



Research Article

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Density Functional Calculations on the Molecular, Electronic Structures of Metal-Free, N,N'-Dideuterio and Magnesium Tetra-3,4-Pyridino-Porphyrazines

Zhongqiang Liu^{1*} and Xianxi Zhang²

Affiliation

¹Research Center of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Qilu Normal University, PR China

²Shandong Provincial Key Laboratory/Collaborative Innovation Center of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, PR China

*Corresponding author: Zhongqiang Liu, Associate Professor, Research Center of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Qilu Normal University, Jinan 250200, PR China, Tel: +86 531 66778025, E-mail: warler2000@163.com

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Abstract

A theoretical calculation of the fully optimized geometries and electronic structures of the metal-free Tetra-2,3-Pyridino-Porphyrazine (TPdPzH₂^{*}), N,N'-Dideuterio (TPdPzD₂^{*}), and Magnesium (TPdPzMg^{*}) tetra-3,4-pyridino-porphyrazine has been conducted with the density functional B3LYP level using the 6-31G(d) basis set. A comparison among the different Phthalocyanine (Pc) derivatives, including Tetra-2,3-Pyridino-Porphyrazine (TPdPzH₂) compounds, for the geometry, molecular orbital, and atomic charge was made. The substitution effect of the N atoms and the isotopic effect of D atoms on the properties of these compounds were discussed. The farther the heterocyclic N atoms in the benzo rings from 16-membered ring are, the smaller it influence the size of the central hole, the bond lengths and bond angles of 16-membered ring, the HOMO-LUMO gaps, and the atomic charges on the core Pz fragment. In other words, the properties of TPdPz^{*} compounds are closer to Pc than TPdPz. With the order of H₂Pc < TPdPzH₂ < TPdPzH₂^{*}, the acidity of the inner N-H bonds in the three molecules increased in turn.

Keywords: Tetra-3,4-pyridino-porphyrazine, DFT method, Molecular structure, Electronic structure, Phthalocyanines.

Abbreviations: DFT-Density Functional Theory, TPdPzH₂-Tetra-2,3-Pyridino-Porphyrazine, Pc-Phthalocyanine, HOMO-Highest energy Occupied Molecular Orbital, LUMO-Lowest energy Unoccupied Molecular Orbital.

Introduction

Phthalocyanines (Pcs) have been widely used as organic dyestuffs since their first synthesis early last century because of their intense absorption of light in the visible and ultra-violet regions and their high chemical and thermal stabilities [1,2]. They have also attracted considerable interest due to their applications in modern science and technology on the basis of their special electric and photoelectric properties: semiconductivity, photoconductivity and luminescence [3].

The benzo rings of Pc compounds can be substituted by heterocycles such as thiophene, thionaphthalene, pyridine, or pyrazine, thus forming heterocyclic Pc analogues. The aza-Analogues of the Phthalocyanines (aza-Pcs) have been extensively studied over the past three decades. Potential applications include their use as textile bleaching agents, photoinactivators for controlling growth of microorganisms, catalysts for oxygen reduction, materials for electrochromic displays, and media for optical data storage with large memory capacity, inhibitor of thermal degradation of polymers and photosensitizers for photodynamic therapy of cancer [4-9].

The synthesis of heterocyclic Pc analogues was initially reported in 1937 by Linstead and co-workers [10,11]. A significant contribution to the development of the aza-Pcs chemistry was made by Galpern and Luk'yanets [12] who described the synthesis and properties of a series of aza-Pcs. Previously, Density Functional Theory (DFT) methods have been extensively employed investigating Pcs and their derivatives by Zhang et al [13-18]. We have also approached the molecular, electronic structures and vibrational spectra for metal-free (TPdPzH₂), N,N'-Dideuterio (TPdPzD₂) and Magnesium (TPdPzMg) tetra-2,3-pyridino-porphyrazines and metal-free (TPyPzH₂), N,N'-Dideuterio (TPyPzD₂) and Magnesium (TPyPzMg) tetra-2,3-pyrazino-porphyrazines [19,20].

