Structural Preferences and Stability of Tin(II)-Porphyrins - A Theoretical Investigation

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Abstract

Tin(II)-porphyrin compounds are rare when compared to those of tin(IV)-porphyrin compounds. But tin(II)-porphyrin compounds are known and exhibit as excellent reducing agents. The stable octaethyl-porphyrinato-tin(II) is known with its crystal structure. The structural preferences and the stability of tin(II)-porphyrin compounds of the type SnP, where, P = porphyrin (**1**); Octamethylporphyrin (**2**); Octaethylporphyrin (**3**); Octa-n-propyl-porphyrin (**4**); Octa-isopropyl-porphyrin (**5**); Octa-n-butyl-porphyrin (**6**) and Octa-tert-butyl-porphyrin (**7**) are studied using the Density Functional Theory (DFT) methods. Computational chemistry tools like DFT methods can aid to study and model compounds with experimental handling difficulties. Here we have studied the viability of the different tin(II)-porphyrin compounds with substitutions at the porphyrin ring. Our results predict the non-viable nature of some selected tin(II)-porphyrins as well as the possible formation of tin(II)-porphyrin complexes in selected cases.

1. Introduction

Tin(II) is an uncommon oxidation state in porphyrin complexes as there is a strong tendency to oxidise to Sn(IV). During the preparation of Sn(IV) porphyrins by treating $SnCl_2$ with free base porphyrins in aerobic conditions, transient green colours appear immediately, to be replaced by the familiar maroon to purple colours of the Sn(IV) complexes. The first well-defined Sn(II) porphyrin was reported by Whitten et al., [1] who prepared Sn(OEP) on a very small scale by treatment of rigorously dried and degassed pyridine solutions of H_2(OEP) with freshly prepared anhydrous $SnCl_2$. The characteristic absorption bands at 495 and 600 nm were recorded and the proton NMR data supported the out-of-plane Sn(II) formulation. Landrum et al. [2] reported the synthesis of Sn(TPP) in 1984 from H_2(TPP) and $SnCl_2$ in THF and pyridine. The visible spectrum shown in this paper indicates that the product was a mixture of Sn(TPP) and H_2(TPP), but the signature bands of the former at 397, 488 and 692 nm were evident. The Guilard group [3] then produced the complete and unambiguous characterisation of Sn(P), (P = OEP, TPP, TpTP, TmTP, TMP), including X-ray structural analysis of Sn(OEP) and electrochemical studies of several derivatives. Their method of preparation was the same as that of Landrum but a longer reaction time ensured complete metallation. The very air-sensitive complexes could be chromatographed under rigorous conditions and yields of 27-76% were achieved. Recently Woo et al. [4] introduced a new method for preparing Sn(II) porphyrins by the reduction of Sn(TpTP)Cl_2 with $NaBEt_3H$ in toluene. This method avoids chromatography and gave 76% yield of the Sn(II) complex. This appears to be the most convenient method so far published and is the only reductive method that has succeeded in producing the divalent complexes rather than inducing the common reaction of ring-reduction to give Sn(IV)chlorins and bacteriochlorins. [5] Although tin-porphyrin

compounds and their applications are well documented and still there are many areas to be explored both experimentally and theoretically [6-18]. Here we have used computational chemistry tools like DFT methods to study the geometrical, electronic structural preferences, stability, spectroscopic properties and molecular orbital studies of tin(II)-porphyrin compounds of the type SnP, where, P = porphyrin (1); Octamethylporphyrin (2); Octaethylporphyrin (3); Octa-n-propyl-porphyrin (4); Octa-isopropyl-porphyrin (5); Octa-n-butyl-porphyrin (6) and Octa-tert-butyl-porphyrin (7). The interesting results obtained are discussed under different sections.

