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## **Theoretical Studies on the Structural Change in the *N*-Protonated $\beta$ -Octamethylporphyrin**

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## Theoretical Studies on the Structural Change in the *N*-Protonated $\beta$ -Octamethylporphyrin<sup>#</sup>

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### Abstract

**Motivation.** The structural changes of four pyrrole-rings and various substituting groups of porphyrin derivatives have great influence on the selectivity to molecular aggregation in DNA helix; the aggregate can stabilize the DNA helix and disable telomerase. It not only can develop new anticancer drugs, but also can distinguish G-quadruplexes. Therefore, researchers are showing increasing interest in searching selective porphyrin compounds and understanding the structural change in acidic medium. In this paper, we report a theoretical calculation of  $\beta$ -octamethylporphyrin ( $\beta$ -OMPH<sub>2</sub>) as well as its diacid ( $\beta$ -OMPH<sub>4</sub><sup>2+</sup>) with an attempt to elucidate the changes of the configuration and property in the protonation process. The results calculated by B3LYP/6-1G\* show that although  $\beta$ -OMPH<sub>2</sub> has various conformations, *D*<sub>2h</sub>L configuration is the only stable equilibrium geometry. After protonation, the stable equilibrium configuration of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> presents *D*<sub>2d</sub> symmetry. The configurational change is determined by a molecular intrinsic attribute and the intermolecular interaction is a secondary factor at least. The *D*<sub>4h</sub> configuration of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> guessed by experimenters is a saddle point of multi-order, not a stable equilibrium configuration. In addition, a decrease in *E*<sub>2u</sub> separation occurs concomitantly with an increase of degeneracy between *a*<sub>1u</sub> and *a*<sub>2u</sub>. These will lead to producing shift and strengthening absorbance of B and Q absorption bands.

**Method.** By means of B3LYP method combining Becke's three-parameter hybrid functional method with Lee-Yang-Parr's correlation functional (LYP) and Berny energy gradient method, the target molecules under reasonable symmetry restriction were optimized at 6-31G\* basis set level. All of the stationary points were confirmed by vibrational analysis. In all calculations GAUSSIAN 98 program was used on a P4 computer.

**Results.** The change of the geometry between  $\beta$ -OMPH<sub>2</sub> and  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> is obvious that leads to a series of property changes, especially, the change of FMO leads to a larger change of molecular absorption spectrum.

**Conclusions.** Although  $\beta$ -OMPH<sub>2</sub> has various conformations, *D*<sub>2h</sub>L configuration is the only stable equilibrium geometry. After protonation, the stable equilibrium configuration of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> presents *D*<sub>2d</sub> symmetry. The configurational change is determined by a molecular intrinsic attribute and the intermolecular interaction is a secondary factor at least. The *D*<sub>4h</sub> configuration of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> guessed by experimenters is a saddle point of multi-order, not a stable equilibrium configuration. In the protonation process, along with the averaged bond lengths, the bond charge populations are also averaged generally. Although the changes are opposite with those of bond lengths in general, the exception exists. As expected, the energies of both the LUMOs and HOMOs of

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$\beta$ - $\text{OMPH}_4^{2+}$  are lower than those in their unprotonated form. In addition, a decrease in  $E_{2u}$  separation occurs concomitantly with an increase of degeneracy between  $a_{1u}$  and  $a_{2u}$ . These will lead to producing shift and strengthening absorbance of B and Q absorption bands. After protonation, the vibrational Raman displacements of the  $C_\alpha$ - $C_\beta$  bonds are shifted to higher frequencies as the populations are increased, while those of the  $C_\beta$ - $C_\beta$  bonds are shifted to lower frequencies as the populations are decreased; and the Raman displacements of the  $C_\alpha$ - $C_m$  bonds do not change in general, and those of the  $C_\alpha$ -N bonds of various positions are shifted to higher or lower frequencies with the population changes. With the equivalence of the pyrrole rings, the IR spectrum of  $\beta$ - $\text{OMPH}_4^{2+}$  is simpler than that of  $\beta$ - $\text{OMPH}_2$  because of the higher symmetry of the former species.

**Keywords.**  $\beta$ -Octamethylporphyrin; *N*-protonated diacid; configurational change; B3LYP/6–31G\* method.

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#### Abbreviations and notations

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$\beta$ - $\text{OMPH}_2$ , $\beta$ -octamethylporphyrin	$\beta$ - $\text{OMPH}_4^{2+}$ , diacid of $\beta$ -octamethylporphyrin
FMO, frontier molecular orbital	HOMO, highest occupied molecular orbital
LUMO, lowest unoccupied molecular orbital	TPPH <sub>2</sub> , tetraphenylporphyrin
TPPH <sub>4</sub> <sup>2+</sup> , diacid of tetraphenylporphyrin	

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## 1 INTRODUCTION

The structural changes of four pyrrole-rings and various substituent groups of porphyrin derivatives have great influence on the selectivity to molecular aggregation in DNA helix [1]; the aggregate can stabilize the DNA helix and disable telomerase. It not only can develop new anticancer drugs, but also can distinguish G-quadruplexes. Therefore, researchers are showing increasing interest in searching selective porphyrin compounds and understanding the structural change in acidic medium. In the past several decades, a large number of theoretical researches on the porphyrin have been carried out. In the mid-90s, with the development of computer techniques and theoretical methods, revolutionary breakthrough on the structures has been found, and the theoretical results, which are consistent with experiments, have been obtained [2]. The study [3] shows that the structural changes of porphine in the protonation process are consistent with experiments [4] by using methods mentioned in this text. For the above-mentioned reasons, in this paper we report a theoretical calculation of  $\beta$ -octamethylporphyrin ( $\beta$ - $\text{OMPH}_2$ ) as well as its diacid ( $\beta$ - $\text{OMPH}_4^{2+}$ ) with an attempt to elucidate the effects of the substituted methyls, which are the typical repulsive electron groups, on the changes of the configuration and property in the protonation process.

