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Research Article

Aromaticity and planarity of zinc phthalocyanine (ZnPc) characterized by splitting of NICS(1) index

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Abstract: The planarity of zinc phthalocyanine (ZnPc) in the gas phase and water, with solute-solvent interactions modeled by polarized continuum model (PCM), has been characterized with new indexes of aromaticity. The aromaticity of individual ring subunits of ZnPc molecule was studied on the basis of nucleus independent chemical shift index (NICS) above and below the molecular plane. Density functional theory (DFT) with selected Pople-type basis sets was used to study the local aromaticity. The calculated NICS(1) and NICS(-1) indexes of aromaticity for a non-planar ZnPc molecule in the polar environment are significantly different.

Keywords: Zinc phthalocyanine; ZnPc; planarity; DFT; aromaticity; NICS(1); NICS(-1); NICS splitting.

1. Introduction

This short theoretical study is devoted to theoretical characterization of zinc phthalocyanine. ZnPc is a fairly large, symmetrical molecule composed of several ring subunits containing a number of conjugated C=C double bonds. Phthalocyanines could be considered as man-made analogs of porphyrins. Due to their characteristic structure, free phthalocyanine (H₂Pc) and its numerous complexes with metal ions (MPc) are popular object of basic research and practical applications. Phthalocyanines are important compounds, used in photodynamic therapy (PDT), dyes and pigments industry, and in modern electronics and photonics [1-13].

On the other hand, chemical reactivity of organic compounds is directly related to the presence of unsaturated C=C bonds, and a possibility to delocalize labile π -electrons in

conjugated systems. Besides, π -electron delocalization in case of ring systems [14] is an important issue. In case of benzene, its six-membered ring forms a relatively stable, flat molecule with all CC (and CH) bonds equal. Moreover, in the presence of external magnetic field, hydrogen and carbon atoms are strongly deshielded. This is due to an induced magnetic field, caused by the ring electrons current. The ring current creates an induced magnetic field, directed against the external field. As result, the corresponding ¹H and ¹³C signals appear at about 7.2 and 128.5 ppm in proton and carbon NMR spectra, respectively. On the other hand, protons located above (or below) the ring plane resonate at highly shielded magnetic field (chemical shifts up to -3 ppm). This anisotropy of chemical shift around benzene and other ring molecules, for example porphyrins, is also observed from theoretical modelling of isotropic nuclear

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magnetic shieldings (σ) and chemical shifts (δ), observed experimentally by nuclear magnetic resonance spectroscopy (NMR).

A very useful theoretical concept, related to structure and reactivity of ring molecules is aromaticity. Being a multidimensional property, aromaticity is described on the basis of several criteria [15-22], including structural, reactivity and magnetic ones. Among popularly used aromaticity indexes are harmonic oscillator model of aromaticity, HOMA [16-17, 20] and NICS [19, 23]. Originally, von Schleyer et al. [19, 23] introduced NICS(0), NICS(1) and NICS(1)zz parameters, calculated as a negative magnetic shielding of Bq atom (in ppm) in the middle of benzene ring, 1 Å above this point, and its corresponding zz-component. All these indexes were calculated at the RHF/6-31+G* level of theory. Recently, Dobrowolski and co-workers [18] reported on splitting of the NICS(1) parameter into two indexes, one above and the other one below the molecular plane: NICS(1) and NICS(-1). As result, calculations of both indexes helped in better characterization of aromaticity on both sides of non-planar molecules.

Recently we demonstrated the sensitivity of benzene NICS aromaticity indexes to the basis set used and method of calculation [24]. We also reported on the impact of the method and basis set on the planarity and aromaticity of free ZnPc and its monohydrated axial complex in the gas phase and in the presence of polar solvents [25] using HOMA and NICS indexes, calculated by DFT.

