COMPUTATIONAL CHEMISTRY OF THE PORPHYRIN RING SYSTEM

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ABSTRACT

Jaguar 4, Gaussian 98, and gOpenMol were used to study the porphyrin ring system. (Schrödinger 2000, Gaussian 1999, Laaksonen 2000) Jaguar was used to perform computational activities on the porphyrin ring system. This molecule is one of the most prevalent bioinorganic molecules. (Marechal 2000, Siegbahn 1999, Siegbahn 2000) Jaguar performed very well with an effective core potential and a symmetry limitation. An oxygen molecule was added to the iron atom to examine the physical properties of the ring with the bound oxygen. The effects of a cyano group and a carbon monoxide group were also analyzed. The molecular orbitals, density, and electrostatic potential were

Keywords

Porphyrin, heme, Jaguar, Gaussian, quantum chemistry

INTRODUCTION

The porphyrin ring system has long been an interest to bioinorganic chemists because of iron center. This is the functional aspect of the heme group. This interesting system is found in many different proteins in the body. This iron center contributes to the electron chain transport by the oxidation and reduction of the iron center. When the iron is in the +2 oxidation state, it is firmly bound in the ring system. When the iron is in the +3 oxidation state, it is out of the ring as a free ion that is capable of being reduced and bound back into the ring system. This project explored the properties of the ring system and later add bound molecules (carbon monoxide, oxygen, and cyanide) to study the physical properties of the system with the different molecules bound. The project initially started using Gaussian, attempting an ONIOM multi-layer calculation. (Marechal, 2000) The project eventually moved to another computational program, Jaguar 4.0. The whole ring system was geometry optimized using a LAV1S* basis set. The density functional method was recommended by Siegbahn. (Siegbahn, 2000) The density and the electrostatic potential were calculated and displayed. The molecular orbitals were also calculated and displayed using gOpenMol. (Laaksonen, 2000)
METHODS

Hyper Chem

All of the necessary molecules were first built in HyperChem and converted to readable files for Gaussian and Jaguar. (Hypercube, 2000, Gaussian, 1999, Schrödinger, 2000)

Gaussian

A multi-layer ONIOM calculation was attempted with a molecular mechanics calculations on the ring system and a STO-3G basis set on the Fe-N bonds. This was attempted several times, but even with a process with parameters that were similar to ones successful in Jaguar 4.0 (LANL2DZ basis set in Gaussian), it still failed in Gaussian. Unfortunately, our approach in Gaussian was not sophisticated enough to handle a system in which a transition metal was introduced. (Gaussian, 1999) The next step was to move onto another program.

Jaguar 4.0

In Jaguar we did not locate a counterpart to the ONIOM hybrid QM/MM method of Gaussian. (Schrödinger, 2000, Gaussian, 1999) In Jaguar, density functional calculations were chosen instead, Becke 3:P86; this is Perdew’s density functional that has a gradient correction along with Becke’s three parameter (exact Hartree-Fock wavefunction, Slater local exchange functional, and Becke’s 1988 non-local gradient correction). This method was picked for a faster convergence. The system was optimized using a LAV1S* basis set because of the effective core potential, chosen because of the substantial number of electrons in the system. This ECP method only optimized the valence electrons of the iron and a total analytic optimization on the rest of the structure with a STO-3G basis set. 100 iterations was required for the total optimization with an initial guess using ligand field theory. A GVB-DIIS convergence was recommended for faster convergence so that was also used in the calculation. The energy convergence was loosened to 1E-03. An oxygen molecule was added to the porphyrin ring system to study the different physical properties that occurred. It is suspected that iron atom comes out of the plane when it is not bound, but it is in the plane of the ring when oxygen is bound. That question was not answered directly, because in order to calculate the original porphyrin ring, the symmetry had to be restricted. A cyanide group and a carbon monoxide group were added to the iron and calculated. These molecules were calculated and eventually converged to optimized structures. Using the *.in files that were generated after each run, the potential and the density and the molecular orbitals were calculated.
gOpenMol

gOpenMol is able to use the *.out files generated from Jaguar to create visual plots of the electrostatic potential, density, and molecular orbitals. (Laaksonen, 2000) The coordinates were imported from Jaguar and converted to readable files for gOpenMol. The *.plt files were made into readable *.gom files. These were plotted on a contour map with red for the positive wavefunction and blue for the negative wavefunction.

