CNDO/2 and Tamm-Dancoff methods for electronic structure evaluation of aluminum porphyrins involved in photodynamic therapy

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The porphyrins are known as ideal singlet oxygen sensitizers, being recognized as most efficient drugs in photodynamic therapy of cancer [1,2]. Metallo-substituted porphyrins yielded promising results when used as photosensitisers in photodynamic therapy (PDT). The addition of a central diamagnetic metal ion such as aluminium or zinc to the core structure of porphyrins changes their photophysical properties by enhancing singlet oxygen production and longer triplet states, while sulphonation increases the solubility of the molecules, increases their antitumoral properties and decreases the tendency of the compounds to aggregate, consequently improving their photosensitising efficacy [3].

In this paper we initiate a study on the mechanistic aspects involved in photochemical processes (Jablonski diagram) for aluminato-porphyrins (Al(III) X TPP) with different axial ligands (X= C2H5, C4H9, C8H17, C12H25).

Calculations were performed by means of semi-empirical CNDO / 2 electronic structures, evaluating the influence of the electronic structure (axial ligand) on the photochemical reactivity of aluminato-porphyrins (constant of photosensibilization reaction rate) by evaluating the deactivation energies, the direct and indirect mixtures and the states involved in electronic transitions. The calculations were performed for the equilibrium geometry of aluminato-porphyrins in the excited state electron, the Tamm-Dancoff approximation approximation, highlighting a radical dissociation of the porphyrin-ligand fragments during photochemical processes. Some correlations between the electronic structure, energy levels and photodynamic activity of these sensitizers, are discussed, too.

1. ION R.M., The use of phthalocyanines and related complexes in photodynamic therapy, in: Photosensitizers in Medicine, Environment, and Security, Springer, Nyokong, Tebello; Ahsen, Vefa (Eds.), 1st Edition., 2012, pp. 315-351
2. ION R.M., New trends in photodynamic therapy-review, *in* Aspects of. Photodynamic medicine Biomedicine Engineering Acta, 3/2008, pp.123-159,. H.Podbielska, A.Sieron, W.Strek, (Eds.), Wroclaw, Poland, 2008
3. MATEI C., TAMPA M., ION R.M., NEAGU M., CONSTANTIN C. – Photodynamic properties of aluminium sulphonated phthalocyanines in human dysplazic oral keratinocytes experimental model - Digest Journal of Nanomaterials and Biostructures, 7(4), October -December 2012, p. 1535-1547