## 2 COMPUTATIONAL METHODS

In order to investigate the relative change of the configuration in the protonation process, on the basis of other similar theoretical studies [3,5–10], we optimized the target large molecules by using B3LYP/6–31G\* method [11–13], with the Berny gradient technique [14], under reasonable symmetry restriction. The B3LYP/6–31G\* method provides an economical means for calculations of the structures and properties of porphyrin systems; and the calculation under symmetry restriction can aid us in studying the indivisible expression of normal modes with less CPU time [2]. Because of the  $D_{2h}$  symmetry of the porphine core, when a hydrogen atom in each  $\beta$ -substituted

methyls is in the porphine core plane, and others are over and under the plane respectively, the symmetry can be retained. Once the  $\beta$ -substituted methyls deviate from this angle, the symmetry of porphine skeleton can be reduced and the whole molecule symmetry would also be reduced. For *N*-protonated diacid, the free rotation of the  $\beta$ -substituted methyls cannot affect the  $D_{2d}$  symmetry of the porphine core and whole molecule, but in acid solution, because of the existence of rapid exchange of the inner hydrogens with solvent protons, the porphine core has a dynamically averaged  $D_{4h}$  symmetry [15,16]. If a hydrogen atom in each  $\beta$ -substituted methyls is in the porphine core plane, and others are over and under the plane respectively, the whole molecule also has  $D_{4h}$  symmetry. In all calculations GAUSSIAN 98 program [17] was used on a P4 computer.

### 3 RESULTS AND DISCUSSION

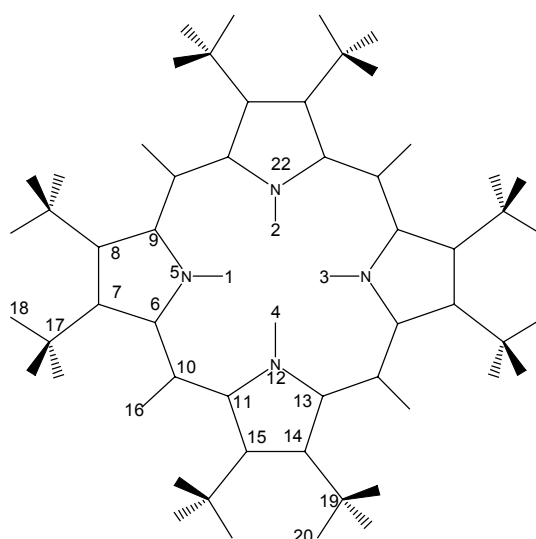


Figure 1. Atomic numbering of the system.

Table 1. The Bond Lengths (nm) of  $\beta$ -OMPH<sub>2</sub> and  $\beta$ -OMPH<sub>4</sub><sup>2+</sup>

Bond Length	OMPH <sub>2</sub> ( <i>D</i> <sub>2h</sub> L)	OMPH <sub>4</sub> <sup>2+</sup> ( <i>D</i> <sub>2d</sub> )	OMPH <sub>4</sub> <sup>2+</sup> ( <i>D</i> <sub>4h</sub> L)	Bond Length	OMPH <sub>2</sub> ( <i>D</i> <sub>2h</sub> L)	OMPH <sub>4</sub> <sup>2+</sup> ( <i>D</i> <sub>2d</sub> )	OMPH <sub>4</sub> <sup>2+</sup> ( <i>D</i> <sub>4h</sub> L)
N <sub>5</sub> -H <sub>1</sub>	0.1015	0.1014	0.0994	C <sub>15</sub> -C <sub>14</sub>	0.1364	0.1392	0.1389
C <sub>6</sub> -N <sub>5</sub>	0.1370	0.1394	0.1379	C <sub>11</sub> -C <sub>10</sub>	0.1400	0.1395	0.13402
C <sub>7</sub> -C <sub>6</sub>	0.1444	0.1435	0.1446	H <sub>16</sub> -C <sub>10</sub>	0.1086	0.1084	0.1085
C <sub>8</sub> -C <sub>7</sub>	0.1381	0.1392	0.1389	C <sub>19</sub> -C <sub>14</sub>	0.1499	0.1496	0.1498
N <sub>12</sub> -C <sub>11</sub>	0.1362	0.1394	0.1379	C <sub>17</sub> -C <sub>7</sub>	0.1500	0.1496	0.1498
C <sub>13</sub> -C <sub>14</sub>	0.1470	0.1435	0.1446	H <sub>20</sub> -C <sub>19</sub>	0.1094	0.1092	0.1091
C <sub>10</sub> -C <sub>6</sub>	0.1370	0.1392	0.1402	H <sub>18</sub> -C <sub>17</sub>	0.1093	0.1092	0.1091

#### 3.1 The Structures of $\beta$ -OMPH<sub>2</sub> and $\beta$ -OMPH<sub>4</sub><sup>2+</sup>

The main axis ( $C_2$ ) of the  $D_{2h}$  configuration of  $\beta$ -OMPH<sub>2</sub> is a line crossing molecular center and perpendicular to the porphine core plane, the two  $C_2$  axes perpendicular to the main axis are two lines crossing the H<sub>1</sub>-H<sub>3</sub> and N<sub>12</sub>-N<sub>22</sub>, respectively; and  $\sigma_h$  is the porphine core plane. In each  $\beta$ -

methyls, when one hydrogen atom is in the porphine core plane, and other two are over and under the plane respectively, then the two  $D_{2h}$  configurations are found:  $D_{2h}H$  and  $D_{2h}L$ . All geometric parameters are given in Tables 1–3 (for the numbering of atoms, see Figure 1). The configurational diagrams are shown in Figure 2.

