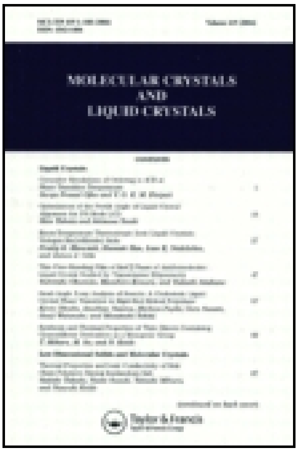

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Piotr Brągiel [a] & Beata Szczepaniak [a]

[a] Institute of Physics, Pedagogical University, Al. Armii Krajowej 13/15, 42-200, Częstochowa, POLAND

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PHTHALOCYANINE AS GAS SENSOR - ELECTRONIC STRUCTURE ON ZDO LEVEL

PIOTR BRĄGIEL AND BEATA SZCZEPANIAK
Institute of Physics, Pedagogical University, Al.Armii Krajowej 13/15, 42-200 Częstochowa, POLAND

Abstract Metal free phthalocyanine (PcH_2) geometry has been fully optimized on MNDO level. For the structure obtained on this way interactions with NO molecule, for which Pc is known to be a very good sensor, have been investigated. It has been found that characteristic for PcH_2 energy gap between the HOMO level and the next below it is absent in the case of PcH_2 - NO system.

INTRODUCTION

Phthalocyanine crystals, due to their electrical, thermoelectrical, photoconducting and optical properties have focused interest since many decades. Phthalocyanines have the advantage of thermal and chemical stability which, in connection with theirs properties, leads to wide field of applications. Phthalocyanines, for instance, are used as dyes in textile industry and in molecular electronic devices.[1,2]
In recent years new interesting features of phthalocyanines have been discovered - they form low-dimensional conducting materials. Doping phthalocyanines with oxidant agents "molecular metals" with conductivity up to 1000 S/cm at room temperature, preserving metallic character even in low temperatures could be obtained.[3] The other interesting property of phthalocyanines is their electrochemical sensivity and the possibility to be used as gas sensors.[4]

In phthalocyanine crystals molecules are stacked in columns in which they lie parallel to one another. As the stacking distance is over 3 Å the interactions between molecules are mainly of van der Waals type, so we can expect that the electronic structure of free molecule is only little influenced by neighbours in crystalline structure. Starting with such a point of view we can expect to find an explanation of electronic structure depending properties on a "molecule level"; also results of interactions of phthalocyanines with gaseous molecules, especially with NO should be possible to see in an electronic structure of a free molecule.

As even metal free phthalocyanine molecule is a large system an ab initio calculations are rather difficult to perform therefore mainly semiempirical methods were applied in PcH_2 studies: Pariser - Parr - Pople[7], EHT[8] and CNDO[9]. Probably the most advanced calculations for PcH_2 are Valence Effective Hamiltonian investigations by Orti and Bredas[10].

The purpose of this paper is, at first, to report the results of H_2Pc geometry optimization on MNDO level which, to our knowledge, has not be done so far, and then compare results for PcH_2 with those obtained for PcH_2 interacting with NO molecule. This last we find to be interacting due to the known fact that PcH_2 is a good sensor for NO.

METHOD

MNDO method, known to be one of the most useful tool for geometry optimization, is a version of NDDO type method, given by Dewar and Thiel[5].

Construction of NDDO type hamiltonian may be briefly described as follows:

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\varepsilon \qquad (1)$$

with **F** the Fock or energy matrix, **S** the overlap matrix,

$$S_{\mu A \nu B} = \delta_{\mu A \nu B} \qquad (2)$$

$$(\mu A \nu B | \lambda C \sigma D) = (\mu A \nu B | \lambda C \sigma D)\delta_{AB}\delta_{CD} \qquad (3)$$

for the NDDO model (A, B, C and D denote different atoms); ε, the diagonal matrix of molecular orbital "energies"; and **C**, a square matrix the columns of which are the molecular orbitals coefficients.