2. Computational Methods

DFT calculations were carried out using the software ORCA developed by Frank Neese and co-workers. [19] All calculations were performed using the BP86 density functional [20-23] and Def2-TZVP basis set included in the ORCA programme, which is free for academic use. Self-Consistent Field (SCF) calculations were performed using the TIGHTSCF convergence criteria. The geometry optimization was carried out and the resulting geometries are confirmed as minima through the frequency calculations. Pictures of the optimized geometries and the Frontier molecular orbitals are taken using the graphics programme ChemCraft. [24]

3. Results and Discussion

The chemistry of tin(II)-porphyrins are less explored when compared to those of tin(IV)-porphyrins. Here we have studied the electronic, geometrical structural preferences, stability, spectroscopic properties and frontier molecular orbital analysis of the tin(II)-porphyrin compounds of the type SnP, where, P = porphyrin (**1**); Octamethylporphyrin (**2**); Octaethylporphyrin (**3**); Octa-n-propyl-porphyrin (**4**); Octa-isopropyl-porphyrin (**5**); Octa-n-butyl-porphyrin (**6**) and Octa-tert-butyl-porphyrin (**7**).

3.1.Geometry

The DFT (BP86/Def2-TZVP) optimized geometries of the tin(II)-porphyrin compounds 1 with selected bond lengths are given in the Figure 1. The DFT (BP86/Def2-TZVP) optimized geometry of the compound tin(II)-octaethylporphyrin (3) is presented in the Figure 2 with two views. The DFT computed selected bond parameters are provided in the Table S1.

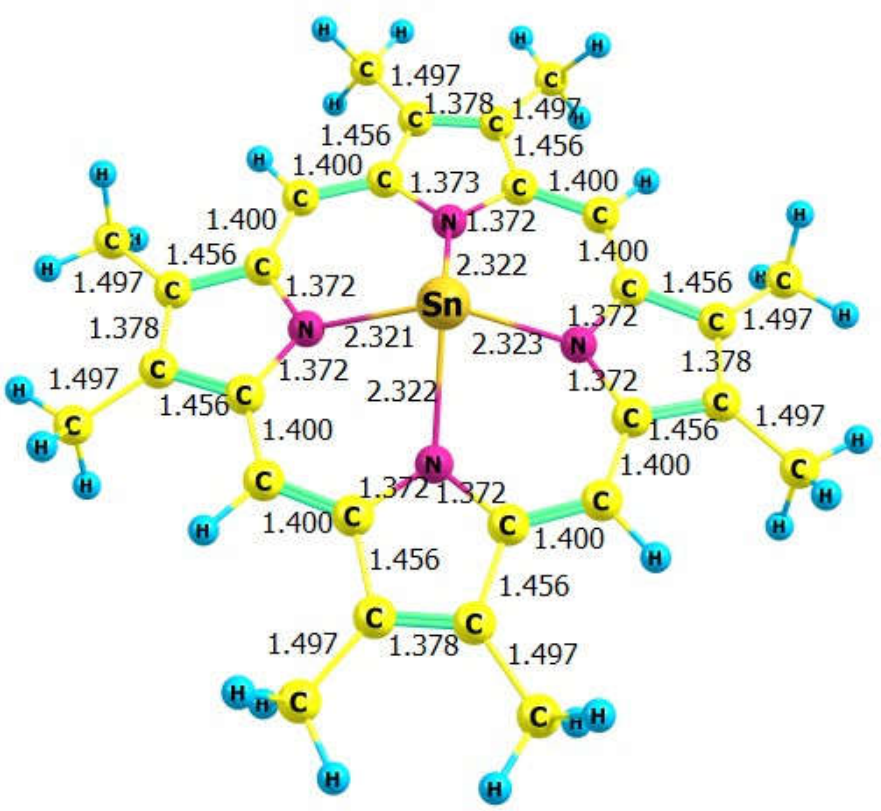

Figure 1. DFT (BP86/Def2-TZVP) optimized geometries of the compound tin(II)-octamethylporphyrin (**2**) with selected bond lengths.