**Table 2.** The Bond Angles ( $^\circ$ ) of  $\beta$ -OMPH<sub>2</sub> and  $\beta$ -OMPH<sub>4</sub><sup>2+</sup>

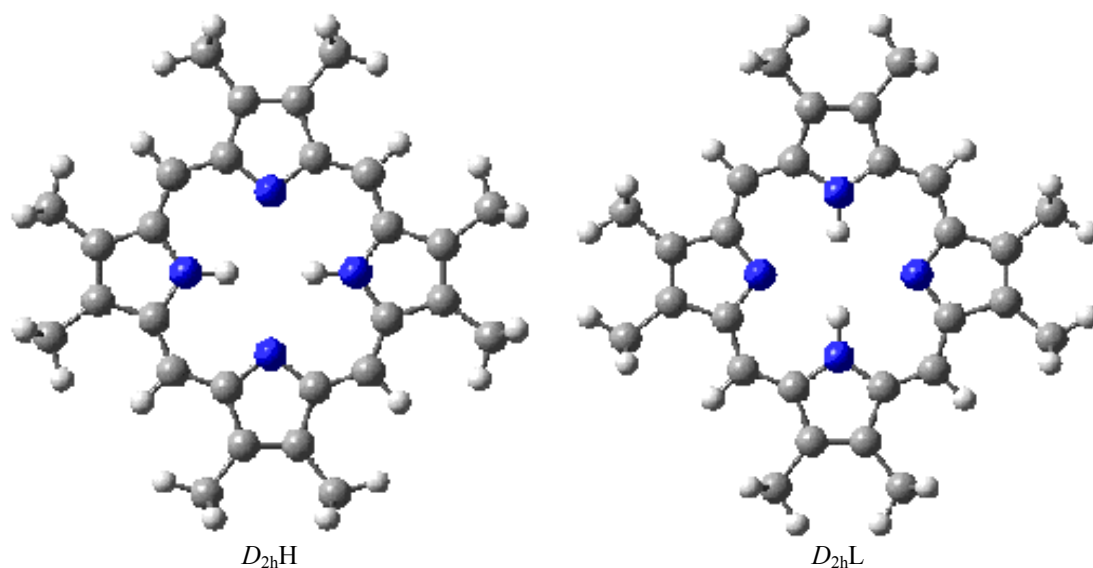
Bond Angle	OMPH <sub>2</sub> ( $D_{2h}L$ )	OMPH <sub>4</sub> <sup>2+</sup> ( $D_{2d}$ )	OMPH <sub>4</sub> <sup>2+</sup> ( $D_{4h}L$ )	Bond Angle	OMPH <sub>2</sub> ( $D_{2h}L$ )	OMPH <sub>4</sub> <sup>2+</sup> ( $D_{2d}$ )	OMPH <sub>4</sub> <sup>2+</sup> ( $D_{4h}L$ )
$\angle C_9N_5H_1$	124.6	119.6	123.7	$\angle C_{13}C_{14}C_{15}$	107.7	107.9	108.0
$\angle C_6C_{10}C_{11}$	127.7	127.9	130.3	$\angle N_5C_6C_{10}$	124.3	125.0	125.9
$\angle C_6N_5C_9$	110.6	108.7	112.3	$\angle N_{12}C_{11}C_{10}$	124.4	125.0	125.9
$\angle C_8C_9N_5$	107.0	107.8	105.6	$\angle H_{16}C_{10}C_6$	116.0	116.5	114.8
$\angle C_7C_8C_9$	107.5	107.7	108.0	$\angle H_{16}C_{10}C_{11}$	116.0	116.5	114.8
$\angle C_{11}N_{12}C_{13}$	105.2	108.7	112.3	$\angle H_{18}C_{17}C_7$	111.3	110.8	111.5
$\angle N_{12}C_{13}C_{14}$	111.5	107.8	105.6	$\angle H_{20}C_{19}C_{14}$	111.3	110.8	111.5

**Table 3.** The Dihedral Angles ( $^\circ$ ) of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> ( $D_{2d}$ )

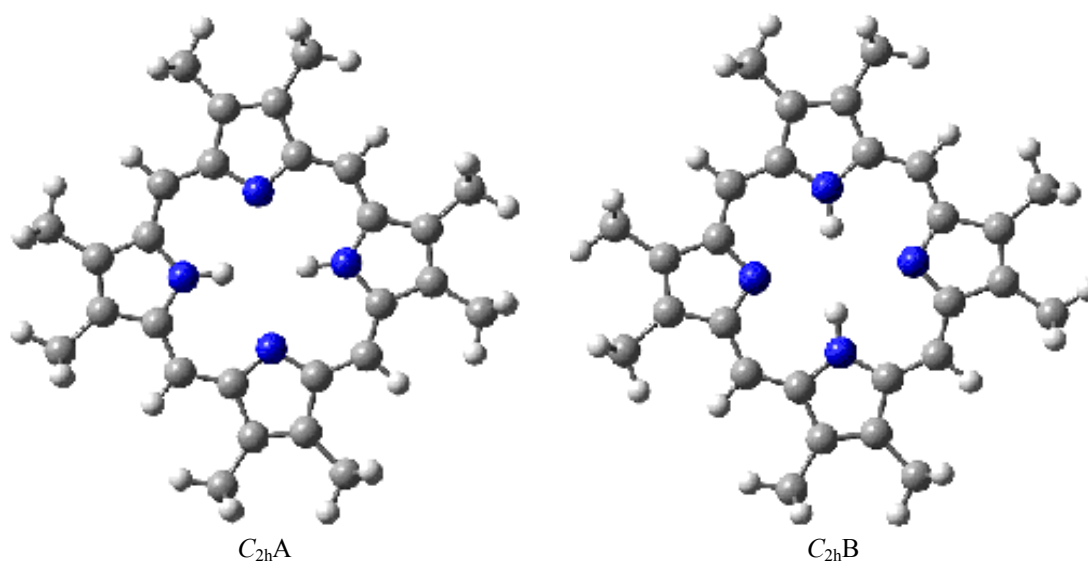
Dihedral Angle	OMPH <sub>4</sub> <sup>2+</sup> ( $D_{2d}$ )	Dihedral Angle	OMPH <sub>4</sub> <sup>2+</sup> ( $D_{2d}$ )
$\angle C_6C_7C_8C_9$	0.0	$\angle H_{16}C_{10}C_6C_7$	8.7
$\angle C_7C_8C_9N_5$	-2.8	$\angle H_{18}C_{17}C_7C_8$	22.8
$\angle C_8C_9N_5H_1$	147.3	$\angle H_{18}C_{17}C_7C_6$	-160.0
$\angle C_6C_{10}C_{11}N_{12}$	9.5	$\angle C_{19}C_{14}C_{13}N_{12}$	174.8
$\angle C_7C_6C_{10}C_{11}$	-171.3		

