INTRODUCTION

Phthalocyanines (PcH₂) are used as photosensitizers, dyes, pigments, fluorescent and electroactive molecules for biomedical and industrial applications. Breley et al. [1] synthesized a novel dимethyl amino phenyl substituted phthalocyanine (dmaphPcH₂) and its Ag(І) complex ([dmaphPcAg]⁺, see Fig. 1) used as a light-absorbing photomultiplier for free-radical and cationic polymerizations.

Figure 1. Structure of [dmaphPcAg]⁺ [1]

Irradiation of the [dmaphPcAg]⁺ solution led to the reduction of Ag(І) to Ag(I) and simultaneously generated the nitrogen-centered radical. In the next step, Ag nanoparticles and aromatic carbon-centered radicals were formed. The proposed photoinitiation mechanisms under light irradiation suppose the existence of [dmaphPc]⁺, Ag⁺ and [dmaphPcAg]²⁻ entities, q = -1, 0 or -1. DFT calculations indicate a D₂ → D₄ symmetry descent due to the Jahn-Teller effect in Ag complexes. The intermediate deprotonated [dmaphPc]⁺ species, q = -2 → 0, are formed during the above redox processes. Our study deals with their DFT study and group-theoretical analysis from the point of view of the Pseudo-Jahn-Teller (PJT) effect in terms of the epimeric principle method [2, 3] with the aim to shed more light on the processes in the above systems. Our study is restricted to the symmetry descent from the highest possible D₄ₐ structures to the stable structures of its maximal symmetry subgroup due to a great number of possible conformations of dimethyl amino phenyl groups.

METHOD

Standard B3LYP [4] geometry optimization with Grimme’s GD3 dispersion correction [5] of [dmaphPcH₂], q = -2 to 0, (single or doublet) ground spin states using the cc-pVDZ basis sets [6] was performed within D₄ₐ and lower symmetry groups. The optimized structures were checked on imaginary vibrations by vibrational analysis. The excited-states energies with the corresponding electron transitions were evaluated using the time-dependent DFT method [7]. All calculations were performed using the Gaussian16 [8] program package.

THEORETICAL BACKGROUND

The epimeric-principle method for pseudodegenerate states [2, 3] is based on the Jahn-Teller active distortion coordinate q of Representation for pseudodegenerate electron states Ψ₁ and Ψ₂ of Γ₁ and Γ₂ representations, respectively, within the parent symmetry group G. A is the non-translationally symmetric part of the symmetrized direct product (Γ₁ ⊕ Γ₂) which corresponds to a non-vanishing value of <Ψ₁ | q | Ψ₂> integrals where q denotes Hamiltonian. According to the epimeric principle, the extrema of a JT energy surface correspond to the kernel KG(G, A) or epimeric E(G, A) subgroups of the parent group G. Kernels contain symmetry operations that leave the A representation invariant, whereas epimeric leaves invariant only some components of the degenerate A representation. The energy difference between the high-symmetry unstable and low-symmetry (stable) structures of the same compound is denoted as the Jahn-Teller stabilization energy EJT.

RESULTS

Table 1. Ground state Γ₂, DFT energy E_DFT representations Ω repay corresponding wavefunctions ψ repay kernels and epimeric kernels of imaginary vibrations in optimized [dmaphPc]⁺ geometries of various groups G.

Table 2. Representations Γ₂ and excitation energies Eexc of low excited electron states in optimized [dmaphPc]⁺ geometries of various symmetry groups.

CONCLUSIONS

PJT symmetry descent can proceed via various symmetry descent paths in multiple steps

PJT symmetry descent paths (PJT interactions in are parentheses):

Table 3. Excitation energies Eexc of low excited electron states in optimized [dmaphPc]⁺ geometries of various symmetry groups.

REFERENCES: