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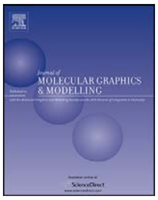

The effect of β-saturated pyrrolic rings on the electronic structures and aromaticity of magnesium porphyrin derivatives: A density functional study

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ABSTRACT

Density functional theory (DFT) calculation on the molecular structures, molecular orbitals, electronic absorption spectra, and magnetic properties of magnesium porphyrin (MgPor) and a series of five hydrogenated magnesium porphyrin complexes with different number of β-saturated pyrrolic rings, namely MgPor-β-1Hy, MgPor-β-opp-2Hy, MgPor-β-adj-2Hy, MgPor-β-3Hy, and MgPor-β-4Hy, clarifies the red-shift of the lowest energy absorption band from chlorophyll *a* to bacteriochlorophyll and reveals the strong chemical stability for both of them. The energy levels of highest occupied molecular orbitals (HOMO) and HOMO−1 for MgPor are reversed upon hydrogenation at β-positions (2 and 3, 7 and 8, 12 and 13, and 17 and 18) of porphyrin ring. Along with the increase of β-saturated pyrrolic rings from 1, 2, 3, to 4, the HOMO energy increases from −4.78 eV to −3.10 eV in a regular manner. In contrast, the lowest unoccupied molecular orbitals (LUMO) energy levels of MgPor, MgPor-β-1Hy, and MgPor-β-opp-2Hy are very similar with each other. As a result, the lowest energy absorption band involving main transition from HOMO to LUMO is red-shifted from MgPor-β-1Hy to MgPor-β-opp-2Hy which is representative of chlorophyll *a* and bacteriochlorophyll, respectively. Natural hydroporphyrins represented by MgPor, MgPor-β-1Hy, and MgPor-β-opp-2Hy have turned out to be aromatic and stable enough, in good accordance with the ubiquity of their derivatives in the nature. In contrast, MgPor-β-adj-2Hy, MgPor-β-3Hy, and MgPor-β-4Hy with relatively weak aromaticity seem to be unstable and therefore were not found in nature.

1. Introduction

Natural metalloporphyrin derivatives have been at the focus of multidisciplinary interest over the last one century due to their diverse functions in biological processes [1–6]. In particular, the two porphyrinato magnesium complexes, chlorophyll *a* and bacteriochlorophyll, play important roles in plant and bacterial photosynthesis, respectively [4–6].

Chlorophyll *a* has strong lowest energy absorption band at ca. 660 nm, while this band is significantly red-shifted to 772 nm in the electronic absorption spectrum of bacteriochlorophyll [7,8]. The primary structural difference between the two molecules is that bacteriochlorophyll has two β-saturated pyrrolic rings at the opposite positions, while chlorophyll *a* has only one (Fig. S1, supplementary data). It seems that hydrogenation of two opposite pyrrole rings could lead to the red-shift of the “orange” peak of chlorophyll *a*. In 2000, Jusélius and Sundholm studied the aromatic pathways of magnesium porphyrin, magnesium chlorin, and magnesium bacteriochlorins by performing aromatic ring current shieldings (ARCS) and nucleus independent chemical shift (NICS) calculations [9]. However, many problems still remain unresolved such as the contradiction of the large current susceptibility with the high-lying energy for Mg4BC (MgPor-β-4Hy) as compared to other magnesium porphyrins. In 2001, Parusel and Grimme concluded that the experimentally observed large intensity of the Q-band for the hydroporphyrins is due to a relaxation of the near-degeneracy of the four frontier molecular orbitals based on their DFT/MRCI calculations [10]. In 2004, Linnanto and Korppi-Tommola found that the Zindo/S CIS method for the structures of chlorophylls and bacteriochlorophylls optimized by PM5 method is a computationally efficient approach to produce acceptable electronic transition energies as compared to experimental results [11]. In 2006, Petit et al. undertook a systematic study on the excited states of metal free porphyrin, metal free chlorine, and metal free bacteriochlorin using the time dependent density functional theory (TDDFT) method [12]. Up to now, there seems still no report on the theoretical investigation towards understanding the relationship between hydrogenation and electronic absorption spectra as well as hydrogenation and aromaticity of derivatives, to the best of our knowledge.

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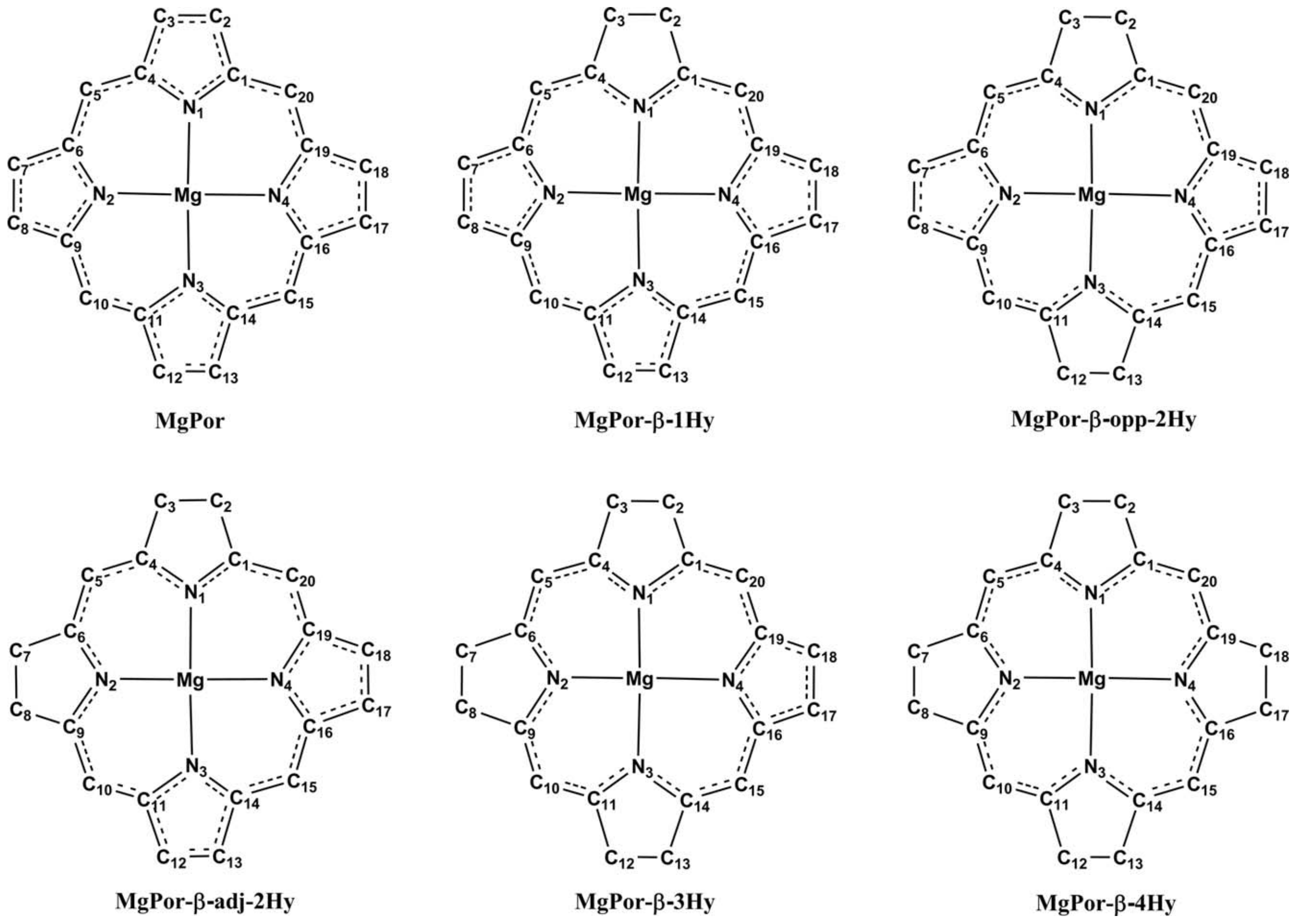
MgPor