RESULTS AND DISCUSSION

Geometry

Table 1. Iron porphyrin complex, calculated as low spin molecule.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Fe-N</th>
<th>Fe-O</th>
<th>Fe-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Porphyrin</td>
<td>1.956818</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron Porphyrin with oxygen</td>
<td>1.892339</td>
<td>1.80703</td>
<td></td>
</tr>
<tr>
<td>Iron Porphyrin with carbon monoxide</td>
<td>1.968281</td>
<td></td>
<td>3.0168</td>
</tr>
<tr>
<td>Iron Porphyrin with cyanide</td>
<td>2.022941</td>
<td></td>
<td>2.3479</td>
</tr>
<tr>
<td>Iron Porphyrin with carbon monoxide, solvated</td>
<td>2.016842</td>
<td></td>
<td>2.27685</td>
</tr>
<tr>
<td>Iron Porphyrin with cyanide, solvated</td>
<td>2.016807</td>
<td></td>
<td>1.93230</td>
</tr>
</tbody>
</table>

Table 2. Iron porphyrin complex, calculated as low spin molecule.

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>N-Fe-N</th>
<th>Fe-X-L (X=C,O I=N,O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Porphyrin</td>
<td>89.93</td>
<td></td>
</tr>
<tr>
<td>Iron Porphyrin with oxygen</td>
<td>88.93</td>
<td>121.39</td>
</tr>
<tr>
<td>Iron Porphyrin with carbon monoxide</td>
<td>90.00</td>
<td></td>
</tr>
<tr>
<td>Iron Porphyrin with cyanide</td>
<td>89.21</td>
<td></td>
</tr>
<tr>
<td>Iron Porphyrin with carbon monoxide, solvated</td>
<td>89.34</td>
<td>180.00</td>
</tr>
<tr>
<td>Iron Porphyrin with cyanide, solvated</td>
<td>89.68</td>
<td>179.77</td>
</tr>
</tbody>
</table>
Experimentally, iron bound to oxygen is typically about 1.8 Å. An iron to carbon bond is typically 1.8-2.0 Å. This is considerably different than what is represented in Table 1. Next, calculations were carried out for the iron porphyrin complex bound to CO, and the Fe-C bond distance shortened considerably for the solvated molecule in comparison with gas phase.

Iron Porphyrin Molecular Orbitals

Figure 1. Fe porphyrin structure.

Figure 2. Fe porphyrin HOMO.  
Figure 3. Fe porphyrin LUMO.
Molecular Orbitals of Iron Porphyrin with Oxygen Bound

Note: the LUMO is predominantly on the $O_2$ ligand.

Iron Porphyrin with Carbon Monoxide Bound
CONCLUSION

The heme group is one of the most widely studied bioinorganic molecules. It is considerably more complex in its actual environment, but the point of interest to the bioinorganic chemist is the iron center. This is the center for the oxidation and reduction that is needed to perform many biological tasks. Jaguar 4.0 performed very well with an effective core potential. The capability of Jaguar to use an initial guess based on ligand field theory is quite helpful and effective. In the gas phase the carbon monoxide group and the cyanide group tended to come away from the iron that it was supposed to be bound. This was surprising so a solvent calculation was run. Jaguar calculated a shorter Fe-C distance for the solvated molecule than for the isolated gas phase molecule.

Further computational procedures would be needed to explore the bonding of the carbon monoxide, the oxygen, and the cyanide group to understand what is actually going on. This project explored the geometries of the different molecules and the molecular orbitals were viewed in gOpenMol.

LITERATURE CITED

Laaksonen, Leif. 2000. gOpenMol software.
http://www.csc.fi/~laaksone/gopenmol/gopenmol.html

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