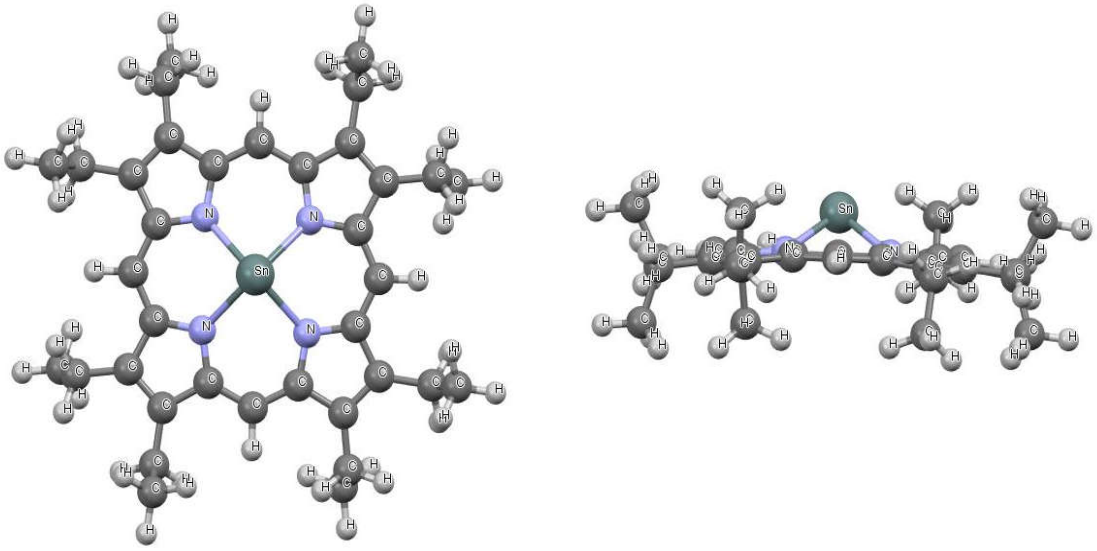

Figure 2. DFT (BP86/Def2-TZVP) optimized geometry of the compound tin(II)-octaethylporphyrin (**3**) is presented in the Figure 2 with two views.

The DFT(BP86/Def2-TZVP) optimized geometries of compound 1-7 show that the tin atom lies above the plane containing the macrocyclic porphyrin unit. The Sn-N bond lengths are around 2.322 A^{O} in the compound 2. This trend is observed in all the compounds studied. The DFT (BP86/Def2-TZVP) optimized geometries of the compounds tin(II)- octa-*iso*propylporphyrin (4) and tin(II)-octa-*tert*-butylporphyrin (7) are provided in the Figure 3. In the compounds 4 and 7 also the the metal-nitrogen bond lengths are around 2.322 A^{O}, similar to other compounds. The central tin atom lies above the plane containing the macrocyclic porphyrin ring.

