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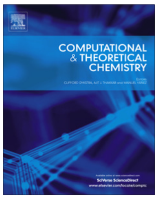

DFT study on deprotonation and protonation of porphyrins: How many protons can the porphyrin core take up?

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ABSTRACT

Deprotonation and protonation are crucial characteristics of porphyrins and porphyrinoids solutions. This report is indicated to investigate all possible deprotonated and protonated species of the porphine ring using DFT. In particular, based on the analysis of the optimized geometries and electronic structures of protonated species, it was confirmed theoretically that aromaticity and stability of the triacid or the tetraacid resulted from further protonation of the porphyrin diacid. Additional hydrogen atoms attached to the inner nitrogen atoms of protonated porphyrins and gave rise to rearrangement of aromatic system involving α-, β-, and meso-carbons. Crowding inner hydrogen atoms attached to the pyrrole nitrogen atoms lead to distortion of porphyrin core. Substituents of porphyrins rendered it to be possible that the final species of the protonation process might be triacid or tetraacid.

1. Introduction

As is well known, two natural chemicals, heme and chlorophyll, which involve the photosynthesis reaction and a variety of biologically vital processes, contain a porphine ring. Consequently, porphyrins and its miscellaneous derivatives have been continuously attracting research interests from multidisciplinary fields, including light harvesting, electron transfer, host–guest chemistry, photodynamic therapy, and design of biological sensors and imaging agents [1,2]. Protonation of macrocycles composed of porphine ring, which is an important phenomena in aqueous solution, influences substantially their structures, configurations, molecular environments, properties and applications [3]. Unfortunately, deprotonation and protonation of porphyrins, involving the interior pyrrole nitrogens bonding to hydrogen, remain some aspects to be realized and manifested explicitly.

Deprotonation means that one or two protons are abstracted from interior pyrrole nitrogen atoms while protonation implies that the interior pyrrole nitrogen atoms take up additional protons. Since the neutral free base of porphyrins has two hydrogen atoms oppositely bonding to two of four interior pyrrole nitrogen atoms in the porphine ring, two hydrogen atoms can be deprotonated sequentially, which is confirmed, as verified by Dong et al. [4], by deprotonation of meso-(p-hydroxyphenyl)porphyrins in DMF + H_2O ($V/V = 1{:}1$) mixture by different concentrated NaOH solution resulting in the appearance of hyperporphyrin spectra.

It is reasonably called monoprotonation or diprotonation that other two imine nitrogen atoms of the porphine ring bond to one or two protons with formation of mono- and di-cations respectively. A neutral water-soluble porphyrin (TCHpH) is protonated in two distinct steps, which is rationalized by a model relating structural changes on the porphyrin macrocycle upon protonation to its basicity [5]. The model is validated by density functional theory (DFT) calculations performed on a planar and non-planar porphyrin. A monoprotonated species of porphyrins has been characterized as having three absorptions in the Q-band region [6,7]. The crystal structures of the octaethylporphyrin and dodecaphenylporphyrin monocations have also been presented [8,9] Recently, spectrophotometric titrations for a full series of para-amino/carbomethoxy/pyridyl-substituted tetraphenylporphyrins provide evidences for a monoprotonated porphyrin, the relative stability of which is proposed to be due to charge delocalization of the first cation and destabilization of the second protonation by the electron-withdrawing substituents [10,11].

In contrast to monoprotonation of porphyrin and its analogues, diprotonation species of porphyrins is well known which is formed as porphyrin diacid in acidic solutions by the free base porphyrin combining with two additional hydrogen atoms on the central nitrogen atom [12,13]. Porphyrin diacids were found to exhibit perturbed photophysical properties compared to their neutral parent compounds, including the substantially lowered quantum