Theoretical prediction of ZnPc molecule non-planarity and its local aromaticity, caused by a polar surrounding (water) is the main aim of the current study. The current work closely follows the concept of NICS(1) splitting [18]. From the calculated NICS(1) and NICS(-1) values we can conclude how the small distortion from planarity influences the magnetic properties above and below ZnPc molecule. However, in this short study, we will not concentrate on experimental aspects of ZnPc and ZnPc...OH₂ planarity or other indexes of aromaticity [26-29].

2. Theoretical Approach

ZnPc complex was optimized in the gas phase and water within a framework of DFT approach. Both B3LYP hybrid density functional [30-32],

and Truhlar's functional M06-2X [33-34] were selected for optimization, subsequent vibrational characterization (all positive frequencies were obtained) and final NICS calculations. All calculations were performed using Gaussian 09 program [35-36] with tight optimization criteria, SCF=tight, NOSYM keyword and grid, specified manually as INT(GRID=150590). The solvent effect was included using PCM [35, 37] for modeling water impact on the fully optimized structures and aromaticity of the studied molecules. For calculation of NICS parameters gauge including atomic orbitals [38-40] (GIAO) approach was used within a keyword NMR in the Gaussian program [35].

NICS(0) was calculated as negative value of nuclear magnetic shielding of Bq atom, placed in the middle of the subunit rings A, B and C (and directly in the ring plane) but similar results, called NICS(1) and its z-component NICS(1)zz, were obtained 1 Å above, and below the molecular plane. It is important to remind that the NICS(1)zz parameter is very sensitive to the electronic structure of the studied molecule [41].

The NICS(-1) parameter, and the other indexes, related to the splitting were obtained following the recent study [18]:

$$\text{NICS(1)}_{\text{av}} = \frac{\text{NICS(-1)} + \text{NICS(1)}}{2} \quad (1)$$

$$\text{NICS(1)}_{\text{diff}} = \text{NICS(1)} - \text{NICS(-1)} \quad (2)$$

$$\text{NICS(1)}_{\text{as}} = \frac{\text{NICS(1)}}{\text{NICS(-1)}} - 1 \quad (3)$$

$$\text{NICS(0)}_{\text{bia}} = \text{NICS(0)} - \text{NICS(1)}_{\text{av}} \quad (4)$$

Due to the size of ZnPc molecule, the calculations were very demanding, time consuming and impractical for better quality basis set types. The following set of systematically changing Pople-type basis sets, including polarization and diffusion functions, was chosen for calculations: 6-31G, 6-31G*, 6-311G**, 6-31+G, 6-31+G*, and 6-311++G**.

3. Results and Discussion

3.1 Planar and non-planar ZnPc molecular structure

A simplified gas phase optimized structural formula of planar ZnPc, with hydrogen atoms omitted for clarity, is shown in **Figure 1**. Due to

symmetry, it is possible to distinguish four sets of ring A, B and C subunits.

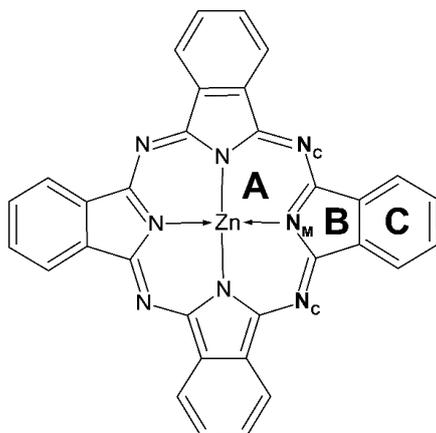


Figure 1. Simplified structure of ZnPc with three different ring subunits A, B and C.

In our recent study we demonstrated a good agreement of our B3LYP and M06-2X predicted structures of ZnPc and ZnPc...OH₂ in the gas phase and water with available experimental gas phase and crystal data^[25]. For brevity, we will not repeat here these results, and the interested reader is referred to the former work.

The magnetic probe atoms Bq, shown as magenta balls in **Figure 2**, were placed below (**Figure 2A**) and above the ZnPc molecule (**Figure 2B**) forming a complex pattern.