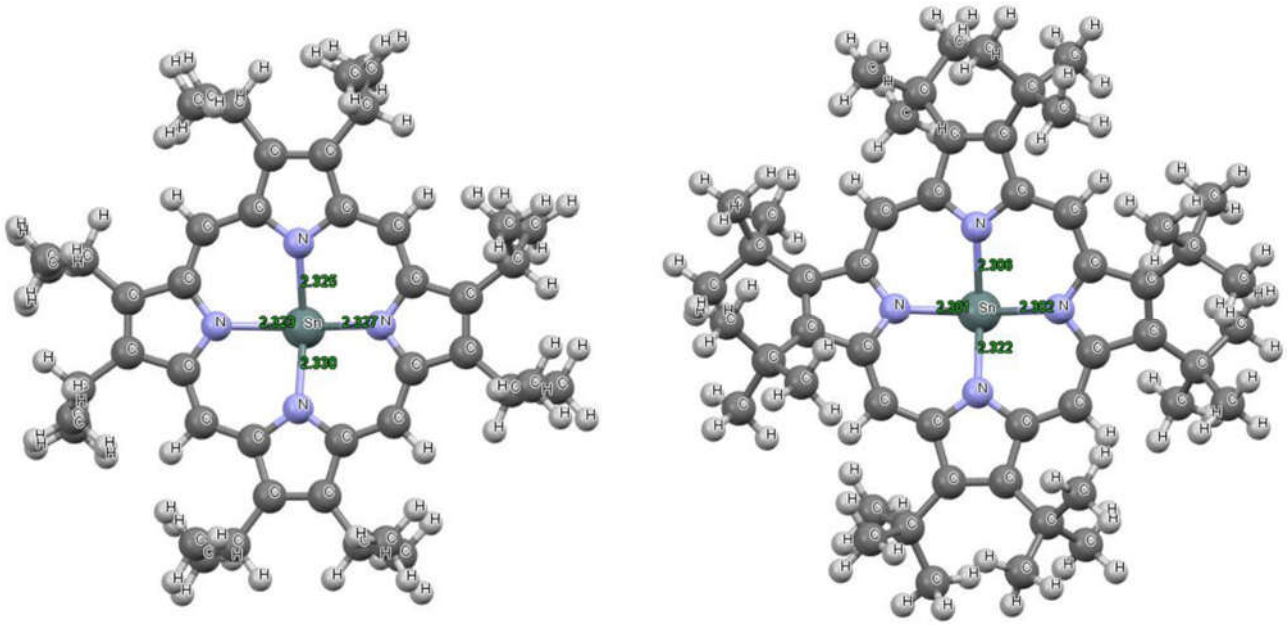

Figure 3. DFT (BP86/Def2-TZVP) optimized geometries of the compounds tin(II)-octa-isopropylporphyrin (4) and tin(II)-octa-*tert*-butylporphyrin (7). The DFT (BP86/Def2-TZVP) computed Mayers bond order values of 0.47 indicate the covalent single bonded nature of the Sn-N bonds in the compounds.

3.2. Electronic Structure

The electronic structural studies on these tin(II)-porphyrin compounds 1-7 resulted in the following conclusions. With the optimized geometry lies in the minima of the potential energy surface and the energy gap between LUMO and HOMO clearly indicate the possible stability of the compounds 1-7. The energy gap $E_{LUMO-HOMO}$ value of 2 eV suggests the possible stability of these compounds 1-7. The frontier molecular orbitals of the compound tin(II)-octamethylporphyrin (2) optimized at DFT(BP86/Def2-TZVP) are provided in Figure 4.

