ON THE ELECTRONIC STRUCTURE OF SOME TRANSITION METAL PHTHALOCYANINES

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INTRODUCTION

Phthalocyanine (Pc) compounds are the most popular organic semiconductors [1,2,3]. As their electrical properties change considerably by the influence of ambient gases [4,5] phthalocyanines are widely used in gas sensor technology, also because of their high chemical and thermal stability.

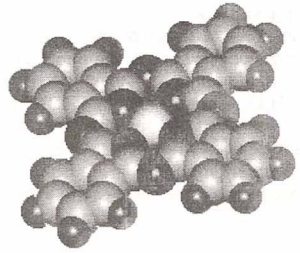
In the field of gas sensors most of the studies concerns an exact electrical characterization of certain materials in the aspect of their industrial application. Although it is well known that the compounds such as CO, CO_2, H_2O, O_2 and NO_2 change the electrical conductivity of phthalocyanines as much as several order of magnitude [6], the nature of the changes still is not obvious. Since both for nano and microelectronics the most important is the band structure of materials used in certain systems we have done some investigations concerning the electronic structure of transition metal ion substituted phthalocyanines. We put special attention on the changes in the electronic structure of investigated phthalocyanines caused by oxygen adsorption.

Quantum chemical computations on molecular level was chosen as an investigation tool. The aim of our study was to find the electronic structure of the iron, nickel and zinc phthalocyanines (each of the elements is characterized by a closed-shell structure). Except examining the electronic structure of isolated Pc molecules we also studied how the presence of oxygen molecule may shift the molecular energy levels in energy scale.

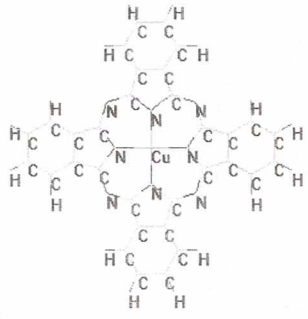
METHOD

Metal-phthalocyanine molecule consists of 57 atoms ($MeC_{32}N_8H_{16}$, Me-metal atom). Metal ion is placed in the middle of the planar molecule inner ring, as is seen in CuPc molecule shown as an example in Figure 1. For the purpose of our study the geometry of the molecule, e.g. bond lengths and bond angles were taken from the literature data [7] and corrected in such a way that symmetry of the investigated isolated molecules was D_{4h}.

All the calculations, which results are reported here, were done with the use of Gaussian 98 program package [8]. First, some calculations were carried out for the isolated MePc molecules (Me=Fe, Ni, Zn) using different methods and basis sets in order to determine what method gives the most accurate results consuming the least computational time. For this purpose the following techniques were applied:
RHF (restricted Hartree-Fock method) with the minimal basis set (STO-3G)
RHF with Lanl2dz basis set (often used for the systems containing transition metal atoms) [9]
B3LYP (a DFT method included local [10] and non-local [11] correlation effects) with the 3-21G basis set used for the calculation of a starting density distribution



a)



b)

Fig.1. Copper phthalocyanine molecule: a perspective (a) and labeled (b) view

In order to compare the advantages and limitations of each method we calculated binding energy (E_b) for iron, nickel and zinc phthalocyanines according to the equation:

$$E_b = -(E_{MePc} - \sum_A E_A)$$

where E_A is the energy of an atom calculated in the same basis set.

Table 1. Binding energy (hartree) calculated with different methods for MePc (Me=Fe, Ni, Zn)

methodsystem	B3LYP/3-21G	RHF/Lanl2Dz	RHF/STO-3G
FePc	4.3445	6.9245	4.9728
NiPc	3.4358	6.7952	3.0303
ZnPc	11.2507	7.2101	9.5811

As a result we determined that the least time-consuming RHF/STO-3G method gives the values comparable to those obtained by using the B3LYP/3-21G one (Table 1.). Therefore we decided to use the RHF method for the purpose of further investigations.
In next step some calculations were provided for the MePc molecules interacting with molecular oxygen. We assumed that the most probable is creation a Pc-O_2 bond through the metal ion orbitals [12] so for the purpose of our study oxygen molecule was placed perpendicularly to Pc plane. Both O-O bond length and distance between O_2 and Pc plane were optimized.

RESULTS AND DISCUSSION

In Figure 1. molecular energy levels (close to HOMO and LUMO) obtained for iron, nickel and zinc Pcs are shown. The most interesting in the aspect of application these materials as gas sensors is to observe how the levels shift in energy scale under the influence of oxygen.