Moreover, theoretical investigation of the molecular, electronic structures and vibrational spectra of a series of transition metal phthalocyanines and naphthalocyanine have been performed using the density functional theory, and ideal results have been achieved [21,23]. All the previous research works demonstrated that the density functional B3LYP method performs well in the calculation for

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phthalocyanines and their analogues, thus it should also be appropriate for the tetra-3,4-pyridino-porphyrazine complexes.

Computer simulation as an attractive alternative to experiment can provide valuable information. So, to get more insights into the molecular and electronic structures, it is worthwhile to conduct quantum chemistry calculations. In the present paper, we report theoretical calculations of molecular, electronic structures of metal-free Tetra-3,4-Pyridino-Porphyrazine (TPdPzH₂^{*}), its N,N'-Dideuterio Derivative (TPdPzD₂^{*}) and Magnesium complex (TPdPzMg^{*}). The substitution effect of the N atoms and the isotopic effect of D atoms on these properties of these compounds were discussed. Some interesting and meaningful results were obtained.

Computational Method

The structures of the tetra-3,4-pyridino-porphyrazine are shown in **Figure 1**. The 6-31G(d) basis set was used at the density functional B3LYP level for geometry optimization and calculations. The default Mulliken method was used for atomic charge calculation. The Berry algorithm using redundant internal coordinates was employed in energy minimization and tight convergence criteria were used throughout [24]. C_{4h} symmetry for TPdPzMg^{*} and C_{2h} for TPdPzH₂^{*} and TPdPzD₂^{*} in the input structures were detected and then enforced by the program. Using the energy-minimized structures generated in the previous step, normal coordinate analyses were carried out. All calculations were carried out using Gaussian09 program.

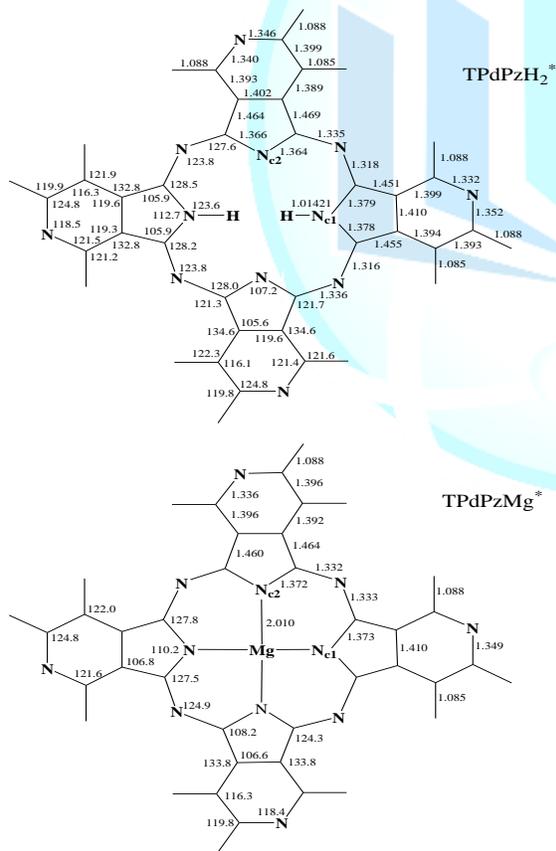


Figure 1: Structure of TPdPzH₂^{*} (H=D for TPdPzD₂^{*}) and TPdPzMg^{*}; bond lengths (Å) and bond angles (°).

Results and Discussion

Molecular structures

At density functional B3LYP level, the energy-minimized structure of TPdPzMg^{*} calculated has C_{4h} symmetry, and both TPdPzH₂^{*} and TPdPzD₂^{*} have C_{2h} symmetry. No imaginary vibration is predicted in the frequency calculations, indicating that the energy-minimized structures are true energy minima. Corresponding structural parameters are illustrated in Figure 1. What's interesting is that N,N'-Dideuterio-Derivative (TPdPzD₂^{*}) cannot change the structural parameters in metal-free-derivative (TPdPzH₂^{*}), thus only the bond lengths and bond angles of TPdPzH₂^{*} herein are discussed. Considering the substitution effect of the N atoms on the molecular structure, except that N-H bond lengths maintain six significant digits to compare, the other structure parameters retain four.