When the  $\beta$ -methyls in  $\beta$ -OMPH<sub>2</sub> ( $D_{2h}H$ ) are rotated by  $180.0^\circ$ , this configuration is changed into  $D_{2h}L$ . In addition, the distance between the H in  $\sigma_h$  plane and the neighboring *m*-H in  $D_{2h}H$  configuration is about 0.205 nm, while the distance between two neighboring Hs in  $\sigma_h$  plane in  $D_{2h}L$  configuration is about 0.208 nm; so it is clear that because the steric repulsion between the neighboring atoms is small,  $D_{2h}L$  configuration is lower in energy (the difference is 17.5 kJ/mol) than that of  $D_{2h}H$  configuration. Normal-mode analysis of  $D_{2h}H$  yields several imaginary frequencies, which shows that  $D_{2h}H$  is not stable; while the normal-mode analysis of  $D_{2h}L$  confirms it to be the correct equilibrium structure (no imaginary frequency exists).

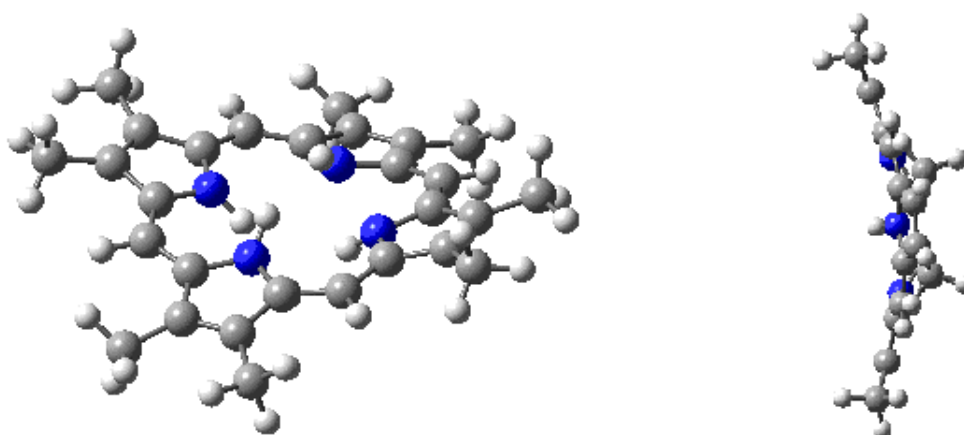
Obviously, considering the different orientations of hydrogen atoms in the plane, also there are two  $C_{2h}$  configurations:  $C_{2h}A$  and  $C_{2h}B$  (the configurational diagrams are shown in Figure 3). And the normal-mode analysis of  $C_{2h}A$  and  $C_{2h}B$  yields several imaginary frequencies, which shows that they are also not stable. In addition, considering of free rotation of the  $\beta$ -methyls, usually  $\sigma_h$  will disappear, and the  $C_{2v}$ ,  $C_2$ ,  $D_2$  configurations of  $\beta$ -OMPH<sub>2</sub> may exist. But the calculated results show that these optimized configurations are similar to the  $D_{2h}L$  configuration. In a word, the  $D_{2h}L$  configuration (the geometric parameters are given in Tables 1–2) is the only stable equilibrium structure.



**Figure 2.** Optimized configuration of  $\beta$ -OMPH<sub>2</sub> ( $D_{2h}H$  and  $D_{2h}L$ ).



**Figure 3.** Optimized configuration of  $\beta$ -OMPH<sub>2</sub> ( $C_{2h}A$  and  $C_{2h}B$ ).



**Figure 4.** Optimized configuration and its side view of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> ( $D_{2d}$ ).

After the protonation, because of the steric effect of the inner neighboring hydrogens, in  $D_{2d}$  configuration, the pyrrole rings flip up and down in alternate directions with the rotation angle being  $9.5^\circ$ , and the dihedral angles of  $\beta$ -methyls and pyrrole ring are  $32.7^\circ$  ( $\angle\text{H}_{20}\text{C}_{19}\text{C}_{14}\text{C}_{13}=147.3$ ). The main axis is unchanged; the two  $C_2$  axes perpendicular to the main axis are diagonals crossing opposite  $C_m$  atoms; the two  $\sigma_d$  planes dividing the angle between the two  $C_2$  axes equally are the planes crossing the main axis and the inner opposite H–H line. The geometric parameters are given in Tables 1–3, and the configurational diagrams with  $D_{2d}$  are presented in Figure 4.