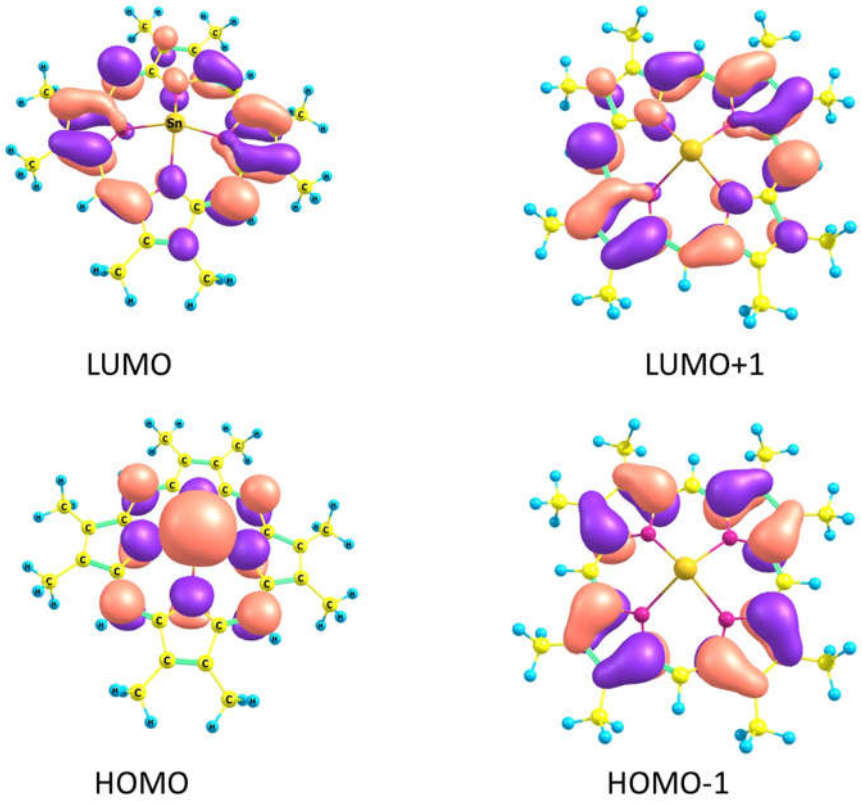

Figure 4. The frontier molecular orbitals of the compound tin(II)-octamethylporphyrin (2) optimized at DFT(BP86/Def2-TZVP).

From the frontier molecular orbital pictures of tin(II)-octamethylporphyrin (2), Figure 3, it is evident that the lone pair of the tin(II) mainly occupied in the HOMO. No significant contribution from the metal atom is observed in the LUMO, LUMO+1 and HOMO-1, but the electrons are delocalized throughout the porphyrin ring.

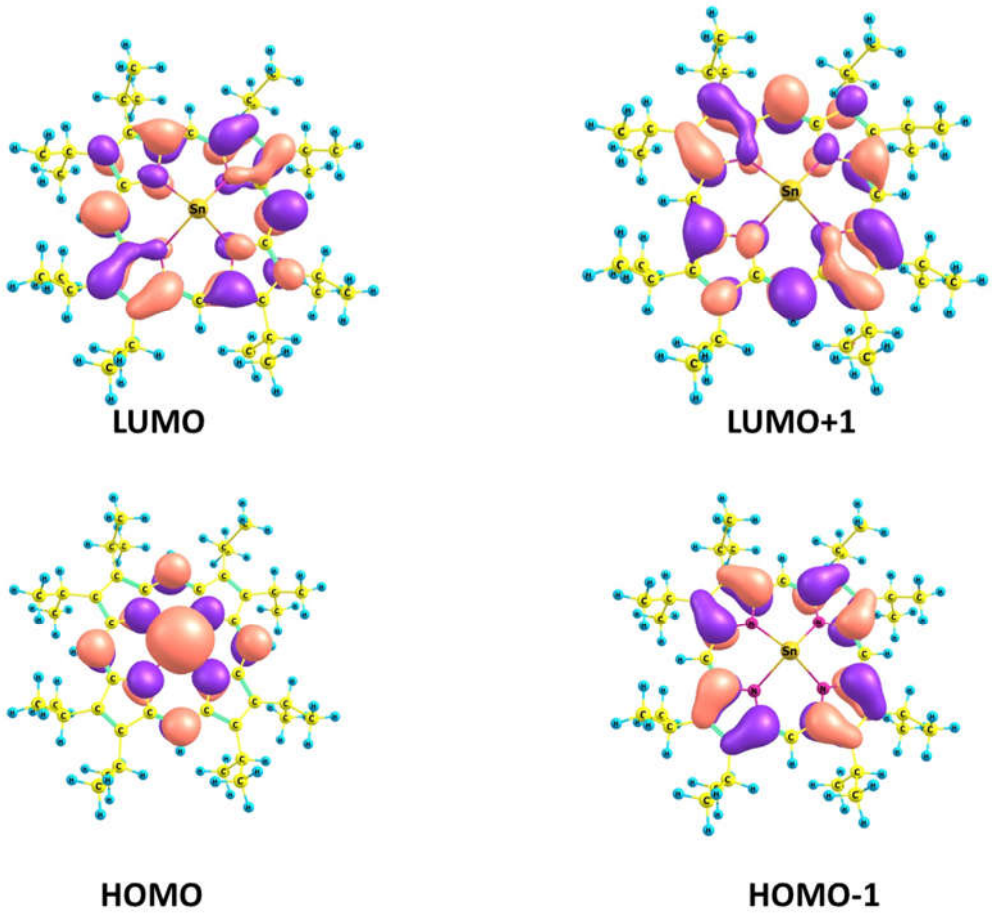

Figure 5. The frontier molecular orbitals of the compound tin(II)-octaisopropylporphyrin (**5**) optimized at DFT(BP86/Def2-TZVP).