As shown in Figure 1, the N-H bond length is 1.01421 Å for TPdPzH₂^{*}, which is slightly longer than that of TPdPzH₂ (1.01418 Å), and longer than that of H₂Pc (1.01399 Å) [24]. These indicate that the N-H bond strengths of the three molecules vary with the sequentially decreasing order of H₂Pc < TPdPzH₂ < TPdPzH₂^{*}, which also implies that the acidity of the inner N-H bonds of the three molecules sequentially increase with the trend of H₂Pc < TPdPzH₂ < TPdPzH₂^{*}. On the other hand, the electron-withdrawing effect of the annulated pyridine ring increases the acidity of the inner N-H bonds, which corresponds to the experimental result [25].

Analysis of the structure parameters of TPdPzMg^{*} shows that the average size of the central hole (Nc-Nc distance) is 4.021 Å, which is larger than those of MgPc (4.017 Å), but smaller than that of TPdPzMg (4.024 Å) [19]. This indicates that the size of the central hole increases with the order of MgPc < TPdPzMg < TPdPzMg^{*}, which implies that the farther the heterocyclic N atoms in the benzo rings from 16-membered ring are, the smaller they influence the size of the central hole. That is to say, the size of 16-membered ring in TPdPzH₂^{*} is nearer to that of H₂Pc.

Electronic structures and molecular orbitals

The energies of the molecular orbitals from HOMO-5 to LUMO+3 of TPdPzH₂^{*} and TPdPzMg^{*} are comparatively listed in **Table 1** and shown in **Figure 2**. Herein, HOMO and LUMO represent the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. **Figure 3** shows the scheme of HOMO and LUMO of TPdPzH₂^{*} and TPdPzMg^{*}. It is worth noting that N, N'-dideuterio-derivative (TPdPzD₂^{*}) cannot change the molecular orbital energy levels in metal-free-derivative (TPdPzH₂^{*}). In this paper, the energies of TPdPzH₂^{*} are only discussed.

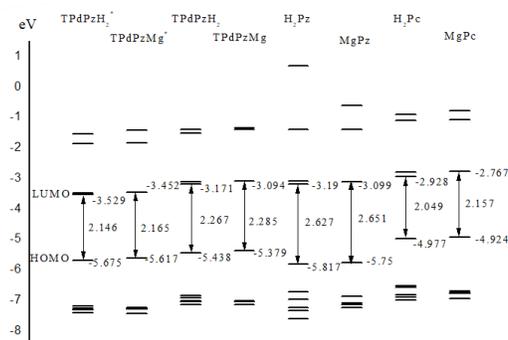


Figure 2: Orbital energies of TPdPzH₂^{*}, TPdPzMg^{*} compared with TPdPzH₂, TPdPzMg, H₂Pz, MgPz, H₂Pc and MgPc.

