction regime has been considered.

CONCLUSION

A theoretical study of the acidity of porphyrin system **I** and some related systems including, on one hand, porphyrin fragments **II** and **III** and the monoanion and dianion of **I** and, on the other, chalcogen porphyrins **IV, V** and **VI** and their anions, as well as cyclic nitrogen derivatives **VII–X,** has been carried out by means of B3LYP/6-31+G(d,p) computations.

Analysis of the electron density indicates the presence of a large number of different interatomic interactions in the inner part of the systems, for instance, chalcogen interactions between sulfur (selenium) and the opposed N anion. Special emphasis has been placed on acid–base equilibria (neutral/anion/dianion). The relationships between the electron density and the Laplacian at the bond critical point show that these interactions are so similar to those encountered in intermolecular interactions that they can be analyzed together.

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