MgPor-β-1Hy

MgPor-β-opp-2Hy

MgPor-β-adj-2Hy

MgPor-β-3Hy

MgPor-β-4Hy

Fig. 1. Schematic molecular structures of MgPor, MgPor-β-1Hy, MgPor-β-opp-2Hy, MgPor-β-adj-2Hy, MgPor-β-3Hy, and MgPor-β-4Hy. The atomic labels are used uniformly in this paper.

In the present paper, a series of hydrogenated magnesium porphyrin complexes with different number of β-saturated pyrrolic rings, namely MgPor-β-1Hy, MgPor-β-opp-2Hy, MgPor-β-adj-2Hy, MgPor-β-3Hy, MgPor-β-4Hy, and MgPor for comparison (Fig. 1) were studied using density functional theory (DFT) and TDDFT methods to reveal the effects of the number and position of β-saturated pyrrolic rings on the electronic structures and aromatic properties of hydrogenated magnesium porphyrin derivatives. The results should be helpful for understanding the red-shift of the "orange" peak from chlorophyll *a* to bacteriochlorophyll and aromatic characteristics of metalloporphyrins, and finally for designing and synthesizing novel hydrogenated tetrapyrrole compounds sensitive to longer wavelength of sunlight.

2. Computational details

The geometries of a serious of hydrogenated magnesium porphyrin complexes (Fig. 1) were fully optimized and characterized to be local minima by harmonic vibrational frequency analysis at the B3LYP [13,14]/6-31G* level of theory. The electronic absorption spectra were simulated with TDDFT method at the same level of theory. The reliability of this method is supported by many previous theoretical works on the porphyrin derivatives [12,15–24].

In order to further verify the reliability of our TDDFT computation results, calculation at B3LYP/6-31G(d) and BP86/6-31G(d) levels for chlorophyll *a* and chlorophyll *b* were performed, respectively (Fig. S2, supplementary data).

On the basis of the above optimized geometries, the molecular orbital energies, ^{1}H NMR, magnetic susceptibility ($\Delta\chi$), and NICSs were computed at the B3LYP/6-311+G(d,p) level of theory.

The NICS values were calculated with the GIAO (gauge invariant atomic orbitals) [25] method at points 1 Å above the magnesium atom which sits in the center of 24 atoms composing the porphyrin framework. The two parameters, NICS(1) and NICS(1)*zz*, were recommended as being a better measure of the π electron delocalization as compared with NICS(0) (i.e. at the ring center) [26]. ^{1}H NMR calculation was carried out for the hydrogen atoms for the series of hydrogenated magnesium porphyrin derivatives with reference to TMS. The magnetic susceptibility (χ) values were calculated with the continuous set of gauge transformations (CSGT) method [27]. The anisotropy of magnetic susceptibility $\Delta\chi$ is defined as the difference between the out-of-plane diagonal term of the magnetic susceptibility tensor [$\chi(zz)$] and the average of the in-plane diagonal terms $\{1/2[\chi(xx)+\chi(yy)]\}$ [28].

All calculations were carried out using the Gaussian 03 program [29] on an IBM P690 system housed at Shandong Province High Performance Computing Center.

3. Results and discussion

The molecular structures of MgPor and the whole series of five hydrogenated magnesium porphyrin derivatives designed with different number of β-saturated pyrrolic rings, namely MgPor-β-1Hy, MgPor-β-opp-2Hy, MgPor-β-adj-2Hy, MgPor-β-3Hy, and MgPor-β-4Hy, are shown in Fig. 1. The atomic labels are used uniformly in this paper.