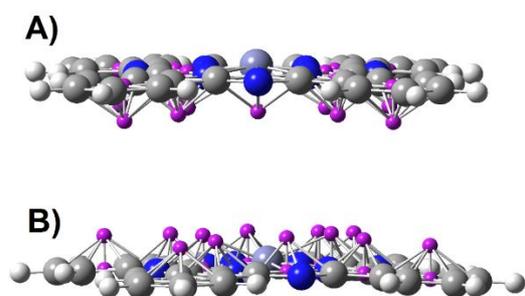


Figure 2. Distribution of Bq atoms (A) below and (B) above the molecular plane of ZnPc

The non-planarity of ZnPc structure, optimized in the presence of water, is clearly visible from **Figure 3**.

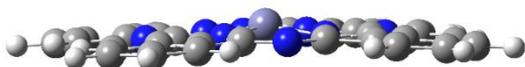


Figure 3. Non-planarity of ZnPc molecule with Zn ion sticking above the plane, formed by four nitrogen atoms.

Interestingly, full optimization of ZnPc yields a planar structure in the gas phase using both B3LYP and M06-2X density functionals and basis sets composed of polarisation, diffuse and mixed functions (the distance between Zn ion and the ring plane, $h = 0 \text{ \AA}$, see **Table 1**). In case of basis sets containing polarisation functions and lacking diffuse ones nonplanar structures are calculated with both density functionals. By adding diffuse functions to the basis sets, the calculations are more balanced, and the distance between the Zn ion and the ring plane slightly drops (from about 0.30 – 0.40 to 0.28-0.29 \AA)

Table 1. The distance h (in \AA) between the zinc ion and the plane, defined by four nitrogen atoms (N_c) in ZnPc.

Basis set	B3LYP		M06-2X	
	Gas phase	Water	Gas phase	Water
6-31G	0.000	0.220	0.000	0.361
6-31G*	0.000	0.245	0.071	0.400
6-311G**	0.000	0.248	0.000	0.311
6-31+G	0.000	0.000	0.000	0.000
6-31+G*	0.000	0.000	0.000	0.283
6-311++G**	0.000	0.000	0.000	0.288

The absolute values of NICS(0) aromaticity index calculated by B3LYP are smaller by up to 1 ppm than those, obtained using M06-2X density functional. However, the relative trends for subunits A, B and C are similar for both density functionals (**Table 2**). The presence of water (polar environment) is reflected by a small increase of ring A aromaticity (by about 0.05 ppm). Keeping in mind the aromatic character of free pyrrole, it is important to note that ring B nearly completely loses its aromatic character [25]. Finally, the aromaticity of ring C is comparable to free benzene [24-25].

The magnitudes of NICS(1) aromaticity indexes for all subunits are significantly larger than the NICS(0) indexes. Besides, the NICS(0) and NICS(1) of B ring are about 50% lower than for the free pyrrole [25] (see also **Table 3**). The impact of water is not uniform and could be probably viewed as a kind of random changes within 0.05 to 0.2 ppm.

Table 2. The B3LYP and M06-2X calculated NICS (0) values (in ppm) for three different ring subunits of ZnPc in the gas phase and in the presence of water using the selected basis sets.

Basis set	A		B		C	
	Gas phase	Water	Gas phase	Water	Gas phase	Water
B3LYP						
6-31G	-12.56	-12.51	-0.02	-0.02	-6.73	-6.74
6-31G*	-14.54	-14.45	-1.12	-1.13	-9.01	-9.03
6-311G**	-15.06	-14.99	-0.88	-0.84	-8.06	-8.08
6-31+G	-12.61	-12.63	0.13	0.47	-5.81	-5.74
6-31+G*	-14.53	-14.58	-0.74	-0.39	-7.83	-7.73
6-311++G**	-14.20	-14.25	-0.60	-0.27	-7.52	-7.43
M06-2X						
6-31G	-13.47	-13.32	0.09	0.03	-6.58	-6.59
6-31G*	-15.50	-15.29	-0.39	-0.50	-8.69	-8.72
6-311G**	-15.97	-15.84	-0.08	-0.08	-7.63	-7.66
6-31+G	-13.42	-13.47	0.19	0.57	-5.68	-5.57
6-31+G*	-15.45	-15.32	-0.07	-0.09	-7.54	-7.53
6-311++G**	-15.08	-14.95	0.15	0.12	-7.12	-7.14

Table 3. The B3LYP and M06-2X calculated NICS (1) values (in ppm) for three ring subunits of ZnPc in the gas phase and water using selected basis sets.