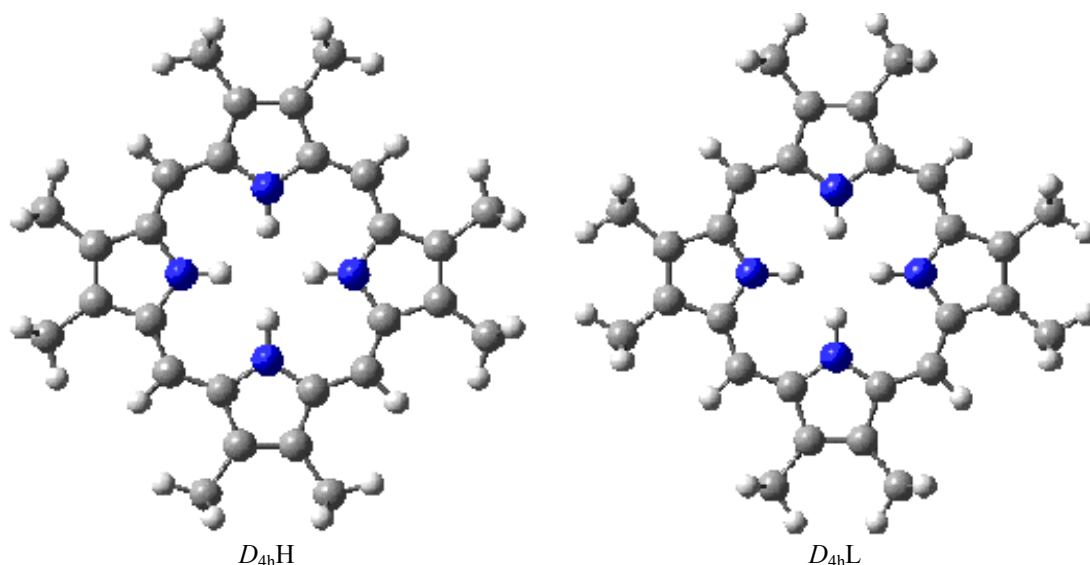


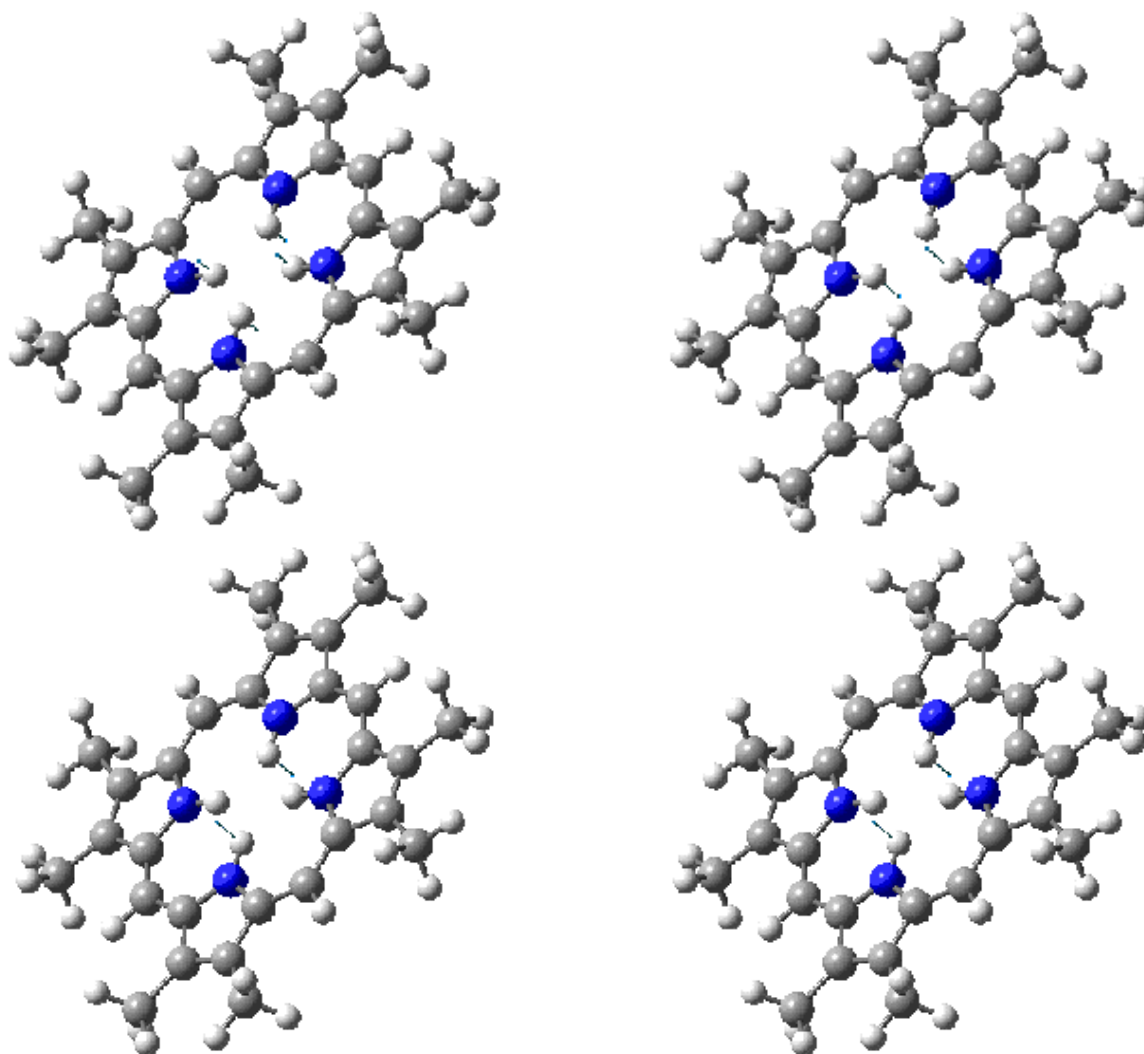
Figure 5. Optimized configuration of  $\beta$ - $\text{OMPH}_4^{2+}$  ( $D_{4hH}$  and  $D_{4hL}$ ).

