



# **PHYSICAL CHEMISTRY 2006**

## *Proceedings*

*of the 8<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry*

September 26-29,  
Belgrade, Serbia

ISBN 86-82139-26-X  
Title: Physical Chemistry 2006. (Proceedings)  
Editors Prof. dr A. Antić-Jovanović  
Published by: The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia  
Publisher: Society of Physical Chemists of Serbia  
For publisher: Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia  
Printed by: "Jovan" Printing and Published Comp;  
250 Copies; Number of Pages: x + 442; Format B5;  
Printing finished in September 2006.  
Text and Layout: Aleksandar Nikolić  
*250 – copy printing*

## STUDY OF C-H... $\pi$ INTERACTIONS WITH PYRROLE AND CHELATE RINGS IN METAL-PORPHYRIN COMPLEXES

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### Abstract

The Cambridge Structural Database (CSD) was screened in order to find and investigate specific C-H... $\pi$  interactions between C-H groups and two types of rings with delocalized  $\pi$ -bonds that exist in porphyrin: pyrrole and six-membered chelate. Statistical analysis of geometrical parameters for interactions in both types of rings was done. In order to determine preferred positions in porphyrinato ring for C-H... $\pi$  interactions fifteen different points distributed over porphyrin ring have been chosen and each of them have been analyzed. Calculations of these interactions by density functional theory (DFT) have been done on three different model systems.

### Introduction

Porphyrin molecule and derivatives of porphyrine possess four pyrrole rings with delocalized  $\pi$ -systems. When porphyrin is coordinated as a tetradentate ligand to a metal, additional four six-membered chelated rings with delocalized  $\pi$ -bonds are formed. In our previous study [1], we have shown that the chelate ring  $\pi$ -systems of the coordinated porphyrin can be involved in C-H... $\pi$  interactions. The Cambridge Structural Database (CSD) was screened in order to find specific C-H... $\pi$  interactions between C-H groups and the  $\pi$ -system of porphyrinato chelate rings in metal complexes. It was found 655 interactions (411 are intermolecular and 244 are intramolecular). Calculations of these interactions by density functional theory (DFT) show energy of the interactions of about 1.5 kcal/mol, and that the strongest interaction occurs when the distance between hydrogen atom and the center of the chelate ring is 2.6 Å. This result is in a good agreement with the distances for intermolecular interactions found in the crystal structures.

The fact that porphyrin possess two different types of rings with delocalized  $\pi$ -bonds, pyrrole and six-membered chelate, prompted us to study and compare C-H... $\pi$  interactions for both of them. In order to determine preferred positions in porphyrinato ring for C-H... $\pi$  interactions we have chosen fifteen different points distributed over porphyrin ring and have analyzed each of them. These fifteen positions include the centroids of five and sixmembered rings, points around the centroids and on the edge of the ring, nitrogen and carbon atoms.

## Results and Discussion

The structures of metal complexes with coordinated derivatives of porphyrin were screened using geometric criteria described briefly below. We searched CSD for structures where the distances between an hydrogen atom and the points of the rings ( $\Omega$ ) were shorter than 3.1 Å, and presenting a C–H... $\Omega$  axis makes narrow cone perpendicular to the ring ( $\alpha > 110^\circ$ ,  $\beta < 6^\circ$ ). The calculations were done using density functional theory (DFT), specifically the PW91, exchange and correlation functional. These calculations were carried out using the Gaussian 98 program. The LANL2DZ basis set was chosen for the nickel atom and 6-31G\*\* basis sets were chosen for the carbon, nitrogen and hydrogen atoms. The bonding energies were calculated as the difference between the energy of the [Ni(por)]–C<sub>2</sub>H<sub>2</sub> system (Figure 1) and the sum of the energies of the [Ni(por)] complex and acetylene. Single point calculations have been done for different H... $\Omega$  distances from 2.2 to 3.0 Å. In order to determine the contribution of electrostatic energy to total energy, the distributed multipole analysis has been used.

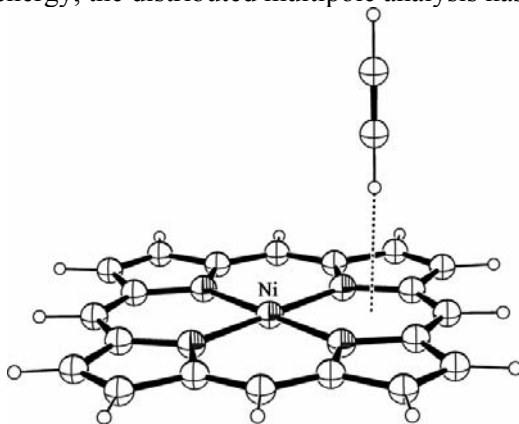
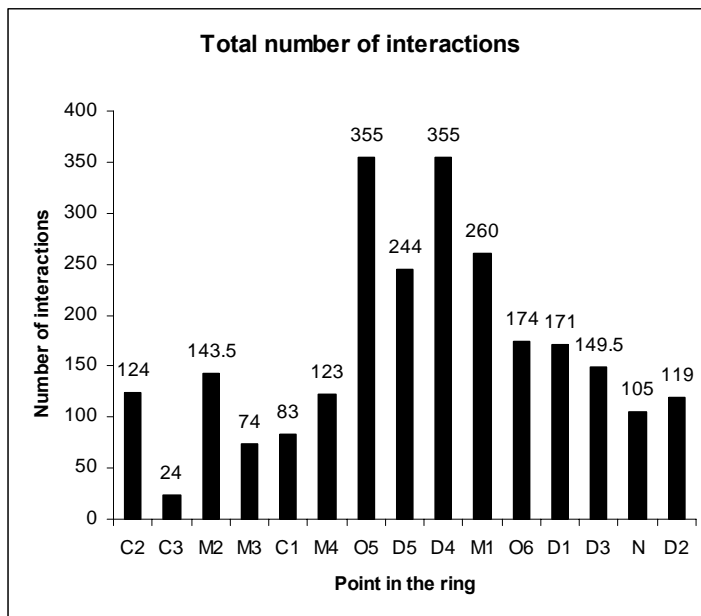


Fig. 1. [Ni(por)]–C<sub>2</sub>H<sub>2</sub> - model system for calculations

In searching crystal structures of transition metal complexes from the CSD for specific intermolecular CH/ $\pi$  interactions, interactions between C–H groups and the  $\pi$ -system of porphyrinato pyrrole and six-membered chelate rings in metal complexes, we found 1746 such interactions. Among them, 1184 are found with five-membered ring and 562 with six-membered ring. Histogram with number of CH/ $\pi$  interactions for every investigated position is shown in Figure 2. The largest number of CH/ $\pi$  interactions have been found for positions O5 and D4, both from the five-membered ring.

However, at the short distances, total number of CH/ $\pi$  interactions is larger for the six-membered ring indicating that the interaction is stronger for six-membered ring. For example, the largest number of interaction for the position O6 (the center of the six-membered ring) is found at the distances between 2.6 and 2.7 Å.



**Fig. 2.** Histogram showing the total number of CH/ $\pi$  interactions for all investigated positions in porphyrinato ring.

The results of DFT calculations show that there is attractive interaction in the investigated range. The differences in interaction energies for different positions are small, and at the minima energies are between -2.83 and -2.05 kcal/mol.

## Conclusion

The crystal structures of transition metal complexes from Cambridge Structural Database (CSD) were screened in order to find CH/ $\pi$  interactions with pyrrole and chelate rings from porphyrine. Statistical analysis show that there is difference in distribution of the geometrical parameters, depending on the presence of the substituents on porphyrinato ring and different positions. In order to investigate the influence of different positions and of side groups of porphyrinato ring, DFT calculations have been done on three different model systems. The results show that the differences in interaction energies for different positions are small, and at the minima interacting energies are between -2.83 and -2.05 kcal/mol.

## References

- [1] V. B. Medaković, M. K. Milčić, G. A. Bogdanović, S. D. Zarić, *Journal of Inorganic Biochemistry*, 2004, **98**, 1867–1873.