Basis set	A		B		C	
	Gas phase	Water	Gas phase	Water	Gas phase	Water
B3LYP						
6-31G	-12.68	-12.28	-4.43	-4.09	-9.93	-9.91
6-31G*	-13.94	-13.48	-4.89	-4.48	-10.71	-10.69
6-311G**	-14.47	-13.83	-4.71	-4.10	-10.43	-10.35
6-31+G	-12.72	-12.71	-4.07	-3.81	-9.12	-9.04
6-31+G*	-13.97	-13.99	-4.32	-4.05	-9.77	-9.67
6-311++G**	-13.99	-14.00	-4.45	-4.18	-9.76	-9.68
M06-2X						
6-31G	-13.78	-12.92	-5.06	-4.44	-10.43	-10.33
6-31G*	-15.32	-14.1	-5.53	-4.6	-11.18	-11.03
6-311G**	-15.61	-14.72	-5.09	-4.34	-10.77	-10.67
6-31+G	-13.74	-13.75	-4.72	-4.42	-9.57	-8.32
6-31+G*	-15.15	-14.28	-4.83	-4.13	-10.16	-10.01
6-311++G**	-15.10	-14.18	-4.89	-4.19	-10.08	-9.92

The largest magnitudes of aromaticity index are obtained for NICS(1)_{zz} (see **Table 4**). As in case of NICS(0) and NICS(1), here also the B ring is significantly less aromatic than free pyrrole. This is evident from a magnitude of NICS(1)_{zz} magnetic index of aromaticity: the B3LYP/6-311++G** calculated value for ring B in the gas phase is -6.8 ppm. In contrary, for free pyrrole this index is -31.0 ppm [25].

3.2 NICS(1) splitting as evidence of ZnPc nonplanarity

Tables 1-4 well characterize the structure and local aromaticity in planar ZnPc molecule in the gas phase. The results also show that the 6-31G

basis set is too small to predict well the NICS indexes of aromaticity and the saturated (converged) results are obtained in case of both polarization and diffuse functions present. However, in order to get an additional insight into the local aromaticity around the molecule of ZnPc (results in **Tables 2-4**) we extended our calculations to specific points in space below (see **Figure 2A**) and above (**Figure 2B**) the molecule. In case of a planar and symmetrical molecule, both NICS(1), and NICS(-1) parameters should be the same. However, if there exists a difference in electronic structure and electron flow above, and below the molecule, for example due to molecular

non-planarity, the calculated parameters should differ. Indeed, a fairly large difference between NICS(1) and NICS(-1) indexes on both sides of ZnPc molecule are observed for the selected basis set used (see Table 5). This is clearly visible from significant values of parameters NICS(1)_{diff}, NICS(1)_{av}, and NICS(1)_{bia}. In addition, from Table 5B a nonzero values of NICS(1)_{as} parameter are also calculated using M06-2X density functional.

In case of B3LYP calculations, the magnitudes of these differences are within 1.6 to 2 ppm for ring A and are significantly smaller for ring B (from 0.7 to 1.1 ppm) and C (from 0.11 to 0.24 ppm). These results confirm the strongest deviation from planarity directly near the zinc ion.

Table 4. The B3LYP and M06-2X calculated NICS (1)_{zz} values (in ppm) for three different ring subunits of ZnPc in the gas phase and the presence of water using selected basis sets.