It is interesting to note that the side views of the configurations show that the molecular skeleton is shaped like a bowl from  $D_{2h}$  to  $D_{2d}$ . These can provide important information concerning molecular aggregation undoubtedly. Generally, the deviation of pyrrole rings from the porphine core plane is unfavorable to molecular aggregation; but  $\beta$ - $\text{OMPH}_4^{2+}$  has a center of symmetry with  $S_4$  axis, and its shape is favorable to orderly aggregation. If there is a rapid exchange between the inner hydrogens and solvent protons, the exchange vibration of the bowl-shaped molecular aggregate is also favorable.

Analyzing their configuration parameters, especially, the changes of  $D_{2d}$  relative to  $D_{2hL}$ , because of the existence of  $S_4$ ,  $C_\alpha$ -N,  $C_\alpha$ - $C_\beta$ ,  $C_\beta$ - $C_\beta$  and  $C_\alpha$ - $C_m$  bonds are averaged. Notably, it changes the parameters of pyrrole rings, especially, on the rings having  $N_{12}$  and  $N_{22}$ .  $C_\alpha$ -N bonds ( $C_6$ - $N_5$  and  $C_{11}$ - $N_{12}$ ) are increased by 2.4 pm and 2.8 pm, and  $C_\beta$ - $C_\beta$  bonds ( $C_8$ - $C_7$  and  $C_{15}$ - $C_{14}$ ) are increased by 1.1 pm and 3.2 pm, while  $C_\alpha$ - $C_\beta$  bonds ( $C_7$ - $C_6$  and  $C_{14}$ - $C_{13}$ ) are reduced by 0.9 pm and 3.5 pm, respectively.  $C_\alpha$ - $C_m$  bonds ( $C_{10}$ - $C_6$  and  $C_{11}$ - $C_{10}$ ) are also increased by 2.2 pm and 0.5 pm. In addition, the bond lengths of C–H in methyls are changed slightly after protonation.

It is obvious that there are two  $D_{4h}$  configurations, which are consistent with two  $D_{2h}$

configurations respectively.  $D_{4h}L$  configuration is lower in energy than that of  $D_{4h}H$  configuration (see Figure 5), and the energy difference is 3.4 kJ/mol, so we only discuss  $D_{4h}L$  configuration. Normal-mode analysis of  $D_{4h}L$  yields four imaginary frequencies (see Figure 6), which is consistent with those calculated results of protonated porphine [5]. So it is expected that  $\beta$ - $OMPH_4^{2+}$  also have three kinds of saddle points of multi-order (two  $C_{2h}$  configurations and one  $C_{4v}$  configuration), as the same as  $PH_4^{2+}$  ( $D_{4h}$ ). In addition, the energy of the dynamic  $D_{4h}L$  configuration of  $\beta$ - $OMPH_4^{2+}$  (for the geometric parameters, see Tables 1–3) is increased by 98.8 kJ/mol over the  $D_{2d}$  configuration. Finally, when the  $S_4$  changes into  $C_4$ , because of the planar restriction of the porphine core, the parameter changes of pyrrole rings are notable. N–H bonds are reduced by 2.0 pm, and  $C_\alpha$ –N bonds are reduced by 1.5 pm while  $C_\alpha$ – $C_\beta$  bonds are increased by 1.1 pm, respectively. The diagonal of porphine ring is increased by 4.3 pm, and the corresponding bond angles are increased and reduced by 0.1~4.1°.



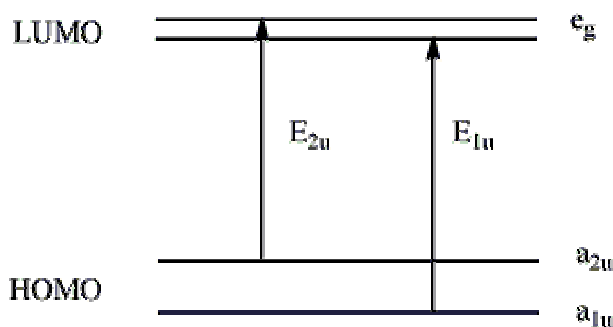
**Figure 6.** The imaginary frequency modes of  $\beta$ - $OMPH_4^{2+}$  ( $D_{4h}L$ ).

### 3.2 The Bond Charge Populations of $\beta$ -OMPH<sub>2</sub> and $\beta$ -OMPH<sub>4</sub><sup>2+</sup>

Seen from the data of GAUSSIAN 98 (see Table 4), it is clear that the bond charge populations are also averaged in protonation process. Although the changes are opposite with those of bond lengths in general, the exception exists, for example, C<sub>6</sub>–N<sub>5</sub> of C <sub>$\alpha$</sub> –N is reduced by 0.0272 *e*, C<sub>8</sub>–C<sub>7</sub> and C<sub>15</sub>–C<sub>14</sub> of C <sub>$\beta$</sub> –C <sub>$\beta$</sub>  are reduced by 0.0140 *e* and 0.0357 *e*, respectively; but N<sub>12</sub>–C<sub>11</sub> of C <sub>$\alpha$</sub> –N is increased by 0.0240*e*, which is same with the increase of bond lengths. The population changes of *D*<sub>4h</sub> relative to *D*<sub>2d</sub> are opposite with the changes of bond lengths, for example, the bond charge populations of C <sub>$\alpha$</sub> –N and C <sub>$\beta$</sub> –C <sub>$\beta$</sub>  are increased by 0.0148 *e* and 0.0038 *e*, respectively while that of C <sub>$\alpha$</sub> –C <sub>$\beta$</sub>  are reduced by 0.0038 *e*. These provide useful insights of changes of the aggregate selectivity.