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orbital	TPdPzH ₂ [*]		TPdPzMg [*]		TPdPzH ₂ ^a		TPdPzMg ^a		H ₂ Pz ^b		MgPz ^b		H ₂ Pc ^b		MgPc ^b	
	Orbital energy	Orbital symmetry	Orbital energy	Orbital symmetry	Orbital energy	Orbital symmetry	Orbital energy	Orbital symmetry	Orbital energy	Orbital symmetry	Orbital energy	Orbital symmetry	Orbital energy	Orbital symmetry	Orbital energy	Orbital symmetry
E _{LUMO+3}	-1.533	A _u	-1.414	B _u	-1.402	A _u	-1.355	B _u	0.701	B _{3u}	-0.610	A _{1g}	-0.909	B _{3u}	-0.785	B _{2u}
E _{LUMO+2}	-1.861	A _u	-1.823	B _u	-1.512	A _u	-1.398	B _u	-1.405	A _u	-1.397	B _{1u}	-1.095	A _u	-1.071	B _{1u}
E _{LUMO+1}	-3.470	B _g	-3.452	E _g	-3.107	B _g	-3.094	E _g	-3.083	B _{2g}	-3.099	E _g	-2.788	B _{1g}	-2.767	E _g
E _{LUMO}	-3.529	B _g	-3.452	E _g	-3.171	B _g	-3.094	E _g	-3.190	B _{1g}	-3.099	E _g	-2.928	B _{2g}	-2.767	E _g
ΔE	2.146		2.165		2.267		2.285		2.627		2.651		2.049		2.157	
E _{HOMO}	-5.675	A _u	-5.617	A _u	-5.438	A _u	-5.379	A _u	-5.817	A _u	-5.750	A _{1u}	-4.977	A _u	-4.924	A _{1u}
E _{HOMO-1}	-7.186	A _g	-7.227	B _g	-6.845	A _u	-7.020	A _u	-6.720	B _{3u}	-6.869	A _{2u}	-6.517	B _{3u}	-6.680	B _{2u}
E _{HOMO-2}	-7.186	B _u	-7.261	E _u	-6.925	B _g	-7.023	B _g	-6.964	B _{1g}	-7.077	B _{2u}	-6.559	B _{1g}	-6.735	A _{2u}
E _{HOMO-3}	-7.267	A _u	-7.261	E _u	-7.009	A _g	-7.042	B _u	-7.237	B _{3u}	-7.141	B _{2g}	-6.816	B _{3u}	-6.768	E _g
E _{HOMO-4}	-7.313	B _g	-7.278	A _g	-7.025	B _u	-7.133	E _g	-7.326	B _{3G}	-7.221	E _g	-6.880	B _{2g}	-6.768	E _g
E _{HOMO-5}	-7.412	A _g	-7.416	B _u	-7.144	A _u	-7.133	E _g	-7.597	B _{2u}	-7.221	E _g	-6.982	A _u	-6.934	E _g

Note: a-Cited from Reference [30], b-Cited from Reference [24].

Table 1: Energy levels (in eV) of some occupied and unoccupied molecular orbital for TPdPzH₂^{*} and TPdPzMg^{*}.

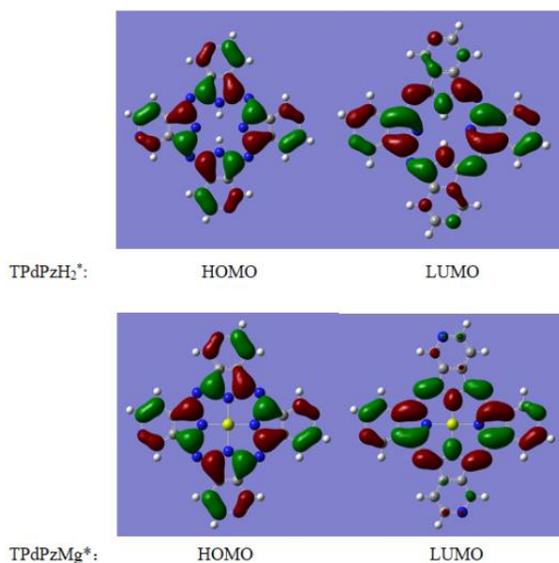


Figure 3: Graphic representation of HOMO and LUMO of TPdPzH₂^{*} and TPdPzMg^{*}.

There are two characteristic absorption bands (the Q band and Soret or B band) in UV-visible spectra of porphyrazines and their analogues with fused heterocycles. The Q band in the visible region originates from the HOMO→LUMO electronic transition [26]. In practical application, people pay attention to Q band.

Due to the extension of π -conjugation, the HOMO-LUMO gaps of TPdPzH₂^{*} and TPdPzMg^{*} (2.146 and 2.165 eV) are smaller than those of H₂Pz and MgPz (2.627 and 2.651 eV), indicating that the Q bands of TPdPzH₂^{*} and TPdPzMg^{*} shift to a longer wavelength side than those of H₂Pz and MgPz [13]. According to Linstead, some Pz derivatives show Q band peaks at 535-617 nm, while the TPdPz^{*} compounds at 574-672 nm [27,28]. These data agree very well with the above-mentioned calculation results.