The frontier molecular orbital pictures of tin(II)-octaisopropylporphyrin (**5**), Figure 5, it is evident that the lone pair of the tin(II) mainly occupied in the HOMO. The LUMO, LUMO+1 and HOMO-1 orbitals are mainly containing the electrons are delocalized throughout the porphyrin ring.

DFT (BP86/Def2-TZVP) computed $E_{LUMO-HOMO}$ energies (eV), chemical potential, hardness, softness, electrophilicity, ionization potential, and electron affinity for the compounds tin(II)-octamethylporphyrin (**2**), tin(II)-octaethylporphyrin (**3**) and tin(II)-octa-iso-propylporphyrin (**5**) are provided in Table 1.

Table 1. DFT computed ELUMO-HOMO energies (eV), chemical potential, hardness, softness, electrophilicity, ionization potential, and electron affinity for the compounds tin(II)-octamethylporphyrin (**2**), tin(II)-octaethylporphyrin (**3**) and tin(II)-octa-*iso*-propylporphyrin (**5**).

Compound	**2**	**3**	**5**
HOMO	-4.3784	-4.3967	-4.3921
LUMO	-2.7817	-2.8021	-2.8032
$E_{LUMO-HOMO}$	1.5967	1.5946	1.5889
Chemical potential (μ)	-3.5801	-3.5994	-3.5977
Hardness (Ƞ)	0.7984	0.7973	0.7945
Softness (S)	1.2525	1.2542	1.2587
Electrophilicity (Ꞷ)	8.0268	8.1247	8.1457
Ionization potential (eV)	4.3784	4.3967	4.3921
Electron Affinity (eV)	2.7817	2.8021	2.8032

The energy gap between the frontier molecular orbitals LUMO and HOMO, ie., $E_{LUMO-HOMO}$ value of 1.6 eV confirms the stable nature of these compounds. Electrophilicity

index value of 8.0 eV suggest the similar electrophilic nature in these compounds. The highest electrophilicity index value has been observed in compound 5 ie., tin(II)-octa-iso-propylporphyrin.

4. Conclusions

The structural preferences and the stability of tin(II)-porphyrin compounds of the type SnP, where, P = porphyrin (1); Octamethylporphyrin (2); Octaethylporphyrin (3); Octa-n-propyl-porphyrin (4); Octa-isopropyl-porphyrin (5); Octa-n-butyl-porphyrin (6) and Octa-tert-butyl-porphyrin (7) are studied using the Density Functional Theory (DFT) methods and the following conclusions are derived. (1) The DFT(BP86/Def2-TZVP) optimized geometries of compound **1-7** show that the tin atom lies above the plane containing the macrocyclic porphyrin unit. (2) The DFT (BP86/Def2-TZVP) computed Mayers bond order values of 0.47 indicate the covalent single bonded nature of the Sn-N bonds in the compounds. (3) The energy gap between the frontier molecular orbitals LUMO and HOMO, ie., ELUMO-HOMO value of 1.6 eV confirms the stable nature of these compounds. (4) The highest electrophilicity index value has been observed in compound 5 ie., tin(II)-octa-iso-propylporphyrin. (**3**). (5) DFT computations show the possibility of the viable synthesis of these compounds in the laboratories except 2 which is already known. (6)Tin(II)-porphyrin derivatives can be used as a strong reducing agents for different reactions.

5. References

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