



International Workshop on Photochemistry of Organic Molecules  
dedicated to the 85-th anniversary of academician G.P. Gurinovich

September 18-20, 2018  
Minsk, BELARUS

## The Use of the DFT PBE/TZVP and INDO/SM Quantum Chemical Methods in the Calculations of Molecules of Porphyrazine and Phthalocyanines

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A modified version of the quantum-chemical method INDO/S, specially designed for the calculations of the excited electronic states of molecules of the class of tetrapyrroles, INDO/Sm, was proposed in paper [1]. The set of parameters of the INDO/Sm method was obtained by the variation of one- and two-electron matrix elements and comparison of calculation results with experimental data for the parent molecule of the series of porphyrins – porphyrin (H<sub>2</sub>P) and its magnesium complex (MgP). The INDO/Sm method was applied to a number of fundamental tetrapyrrole structures, including porphyrazine (tetraazaporphyrin) (H<sub>2</sub>TAP) as well as chlorin and bacteriochlorin. It was used for the consideration of the experimental data on the electronic absorption and luminescence spectra of a number of new compounds of the class of tetrapyrroles, in particular, phenyl-substituted porphyrazines with a chalcogen-containing heterocycle, bacteriochlorophyll analogs, phenyl-substituted tetraazachlorins and their analogues with annelated benzene rings (see [2] and references therein). It was also found that the use of the geometry of molecules obtained as a result of its optimization in the framework of the DFT PBE/TZVP method [3] gives for INDO/Sm spectroscopic data improved agreement with experiment.

The geometrical structure of the porphyrazine (MgTAP, H<sub>2</sub>TAP) and phthalocyanine (MgPc, H<sub>2</sub>Pc) molecules and their octaphenyl derivatives has been calculated by the DFT PBE/TZVP method, and the calculations of the excited electronic states have been carried out by the INDO/Sm method. A detailed analysis of the bond lengths has been performed for the series of compounds MP – MTAP – MTAPPh<sub>8</sub> – MPc – MPcPh<sub>8</sub>, M=Mg, H<sub>2</sub>. It has been shown that the weight of the internal 16-atom macroheterocycle in the electronic structure of MgPc and MgPcPh<sub>8</sub> increases as compared to MgTAP, while the contribution of the 18-atom azacyclopolyene for the free bases H<sub>2</sub>Pc and H<sub>2</sub>PcPh<sub>8</sub> becomes weaker as compared to H<sub>2</sub>TAP.

For the phthalocyanine molecules, the two lowest unoccupied MOs and the highest occupied MO are 70% localized on the internal 16-atom macrocycle; as to the lower-energy filled MOs, there is strong mixing of the  $\pi$  AOs of 16-atom macrocycle with the  $\pi$  MOs of the annelated benzene rings (MgPc and H<sub>2</sub>Pc) and additionally with the  $\pi$  MOs of the phenyl rings (MgPcPh<sub>8</sub> and H<sub>2</sub>PcPh<sub>8</sub>). The Q state energies calculated by the INDO/Sm method agree with the experimental values with an accuracy of 200–400 cm<sup>-1</sup>. It is emphasized that the observed broad absorption spectrum in the region of 27000–37000 cm<sup>-1</sup> (Soret band) of phthalocyanines should be primarily assigned to several  $\pi\pi^*$  transitions for which both local excitation of the 16-atom macrocycle and electron transfer of the type of the 16-atom ring  $\leftrightarrow$  the benzene fragments are characteristic. If only two most intense  $\pi\pi^*$  transitions are taken into account, there is a qualitative agreement between the calculation and experiment, but the calculated energies are overestimated by  $\sim$ 3000 cm<sup>-1</sup>.

### REFERENCES

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