Equation (1) refers to the closed - shell case. Open - shell cases can be treated by the unrestricted Hartree - Fock theory.[6]

Using (2) and (3) conditions to simplification HFR equations and assuming that LCAO basis is formed from s and p type valence orbitals we obtain following equations for matrix elements of HFR operator in the NDDO approximation:

$$F_{\mu_A\mu_A} = H^c_{\mu_A\mu_A} + \sum_{\lambda_A} P_{\lambda_A\lambda_A}[(\mu_A\mu_A|\lambda_A\lambda_A) - \frac{1}{2}(\mu_A\lambda_A|\mu_A\lambda_A)] +$$
$$+ \sum_{B\neq A}\sum_{\lambda_B\sigma_B} P_{\lambda_B\sigma_B}(\mu_A\mu_a|\lambda_B\sigma_B)$$

$$F_{\mu_A\nu_A} = H^c_{\mu_A\nu_A} + \frac{1}{2} P_{\mu_A\nu_A}[3(\mu_A\nu_A|\mu_A\nu_A) - (\mu_A\mu_A|\nu_A\nu_A)] +$$
$$+ \sum_{B\neq A}\sum_{\lambda_B\sigma_B} P_{\lambda_B\sigma_B}(\mu_A\nu_A|\lambda_B\sigma_B) \qquad \text{when } \mu_A \neq \nu_A$$

$$F_{\mu_A\nu_B} = H^c_{\mu_A\nu_B} - \frac{1}{2}\sum_{\lambda_A\sigma_B} P_{\lambda_A\sigma_B}(\mu_A\lambda_A|\nu_B\sigma_B) \qquad \text{when } A \neq B$$

In the above, **P** is the first order density matrix.

Some of errors introduced due to the ZDO approximation can be avoided when we treat some of the integrals as empirical parameters, fitted to experimental data.

CALCULATIONS

Calculations were performed with MOPAC (version 5.0) code, with standard parametrization[11]. Criterion for the optimization was gradient norm little then one. All the interatomic bonds and angles were taken as parameters for optimization. Location of inner hydrogen atoms has been assumed to be on opposite to nitrogen atoms[12] i.e. according "hydrogen bridged" model.

At the second step, calculations have been repeated for system PcH_2 - NO. Several distances (fixed) of NO from the plane of PcH_2 and different orientations have been considered (Figure 1).

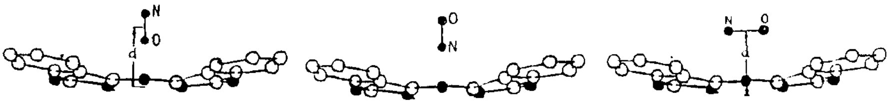

FIGURE 1 Schematic view of the PcH_2 - NO system.

It should be mentioned that this second part of calculations has not been oriented on searching for the optimized geometry of such the system but only on elucidating if it is energetically stable and, if it the case, what are the changes in the electronic structure of PcH_2.

GEOMETRY OPTIMIZATION

Geometry obtained from optimization procedure for PcH_2 is summarized on Figure 2b. On Figure 2a, for comparison averaged experimental results are presented.[13] Both this data are in rather good agreement though almost all bond lengths are overestimated, ca. 0.02 Å. The same effect is observed for pyrrole: experimental bond lengths are 1.417 Å, 1.394 Å and 1.370 Å while this from MNDO geometry are 1.439 Å, 1.394 Å and 1.398 Å respectively.[14,15]

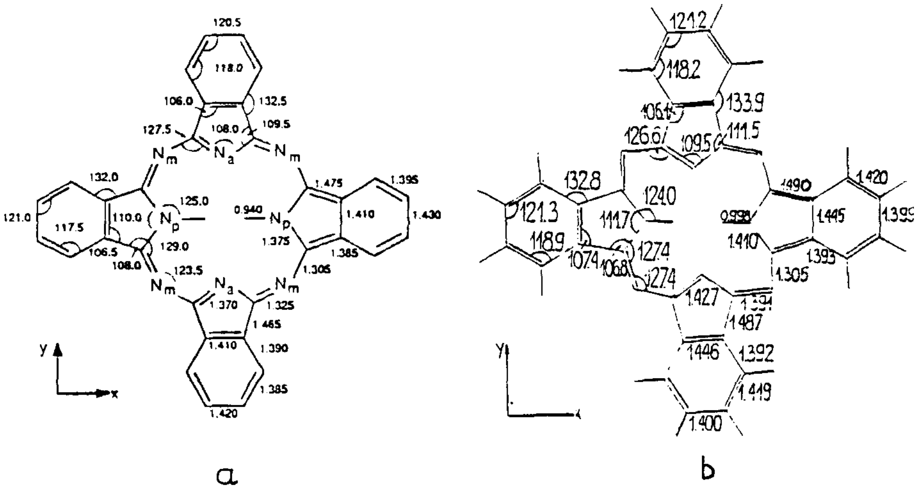

FIGURE 2 PcH_2 molecular geometry: a) experimental data[13], b) MNDO optimized

Our results confirm also deference between isoindole unit in PcH_2 and isoindole molecule[16]. While geometry of pyrrole part in isoindole is almost the same as in a pyrrole molecule in PcH_2 bonds are much longer. Similarly to experimental calculated structure also preserves very small differences between isoindole units containing pyrrole and pyrrole aza nitrogen atoms.

PcH_2 - NO INTERACTION

The PcH_2- NO complex has been analyzed for phthalocyanine - NO distance in the range 0 - 0.7 Å. In the case of NO molecule oriented parallely to Pc plane this "supermolecule" is always stable (in this range) and its heat of formation is unexpectedly increase relative to the value calculated for PcH_2 (256 kcal). The picture is more complicated in the case of molecule oriented perpendiculary to the PcH_2 plane. Both for "O - end" and "N - end" oriented molecule the system in instable on MNDO level when NO molecule is between 0.4 - 0.5 Å from Pc.
Changes of the heat of formation (HF) with NO -Pc distance (d) are ilustrated on figure, 3a -3c.

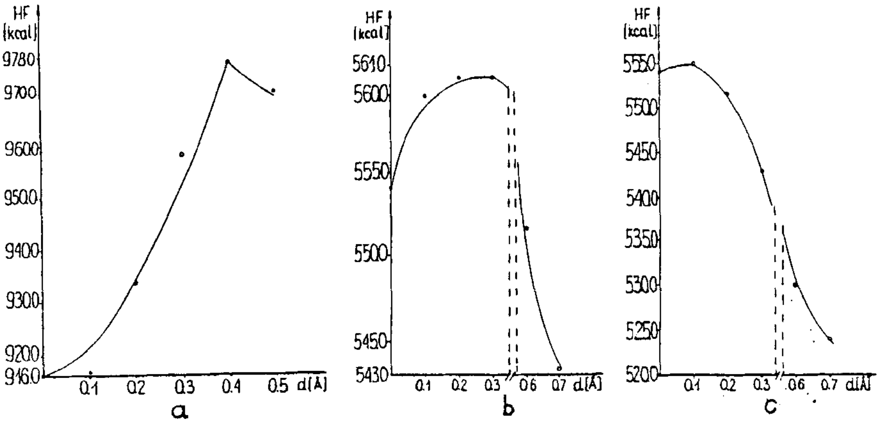

FIGURE 3 Heat of formation changes with Pc - NO distance.
a) NO axis parallel to Pc plane
b) c) NO axis perpendicular to Pc plane, O and N oriented to Pc respectively

PcH_2 electronic structure obtained from this calculations is similar to VEH one reported by Orti and Brédas[10].
The HOMO orbital is laying at -7.03 eV and the followin one 1.88 eV below. This gap, characteristic for PcH_2 is in good accordance with the value of 2.36 in VEH calculations (energies -6.41 eV and -8.77 eV[10]; this values are the energies of centers of bands obtained in colvolution of discrete eigenvalues by Gaussian function). Also some next values are in quite good correlation: -9.46 eV, -10.37 eV, -11.51

eV, -12.51 eV and -9.83 eV, -11.06 eV, -12.99 eV from MNDO and VEH results (MNDO results are given as mean values for very near laying orbitals). The LUMO orbital is at -1.79 eV.

Different situation is in PcH_2 - NO case (values for NO parallel to Pc, 0.4 Å from the plane). The HOMO, partialy filled orbital is laying at -7.803 eV and the next is only -0.22 eV below it. The LUMO orbital is at -1.37 eV and the resulting LUMO - HOMO gap is wider then in PcH_2 case. What is interesting it is gap between the HOMO orbital and the group of orbitals laying below it (1.88 eV in PcH_2).
After broadening of the discrete levels convoluting them with Gaussian functions - typical width at half maximum is 0.7 eV - HOMO and the next below it levels will be in the same, not completly filled, band.
In conclusion: NO molecule is strongly interacting with PcH_2. Resulting from this interaction electronic levels rearengament may lead in solid samples, to conducting states. On the other hand it is seen that Pc sensivity on NO is strictly molecular feature.

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