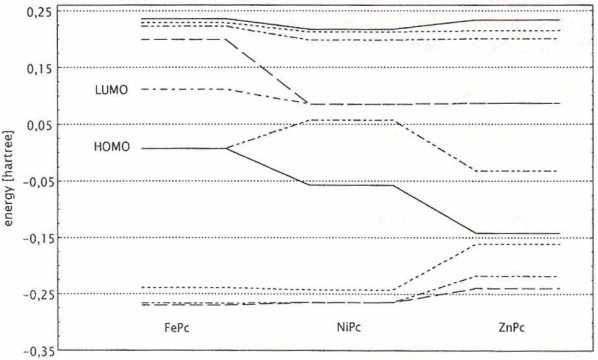


Fig.2. FePc, NiPc and ZnPc molecular orbital energy calculated with RHF method (STO-3G basis set)

Such effect is seen in Figure 3. The presented results were obtained for the optimized O_2 and O-O distances listed in Table 2. It is clear that interaction with the phthalocyanine molecule causes considerable stretching of the oxygen bond, especially in the case of iron and nickel Pcs.

Table 2. Optimized parameters values for the investigated systems

Parameter system	O_2-MePc distance [Å]	O-O bond length [Å]
O_2		1.221
FePc-O_2	1.531	1.570
NiPc-O_2	1.456	1.607
ZnPc-O_2	1.606	1.332

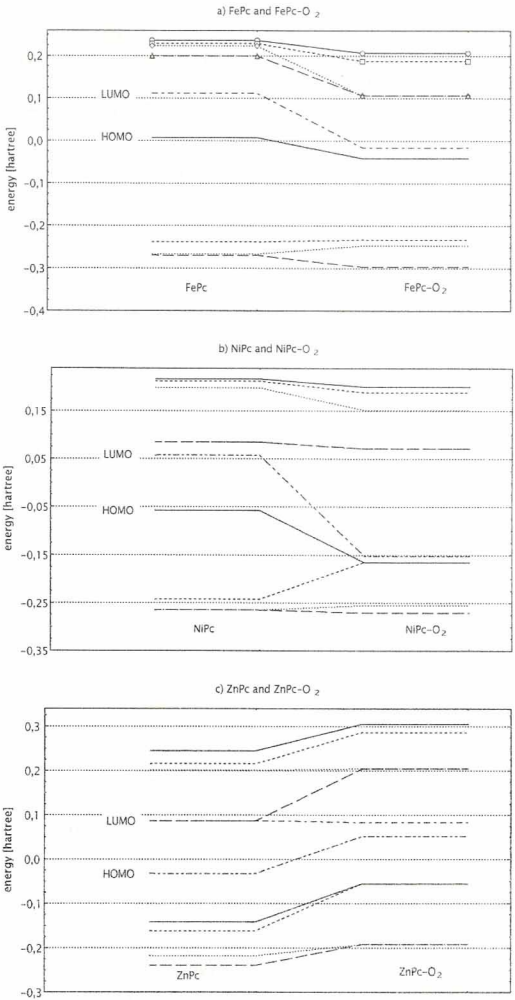


Fig.3. Molecular energy levels shift under the influence of oxygen

In all the cases presented in Figure 3 HOMO-LUMO gap decreases when phthalocyanine molecule interacts with oxygen. The decrease is caused through either lowering the LUMO level (as in the case of FePc and NiPc) or lifting the HOMO level (ZnPc). The exact changes are presented in Table 3.

Table 3. The energy of HOMO and LUMO levels of the investigated systems and the HOMO-LUMO energy gap (ΔE) magnitude

system level	FePc	FePc-O_2	NiPc	NiPc-O_2	ZnPc	ZnPc-O_2
LUMO [hartree]	0.112	-0.016	0.043	-0.153	0.087	0.084
HOMO [hartree]	-0.007	-0.041	-0.047	-0.182	-0.032	0.052
ΔE [hartree]	0.119	0.025	0.090	0.029	0.119	0.032
[eV]	3.24	0.68	2.45	0.79	3.24	0.87

The observed changes of HOMO-LUMO energy gap in all the investigated systems indicate possible transition of iron, nickel and zinc phthalocyanines from insulating materials to doped-like semiconductors when they interacted with oxygen.
In fact, it was found experimentally that adsorption of oxygen on phthalocyanine thin films surface causes creation of the new electronic states in the material's energy gap [13].

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