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Theoretical studies of zinc phthalocyanine monomer, dimer and trimer forms

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ABSTRACT

A theoretical study of the electronic structure of zinc phthalocyanine (ZnPc) ground state was carried out using ab initio and DFT methods. The DFT and MP2 methods indicated a D_{4h} structure, while HF predicted a slightly distorted geometry. The DFT infrared spectra with the corrected wave number values presented good agreement with experiment. The solvation influence on the geometrical parameters, atomic charges and HOMO–LUMO energies was estimated with the use of PCM method and DMSO as solvent. The presence of solvent did not alter these parameters, but affected the orbital energies. The aggregation phenomena were studied with ZnPc dimer and trimer structures. The previously unknown ZnPc dimer infrared spectrum was obtained and compared to the one from monomer. The dimer and trimer stabilization energies are indicative that the formation of stacked structures with several ZnPc is a favorable process.

1. Introduction

Metal-phthalocyanines form a class of aromatic compounds traditionally used as dyes due to their intense absorption in the visible region. Recently, a new series of applications have been discovered, leading to their use in different areas: photodynamic therapy (PDT) [1–4], corrosion inhibitors [5], antimycotic materials [6], solar cell functional materials [7,8], non-linear optical limiting devices [9–15], laser printers and materials for optical storage [16–19], electro-optics [20], electro-catalysts [21], sensors [22,23], displays [24] and others applications. Zinc phthalocyanine (ZnPc) has been extensively studied due to the fact that the d^{10} configuration of the central Zn^{2+} ion results in optical spectra which is less complicated than others transition-metal phthalocyanines.

The first X-ray study of ZnPc was performed by Robertson [25,26]. A distorted structure with zinc atom located at 0.28 Å above the molecular plane was obtained by Mihill et al. [27] in an electron diffraction experiment in gaseous phase. With the same technique, in a more recent experiment, Ruan et al. obtained a planar geometry [28]. A supersonic jet laser induced fluorescence study also indicated that ZnPc molecule presents a planar structure [29]. The infrared spectra of ZnPc and other phthalocyanines, obtained with FTIR, were investigated by Seoudi et al. [30] and Tackley et al. [31]. Tackley et al. studied the ZnPc molecule using Raman scattering technique [32].

The ZnPc ground state has been studied theoretically by several groups. Piet et al. [33] estimated ionization potentials using semi-empirical AM1 and PM3 methods. Energy minimized structures were calculated using AM1 [34], MNDO [35] and PM3 [36]. Gantchev et al. [37] performed AM1 computations on ground and excited states, and applied the MM solvation technique to estimate the solvent reorganization energies. Ding et al. [36] determined the structure and vibrational spectrum of ZnPc using PM3 method. DFT method has been used in many studies on ZnPc properties [31,32,38–40]. Liao and Scheiner [38] studied the electronic structure and bonding of several metal phthalocyanines and some of their ions. Nguyen and Pachter [39], in a B3LYP/6-31G(d) calculation, predicted the structure of zinc porphyrins and phthalocyanine ground state. The geometry of the ground state was also determined by Ricciardi et al. [40]. Tackley et al. [31,32] predicted a non-planar ZnPc structure, in a DFT calculation, and obtained the IR and Raman spectra to compare with the experimental ones.

As other large planar molecules, phthalocyanines may form stacked aggregates in many solvents [37,41–43], resulting in a very different photochemical and photophysical behavior in comparison to the isolated molecule or in a very diluted solution [44]. In photodynamic therapy, phthalocyanine dimers appear to be much less active as sensitizers than their monomers [45]. These dimers are normally found to be non-fluorescent [46,47], and works have being done to develop materials with fluorescence properties [43,48]. A review on phthalocyanine dimers, trimers and oligomers properties can be found in the work of Kobayashi [49].

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In this article, we present a study on the ZnPc ground state properties. The geometry was evaluated using HF, DFT and MP2 methods, with and without solvent (DMSO) influence. The monomer infrared spectrum was simulated and compared to the experimental one. The ZnPc aggregation was studied with the optimization of the dimer and trimer structures. The infrared spectrum of the ZnPc dimer was obtained and compared to the one from monomer.

2. Theoretical approach

The ZnPc was optimized using Hartree–Fock (HF) method [50,51], Second Order Møller–Plesset Perturbation Theory (MP2) [52] and Density Functional Theory (DFT) [53–55]. In DFT calculation, the B3LYP hybrid functional, which includes the non-local exchange term with three parameters of Becke and the correlation term of Lee–Yang–Parr, was used [56,57].

The basis set employed for the study of a single ZnPc molecule was 6-31G (d) [58], resulting in a total of 626 functions (1288 primitives). The Hessian matrix was calculated for the optimized structures obtained with HF and DFT, in order to verify the nature of the stationary state, that is, if it corresponds to a minimum, transition state or higher order saddle point.

The Polarizable Continuum Model (PCM) [59–61] was used to evaluate solvent effects on ZnPc properties. In this model, the solvent is represented as a structureless material involving each solute atom with small spheres. The continuum is characterized by its dielectric constant as well as other parameters. In all PCM calculations, dimethylsulfoxide (DMSO) was considered as solvent. The ZnPc solvated structure was optimized with HF and DFT methods, whereas with MP2 only a single point calculation was carried out with the optimized geometry without solvent.