The HOMO-LUMO gaps of TPdPzH₂^{*} and TPdPzMg^{*} (2.146 and 2.165 eV) are found to be a bit larger than those of H₂Pc and MgPc (2.049 and 2.157 eV), and smaller than those of TPdPzH₂ and TPdPzMg (2.266 and 2.285 eV) [13,19]. This straightens out the hypsochromic shift of the Q band in the electronic spectra of these aza phthalocyanine analogues, on the other hand, interprets electronic spectra in the visible region of TPdPz^{*} compounds are identical to the spectra of the corresponding Pcs due to the HOMO-LUMO gaps of them are near each other [27,29]. According to Galpern, the substitution of the CH groups in the Pc benzo rings adjacent to the porphyrazine macrocycle with N atoms causes a remarkable

hypsochromic shift in the visible part of the electronic absorption spectrum. The magnitude of this shift increases from tetra-aza-Pcs (20-25 nm, 550-780 cm⁻¹) to the octa-aza derivatives (40-60 nm, 870-1260 cm⁻¹) depending on the nature of the central metal atom [30,31].

The energy levels of the HOMO-5 to LUMO+3 orbitals for TPdPz^{*} compounds all decrease compared with those of the corresponding Pc and TPdPz compounds. Moreover, the magnitude of all the energy levels is in the order of TPdPz^{*}<TPdPz<Pc, which indicates that the farther the heterocyclic N atoms in the benzo rings from the 16-membered ring are, the lower the orbital energy level decrease.

Compared with H₂Pc and MgPc, the reduction of HOMO of TPdPzH₂^{*} and TPdPzMg^{*} are 0.698 and 0.693 eV, while the reduction of LUMO are 0.601 and 0.685 eV, respectively, and the decrease of HOMO are slightly larger than those of LUMO [13]. This is due to the presence of the π -deficient annulated pyridine rings in the TPdPz^{*} unit as compared with the isoelectronic benzene rings in the Pc unit. The lowering of HOMO for TPdPzH₂^{*} and TPdPzMg^{*} compared with those of TPdPzH₂ and TPdPzMg are 0.238 and 0.238 eV, which are smaller than those of LUMO, 0.358 and 0.358 eV, respectively [19]. The possible reason is that the heterocyclic N atoms on TPdPz^{*} compounds are farther from the central 16-membered ring than those on TPdPz compounds, and they affect the energy levels of the LUMO orbitals are larger than those of the HOMO ones. This interprets the HOMO-LUMO gaps of TPdPzH₂^{*} and TPdPzMg^{*} are smaller than those of TPdPzH₂ and TPdPzMg.

Atomic charges

Both phthalocyanine and aza-Pcs compounds contain basic porphyrazine structural units and additional π -conjugated rings. This sequential increase in the number of π -conjugated aromatic rings gives rise to increased polarization of basic porphyrazine ring, which causes the change of π -electron energy. The atomic charge of the core Pz fragment and the external N atoms for TPdPzH₂^{*} and TPdPzMg^{*} compounds are comparatively listed in **Table 2**.

It is worth noting that N,N'-dideuterio-derivative (TPdPzD₂^{*}) cannot change the atomic charge in metal-free-derivative (TPdPzH₂^{*}), thus the atomic charge of TPdPzD₂^{*} herein is not discussed. In order to show the difference between TPdPzH₂^{*} and TPdPzH₂, the significant digits of the atomic charges are maintained three except that four significant digits retained by Hc. The atom symbols for TPdPzH₂^{*} and TPdPzMg^{*} are shown in **Figure 4**.

Compared with the TPdPz compounds, the charges of the central Nc for the TPdPz^{*} compounds become less negative, while the meso-N atoms (N_m) become more negative, which means that the charges of these atoms for TPdPz^{*} compounds are nearer to those of Pc compounds [19].



Atom	N _{c1}	N _{c2}	C _{a11}	C _{a12}	C _{a21}	C _{a22}	N _{m1}	N _{m2}	C _{β11}	C _{β12}	C _{β21}	C _{β22}	N _{γ1}	N _{γ2}	H _c	Mg
TPdPzH ₂ ⁺	-0.746	-0.661	0.528	0.516	0.471	0.457	-0.550	-0.552	0.089	0.036	0.107	0.058	-0.414	-0.416	0.4355	
TPdPzMg ⁺	-0.683	-0.683	0.494	0.482	0.494	0.482	-0.547	-0.547	0.091	0.041	0.091	0.041	-0.415	-0.415		0.894
TPdPzH ₂ ^a	-0.753	-0.668	0.506	0.56	0.448	0.5	-0.530	-0.534	0.091	0.185	0.11	0.198	-0.488	-0.494	0.4348	
TPdPzMg ^a	-0.690	-0.690	0.472	0.527	0.472	0.527	-0.529	-0.529	0.093	0.185	0.093	0.185	-0.492	-0.492		0.888
H ₂ Pc ^b	-0.745	-0.662	0.511	0.511	0.456	0.456	-0.560	-0.560	0.064	0.064	0.082	0.082			0.4345	
MgPc ^b	-0.680	-0.680	0.479	0.479	0.479	0.479	-0.556	-0.556	0.067	0.067	0.067	0.067				0.876

Note: a-Cited from Reference [30], b-Cited from Reference [24].

Table 2: Atomic charge (in e) for TPdPzH₂⁺ and TPdPzMg⁺.

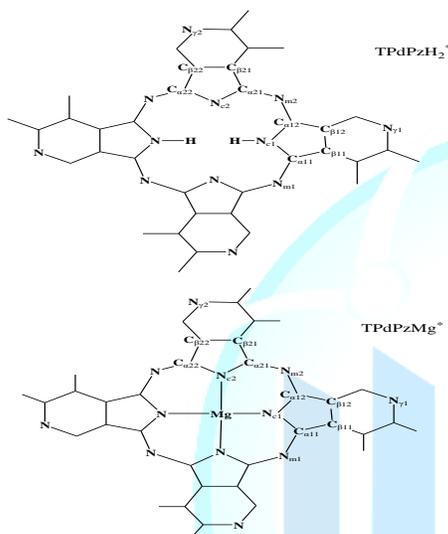


Figure 4: Atom symbols of TPdPzH₂⁺ and TPdPzMg⁺.

In addition, all the other charges of the corresponding atoms in the core Pz fragment for TPdPz⁺ compounds are nearer to those of Pc compounds. This implies that the farther the heterocyclic N atoms in the benzo rings from the central 16-membered ring are, the smaller they influence the charges of the atoms on the core Pz fragment. That is to say, the atom charges of the core Pz fragment in TPdPz⁺ compounds are nearer to those of Pc, which basically agree with the experimental electronic spectra in the visible region of TPdPz⁺ compounds being identical to the spectra of the corresponding Pcs [29].

The atomic charge of the central Hc (0.4355 e) of TPdPzH₂⁺ is larger than that of TPdPzH₂ (0.4348 e) and H₂Pc (0.4345 e), which is consistent with the acidity of the atoms on the inner N-H bonds of the three molecules (H₂Pc < TPdPzH₂ < TPdPzH₂⁺) mentioned above in the molecular structure. In addition, the atom charge of the magnesium (0.894 e) is larger than that of TPdPzMg (0.888 e), which is larger than that of MgPc (0.876 e).

Conclusions

According to our calculation, we found that the farther the heterocyclic N atoms in the benzo rings from 16-membered ring are, the smaller it influence the size of the central hole, the bond lengths and bond angles of 16-membered ring, the HOMO-LUMO gaps, and the charges of the atoms on the core Pz fragment. That is to say, TPdPz⁺ compounds are nearer to Pc compounds than TPdPz in structure, energies of the molecular orbitals, and atomic charges. The acidity of the inner N-H bonds of the three molecules sequentially increase with the order of H₂Pc < TPdPzH₂ < TPdPzH₂⁺.

Acknowledgements

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