**Table 4.** The bond charge populations (*e*) of  $\beta$ -OMPH<sub>2</sub> and  $\beta$ -OMPH<sub>4</sub><sup>2+</sup>

bond	OMPH <sub>2</sub>	OMPH <sub>4</sub> <sup>2+</sup>	OMPH <sub>4</sub> <sup>2+</sup>	bond	OMPH <sub>2</sub>	OMPH <sub>4</sub> <sup>2+</sup>	OMPH <sub>4</sub> <sup>2+</sup>
	( <i>D</i> <sub>2h</sub> L)	( <i>D</i> <sub>2d</sub> )	( <i>D</i> <sub>4h</sub> L)		( <i>D</i> <sub>2h</sub> L)	( <i>D</i> <sub>2d</sub> )	( <i>D</i> <sub>4h</sub> L)
N <sub>5</sub> –H <sub>1</sub>	0.2941	0.2912	0.3043	C <sub>15</sub> –C <sub>6</sub>	0.4533	0.4523	0.4519
C <sub>6</sub> –N <sub>5</sub>	0.3743	0.3471	0.3619	C <sub>11</sub> –C <sub>10</sub>	0.4500	0.4523	0.4519
C <sub>7</sub> –C <sub>6</sub>	0.4165	0.4190	0.4152	H <sub>16</sub> –C <sub>10</sub>	0.3831	0.3755	0.3757
C <sub>8</sub> –C <sub>7</sub>	0.5078	0.4938	0.4974	C <sub>17</sub> –C <sub>7</sub>	0.3474	0.3418	0.3415
N <sub>12</sub> –C <sub>11</sub>	0.3231	0.3471	0.3619	C <sub>19</sub> –C <sub>14</sub>	0.3477	0.3418	0.3415
C <sub>13</sub> –C <sub>14</sub>	0.3785	0.4190	0.4152	H <sub>18</sub> –C <sub>17</sub>	0.3659	0.3627	0.3685
C <sub>15</sub> –C <sub>14</sub>	0.5295	0.4938	0.4974	H <sub>20</sub> –C <sub>19</sub>	0.3656	0.3627	0.3685



**Figure 7.** Sketch diagram of frontier orbital energy levels of porphyrins.

### 3.3 The Effects of *N*-Protonated Structure Change on Molecular Spectra

Gouterman's four-orbital model of porphyrin derivatives can be used as a tool for explaining their absorption spectra. The model [18] shows that in an ideal *D*<sub>4h</sub> point group, the HOMO has two near energy levels (*a*<sub>1u</sub> and *a*<sub>2u</sub>), and the LUMO has two degenerate *e*<sub>g</sub> energy levels. They factitiously define two transitions of single excitation (see Figure 7): *E*<sub>1u</sub> (*a*<sub>1u</sub>→*e*<sub>g</sub>) and *E*<sub>2u</sub> (*a*<sub>2u</sub>→*e*<sub>g</sub>). The two transition moments having the same direction interact and produce the B absorption band (near 420 nm), and those having opposite direction interact and produce the Q absorption band (near 514 nm). The frontier molecular orbital (FMO) levels of the various configurations of  $\beta$ -OMPH<sub>2</sub> and  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> are given in Table 5.

**Table 5.** The FMO Levels (eV) of  $\beta$ -OMPH<sub>2</sub> and  $\beta$ -OMPH<sub>4</sub><sup>2+</sup>

FMO	orbital number	OMPH <sub>2</sub> ( <i>D</i> <sub>2h</sub> L)	OMPH <sub>4</sub> <sup>2+</sup> ( <i>D</i> <sub>2d</sub> )	OMPH <sub>4</sub> <sup>2+</sup> ( <i>D</i> <sub>4h</sub> L)
LUMO	115	B <sub>2g</sub> -1.89	E -8.88	E <sub>g</sub> -8.96
	114	B <sub>3g</sub> -1.90	E -8.88	E <sub>g</sub> -8.96
HOMO	113	B <sub>1u</sub> -4.82	B <sub>2</sub> -11.77	A <sub>2u</sub> -11.86
	112	A <sub>u</sub> -4.88	B <sub>1</sub> -11.78	A <sub>1u</sub> -11.95

We can see from Table 5 that the two LUMOs are degenerate while the two HOMOs are closely spaced, which is in accordance with Gouterman's model. In addition, the transition energy level differences also change after protonation (for data see Table 6), mainly the  $E_{2u}$  is reduced. As expected, the quantitative analysis of the changes in the protonation process further reveals that the energies of both the LUMOs and HOMOs of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> are lower than those in their unprotonated form. In addition, a decrease in  $E_{2u}$  separation occurs concomitantly with an increase of degeneracy between  $a_{1u}$  and  $a_{2u}$  (see Table 6). According to Gouterman's theory, these will lead to producing shift and strengthening absorbance of B and Q absorption bands.

**Table 6.** The Separations of Transition Energy Level (eV) of  $\beta$ -OMPH<sub>2</sub> and  $\beta$ -OMPH<sub>4</sub><sup>2+</sup>

$E_u$	OMPH <sub>2</sub> ( <i>D</i> <sub>2h</sub> L)	OMPH <sub>4</sub> <sup>2+</sup> ( <i>D</i> <sub>2d</sub> )	OMPH <sub>4</sub> <sup>2+</sup> ( <i>D</i> <sub>4h</sub> L)
$E_{2u}$	2.93	2.88	2.90
$E_{1u}$	2.98	2.89	2.99

Meanwhile, one can infer the changes of molecular Raman displacement from the changes of the bond charge population on the porphine skeleton in the protonation process. After the protonation, the population changes on the C–C and C–N bonds are notable (see the analysis in Section 3.2) because the bond charge population on the neighboring pyrroles is averaged. Since the population change determines the change in the intervals of vibrational energy levels and further determines their Raman displacements, one can predict that the vibrational Raman displacements of the C<sub>α</sub>–C<sub>β</sub> bonds are shifted to higher frequencies as the populations are increased while those of the C<sub>β</sub>–C<sub>β</sub> bonds are shifted to lower frequencies as the populations are decreased; and the Raman displacements of the C<sub>α</sub>–C<sub>m</sub> bonds do not change in general and those of the C<sub>α</sub>–N bonds of various positions are shifted to higher or lower frequencies with the population changes.