To study the aggregation process, the optimization of ZnPc dimer and trimer was done with DFT/B3LYP method. For the dimer, the optimization was made with 6-31G* basis set, generating 1252 functions (2576 primitives), but for the vibrational spectra calculation the structure was re-optimized with a smaller basis: 6-31G(d) for zinc and 6-31G for the remaining atoms. For the ZnPc trimer, the basis set used was LanL2MB, generating a total of 675 functions (2061 primitives).

All calculations were made using the Gaussian03 [62] program and the computational resources from Photochemistry Laboratory (LAFOT).

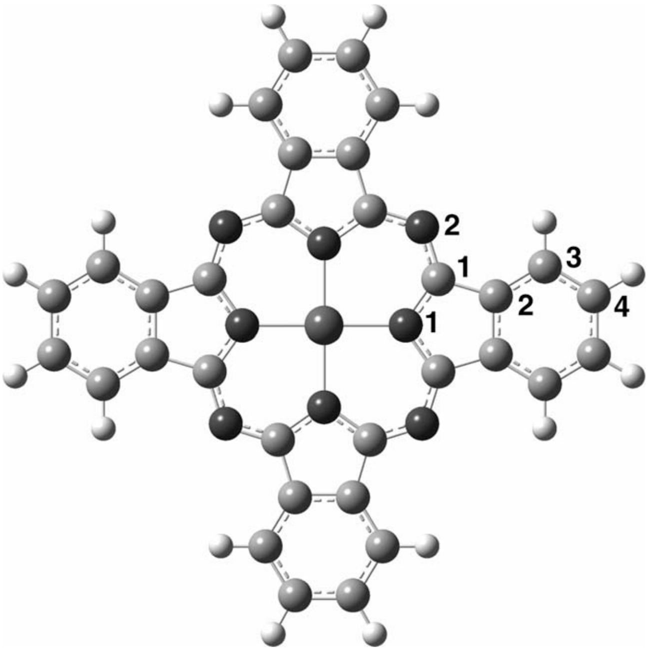

Fig. 1. Molecular structure of zinc phthlalocyanine.

3. Results and discussion

The ZnPc molecule is highly symmetrical, belonging to D_{4h} point group. The electronic configuration of the ground state ($(1)^1A_{1g}$) obtained with B3LYP/6-31G(d) calculation is $\ldots 14(b_{2g})^2\ 2(b_{1u})^2\ 5(e_g)^2\ 6(a_{2u})^2\ 6(e_g)^2\ 3(b_{2u})^2\ 16(b_{1g})^2\ 2(a_{1u})^2$. The ZnPc molecular structure is illustrated in Fig. 1.

In all calculations, ZnPc molecule was optimized to a highly symmetric planar structure (D_{4h}). Vibrational wave numbers calculations were made with HF and DFT methods in order to evaluate the nature of the stationary state. With HF, the molecule presented two imaginary wave numbers related to degenerated mode E_u (881i cm^{-1}). With some changes in the geometric parameters, with a consequent symmetry reduction, a C_{2v} structure was found, with geometry very close to D_{4h}, and corresponding to a species located in a minimum on the potential energy surface. A small energy difference (4.53 kJ/mol) was esti-

Table 1
ZnPc geometric parameters obtained with HF, DFT and MP2 methodologies, compared with experimental data. Distances are given in Angstrom (Å) and angles in degrees (°).

Geometric parameter	HF	B3LYP	MP2	HF PCM	B3LYP PCM	Exp.[a]	Exp.[b]	Theor.[c]	Theor.[d]	Theor.[e]
Zn–N1	1.991	1.992	1.987	2.001	2.001	1.980	1.954	2.012	2.006	1.984
N1–C1	1.350	1.373	1.376	1.347	1.370	1.369	1.374	1.367	1.377	1.371
C1–N2	1.316	1.330	1.337	1.319	1.333	1.331	–	1.334	1.335	1.324
C1–C2	1.459	1.461	1.458	1.462	1.464	1.455	1.420	1.464	1.463	1.451
C2–C3	1.390	1.395	1.396	1.391	1.396	1.393	1.370	1.396	1.397	1.386
C3–C4	1.380	1.395	1.396	1.381	1.396	1.391	1.369	1.397	1.399	1.387
C2–C2	1.393	1.410	1.410	1.395	1.412	1.400	1.550	1.414	1.415	1.405
C4–C4	1.402	1.408	1.409	1.403	1.408	1.396	1.383	1.408	1.410	1.399
C1–N2–C1	125.1	124.4	123.4	125.4	124.6	123.5	125.6	–	124.5	124.2
C1–N1–C1	110.5	109.5	109.0	110.8	109.7	109.1	106.9	110.0	109.9	109.1
C2–C1–N1	108.4	108.7	108.9	108.3	108.7	108.8	113.0	108.3	108.4	108.8
C2–C2–C1	106.4	106.5	106.6	106.3	106.4	106.6	103.5	–	106.7	106.6
C2–C3–C4	117.6	117.8	117.4	117.7	117.9	117.3	121.6	–	117.9	117.9
C3–C4–C4	121.2	121.2	121.3	121.2	121.1	121.5	–	–	121.1	121.1

[a] Ref. [64].
[b] Ref. [28].
[c] Ref. [38].
[d] Ref. [40].
[e] Ref. [31].