QUANTUM-CHEMICAL ANALYSIS OF ACID-BASE PROPERTIES OF METAL COMPLEXES OF AZAPORPHYRINS BY THE INDO METHOD

K. A. Kon'kov, G. M. Zhigomirov, O. L. Kaliya, V. I. Khleskov, and Yu. V. Ivanov

Calculations of monoprotonated forms of complexes of tetraazaporphyrin with Cu, Ni, Co, Fe were carried out by the LCAO MO method in an INDO valence approximation. The possible positions of the proton with respect to the complex were analyzed. Good agreement was obtained between the theoretical and experimental values of the energies of the long-wave electronic transitions. An explanation has been proposed for the dependence of the basicity of the complex on the nature of the complex forming metal.

In addition to their common application as pigments and dyes, azaporphyrins (AP), and particularly, tetraazaporphyrins (TAP), phthalocyanins (Pc) and their substituted derivatives and structural analogs are widely used as catalysts of chemical and electrochemical processes, materials for quantum electronics and electrophotography, active media for transformation of solar energy, as well as many other current technological fields. It should be noted, however, that the degree of knowledge of the electronic structure of AP, the forms of its existence in solutions, and mutual transformations of their forms gravely lags behind the practical problems encountered.

One of the most important aspects in AP chemistry is their acid-base properties, since strong acids are often important components on the compositions in technical applications of AP. However, in the treatment of the manifestation of these properties, there are contradictory points of view that require theoretical approbation. According to one hypothesis (the postulates of which are most fully covered in [1]), the metallocomplexes of AP are weak organic bases and are once protonated even in concentrated solutions of strong acids at one of the nitrogen meso-atoms. The long-wave Q-band in the absorption spectrum of sulfuric acid solutions of AP, resembling in form a similar band in organic solvents, but shifted by more than 100 nm with respect to it, is in particular ascribed to this monoprotonated form. The authors of this hypothesis recently modified it by taking the position that the remaining meso-atoms of nitrogen are bound in this form with the acid molecules by stable hydrogen bonds [2].
Fig. 1. Possible positions of the proton with respect to pyridine in the PyH⁺ system.

Fig. 2. Diagram of formation of the Cu...H⁺ "bond": position of 3d-AO of metals relative to MO including an ls-AO of a proton.

An alternate point of view (presented in [3, 4]) assumes a successive (with increase in the concentration of the acid) protonation of the four nitrogen meso-atoms. Thus, a two-band absorption spectrum in the visible region, shifted by 20-30 nm bathochromically with respect to the Q-band in the spectra of nonprotonated MTAP and MPC, is ascribed to the monoprotonated form.

In the present work, an attempt has been made to quantum-chemically calculate the monoprotonated forms of MTAP by the intermediate neglect of differential overlap (INDO) method in order to evaluate the spectral effects of protonation. Moreover, it was of interest to follow as far as possible the influence of the central metal atom on the basicity series of AP, in which, according to the data in [3, 4], the copper complexes separate out.

Such calculations have not been carried out up to the present time. The results of the available quantum-chemical calculations of the starting nonprotonated forms [5-7] do not give unequivocal answers to the problems related to the properties of the ionic forms of AP. Thus, the position and characters of the MO responsible for intense π → π* transitions, are not sufficient to explain the expected changes in the absorption spectra, while the calculated charges on the donor centers, which are more dependent on the specific features of the method used than on the structure do not correlate with the experimentally known tendencies of changes in the acid-base properties.

The greatest difficulties in the quantum-chemical analysis of the protonated forms (PF) of TAP are encountered attempting to correctly assign the atom coordinates. To carry out the optimization of the geometry of such large molecules is far too great labor consuming task. A simplification has been proposed with respect to the rigidity of the initial macroring framework, and only the position of the proton with respect to it was varied.

Earlier attempts to describe the action of protons on the one-electronic MO energies within the perturbation theory showed that the protonation qualitatively describes the observed features in the absorption spectra [9]. However at the valence distance (\(r_{\text{N-H⁺}} = 1.03 \AA\)), the effect was found to be too strong, since the calculation method used did not take into account the changes in the electronic structure of TAP. For a more adequate description of the experiment, it was necessary to resort to direct quantum chemical calculations of PF. Individual results obtained within the scope of the iterative extended Huckel method (IEHM) program have already been published in [8, 9].

To determine the position of the proton with respect to the bridging nitrogen atom, several additional investigations have been undertaken for the molecule of pyridine (Py), which is a good model for the TAP fragment, since it has a similar geometry. Because of its relatively small size, it is possible to study this problem in very great detail. To clarify the character of the pyridine-proton bond, we used the CNDO/BW (complete neglect of differential overlap/Boyd-Whitehead) [10] and INDO/C methods [11].