Finally, the infrared spectra of  $\beta$ -octamethylporphyrin also change in the protonation process. After protonation, with the equivalence of the pyrrole rings, the IR spectrum of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> is simpler than that of  $\beta$ -OMPH<sub>2</sub>, due to the higher symmetry of the former species.

### 3.4 The Change in the Orientation of Pyrrole Rings

We found that in the configurational optimization of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> when the pyrrole rings deviate from the porphine core plane, the energy is favorable. In fact, the energy of *D*<sub>2d</sub> configuration of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> is reduced by 98.8 kJ/mol in comparison with the *D*<sub>4h</sub>L configuration. Why there is this large reduction in energy as the molecule deviates from a stable conjugate system? In studying the

crystal structure of tetraphenylporphyrin and its diacid (TPPH<sub>2</sub> and TPPH<sub>4</sub><sup>2+</sup>), Stone *et al.* [19] have proposed that there are two main causes for the non-planar configuration of the gas phase TPPH<sub>4</sub><sup>2+</sup>: one is the steric hindrance of the inner neighboring hydrogens, and the other is their electrostatic interaction. But Scheidt [20] considered that the cause is intermolecular interaction and is not an intrinsic attribute. Although these conclusions are made in studying the crystal structure of tetraphenylporphyrin, we can infer from them that in  $\beta$ -octamethylporphyrin, the phenomenon of pyrroles deviating from the porphine core plane results from intermolecular or intramolecular interactions. The calculations of this paper are done for the gas phase and isolated molecular condition. The preceding analyses show that the configurational change is determined by a molecular intrinsic attribute and the intermolecular interaction is a secondary factor, at least.

Table 7 gives the data of distances between inner hydrogens in  $\beta$ -OMPH<sub>4</sub><sup>2+</sup>. Because the effective Van der Waals diameter of hydrogen is 0.22~0.24 nm [21], the Van der Waals interaction between the opposite hydrogens (H<sub>1</sub>-H<sub>3</sub>, H<sub>2</sub>-H<sub>4</sub>) in a planar porphine skeleton (*D*<sub>4h</sub>L) does not exist but a stronger interaction between the neighboring hydrogens (H<sub>1</sub>-H<sub>2</sub>, H<sub>1</sub>-H<sub>4</sub>, H<sub>3</sub>-H<sub>2</sub>, H<sub>3</sub>-H<sub>4</sub>) exists.

**Table 7.** The distances (nm) of inner hydrogens of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup>

$\beta$ -OMPH <sub>4</sub> <sup>2+</sup>	H <sub>1</sub> -H <sub>3</sub>	H <sub>2</sub> -H <sub>4</sub>	H <sub>1</sub> -H <sub>2</sub>	H <sub>3</sub> -H <sub>2</sub>	H <sub>1</sub> -H <sub>4</sub>	H <sub>3</sub> -H <sub>4</sub>
( <i>D</i> <sub>4h</sub> L)	0.2360	0.2360	0.1660	0.1660	0.1660	0.1660
( <i>D</i> <sub>2d</sub> )	0.2685	0.2685	0.2301	0.2301	0.2301	0.2301

In addition, H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub> and H<sub>4</sub> of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> all have net positive charges (0.3216e (*D*<sub>2d</sub>) and 0.2794e (*D*<sub>4h</sub>L), respectively). As the neighboring hydrogens in a planar molecule are near, the electrostatic interaction is notable. These results are consistent with Stone's guess.

## 4 CONCLUSIONS

Although  $\beta$ -OMPH<sub>2</sub> has various conformations, *D*<sub>2h</sub>L configuration is the only stable equilibrium geometry. After protonation, the stable equilibrium configuration of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> presents *D*<sub>2d</sub> symmetry. The configurational change is determined by a molecular intrinsic attribute and the intermolecular interaction is a secondary factor at least. The *D*<sub>4h</sub> configuration of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> guessed by experimenters is a saddle point of multi-order, not a stable equilibrium configuration. In protonation process, along with the averaged bond lengths, the bond charge populations are also averaged generally. Although the changes are opposite with those of bond lengths in general, the exception exists. As expected, the energies of both the LUMOs and HOMOs of  $\beta$ -OMPH<sub>4</sub><sup>2+</sup> are lower than those in their unprotonated form. In addition, a decrease in *E*<sub>2u</sub> separation occurs concomitantly with an increase of degeneracy between a<sub>1u</sub> and a<sub>2u</sub>. These will

lead to producing shift and strengthening absorbance of B and Q absorption bands. After protonation, the vibrational Raman displacements of the  $C_{\alpha}$ – $C_{\beta}$  bonds are shifted to higher frequencies as the populations are increased, while those of the  $C_{\beta}$ – $C_{\beta}$  bonds are shifted to lower frequencies as the populations are decreased; and the Raman displacements of the  $C_{\alpha}$ – $C_m$  bonds do not change in general, and those of the  $C_{\alpha}$ –N bonds of various positions are shifted to higher or lower frequencies with the population changes. With the equivalence of the pyrrole rings, the IR spectrum of  $\beta$ – $OMPH_4^{2+}$  is simpler than that of  $\beta$ – $OMPH_2$  because of the higher symmetry of the former species.

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