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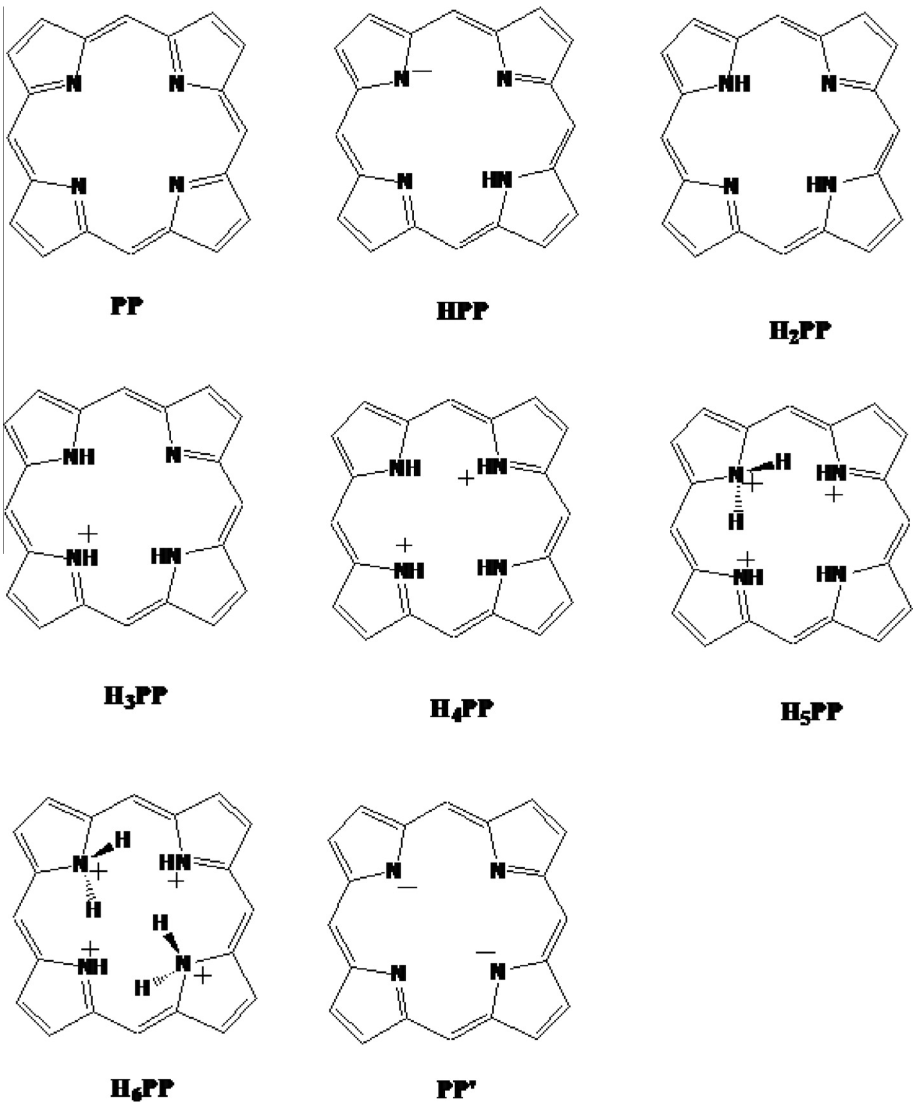
yield of triplet-state formation, altered electronic absorption spectra, increased Stokes-shifts in fluorescence spectra [14–19].

In an attempt to grasp the nature of the protonation of macrocycles, DFT calculations have been employed which have been quite successfully applied to study diverse aspects of porphyrin compounds including molecular geometries, electronic structures, vibrational spectra, etc. [20–24].

The ground-state structure, electronic spectrum and conformational inversion of porphyrin diacid, including OEP (octaethylporphyrin), TPP(meso-tetraphenylporphyrin), TPyP (meso-tetrapyridylporphyrin), OETPP (octaethyltetraphenylpor phyrin), and TCHP (tetracyclohexaporphyrin), have been studied with the density functional theory, which resulted in the most stable structure of porphyrin diacid bearing a saddle-distorted porphyrin ring along with the structures of transition states and intermediates as well as the inversion barriers [25]. Using DFT calculations along with UV–vis and magnetic circular dichrosim spectroscopies, N-confused porphyrin (NCP) and its externally methylated variant were investigated, and then the sites of protonation/deprotonation for tautomeric forms of NCP were determined [26]. Recently, the investigation of the acid-base properties of a series of meso-aryl-substituted N-confused porphyrins (NCPs) in aqueous sodium dodecyl sulfate (SDS) micellar solutions using both spectrophotometric methods and theoretical calculations demonstrated that NCPs are easily protonated and deprotonated compared to the corresponding regular congeners [27].

However, in these studies, there are at least two fundamental questions, whether the porphyrin diacid further bond other hydrogen atoms and which protonation step is energetically beneficial, are not extensively explored, which render us the opportunity to investigate them. It is known that the interior pyrrole nitrogens of the free base of porphyrins can be deprotonated or protonated to afford four possible derivatives, named herein as dianionic-, monoanionic-, monocationic- and dicationic species respectively, with moderately to strongly distorted core conformations [28,29]. In general, further protonation of pyrrole nitrogen is not considered because protonation of pyrrole, as is well known, results in loss of aromaticity of the five-membered heterocycle and is therefore unfavorable. Even though protonation does not occur at nitrogen, however, it does occur at carbon and the protonated pyrrole then adds another molecule like this [30]. Taking into account four pyrrole cycles existed in the porphyrin core and differences of conjugation system of porphyrins from that of annulene, the protonation of protonated pyrrole nitrogen can be



Scheme 1. All possible protonated and deprotonated forms of the porphyrins.