Basis set	A		B		C	
	Gas phase	Water	Gas phase	Water	Gas phase	Water
B3LYP						
6-31G	-31.24	-30.04	-4.93	-3.99	-23.32	-23.15
6-31G*	-35.47	-34.02	-6.74	-5.7	-25.98	-25.81
6-311G**	-36.33	-34.52	-6.17	-4.47	-25.73	-25.33
6-31+G	-31.10	-31.20	-5.06	-4.22	-23.05	-22.81
6-31+G*	-35.21	-35.39	-6.82	-5.95	-25.62	-25.35
6-311++G**	-35.34	-35.48	-6.79	-5.96	-25.74	-25.51
M06-2X						
6-31G	-34.25	-31.81	-6.29	-4.59	-24.55	-23.97
6-31G*	-39.32	-35.82	-8.21	-5.80	-27.39	-26.56
6-311G**	-39.76	-37.23	-7.12	-5.02	-26.98	-26.38
6-31+G	-34.05	-34.17	-6.42	-5.45	-24.36	-24.08
6-31+G*	-38.58	-36.37	-7.93	-6.22	-26.93	-26.40
6-311++G**	-38.65	-36.31	-7.85	-6.10	-27.02	-26.44

Table 5. (A) B3LYP calculated individual NICS(0) and NICS(1) aromaticity indexes indicating splitting and differentiating of magnetic field above and below ZnPc molecule^a and (B) the corresponding M06-2X results^b. All the different NICS parameters, calculated with formulas 1-4 are also shown.

Tab. A.							
Basis	NICS(0)	NICS(-1)	NICS(1)	NICS(1) _{diff}	NICS(1) _{av}	NICS(0) _{bia}	NICS(1) _{as}
A							
6-31G	-12.51	-13.04	-12.28	0.76	-12.66	0.15	-0.06
6-31G*	-14.45	-14.32	-13.48	0.85	-13.90	-0.55	-0.06
6-311G**	-14.99	-15.07	-13.83	1.23	-14.45	-0.54	-0.08
B							
6-31G	-0.02	-4.74	-4.09	0.66	-4.41	4.39	-0.14
6-31G*	-1.13	-5.29	-4.48	0.80	-4.88	3.75	-0.15
6-311G**	-0.84	-5.23	-4.10	1.14	-4.67	3.82	-0.22
C							
6-31G	-6.74	-10.02	-9.91	0.11	-9.96	3.22	-0.01
6-31G*	-9.03	-10.81	-10.69	0.12	-10.75	1.72	-0.01
6-311G**	-8.08	-10.60	-10.35	0.24	-10.48	2.39	-0.02

a) Only results for nonplanar geometry, showing the corresponding splitting, are given

Table 5 continue.

Tab. B.							
Basis	NICS(0)	NICS(-1)	NICS(1)	NICS(1) _{diff}	NICS(1) _{av}	NICS(0) _{bia}	NICS(1) _{as}
A							
6-31G	-13.32	-14.60	-12.92	1.68	-13.76	0.43	-0.11
6-31G*	-15.29	-16.11	-14.10	2.01	-15.10	-0.19	-0.12
6-311G**	-15.84	-16.44	-14.72	1.72	-15.58	-0.26	-0.10
6-31+G*	-15.32	-15.91	-14.28	1.63	-15.10	-0.23	-0.10
6-311++G**	-14.95	-15.91	-14.18	1.73	-15.04	0.09	-0.11
B							
6-31G	0.03	-5.84	-4.44	1.40	-5.14	5.18	-0.24
6-31G*	-0.50	-6.35	-4.60	1.74	-5.48	4.98	-0.27
6-311G**	-0.08	-5.85	-4.34	1.51	-5.10	5.01	-0.26
6-31+G*	-0.09	-5.46	-4.13	1.32	-4.80	4.71	-0.24
6-311++G**	0.12	-5.54	-4.19	1.36	-4.87	4.98	-0.24
C							
6-31G	-6.59	-10.66	-10.33	0.33	-10.50	3.90	-0.03
6-31G*	-8.72	-11.43	-11.03	0.41	-11.23	2.51	-0.04
6-311G**	-7.66	-11.02	-10.67	0.35	-10.85	3.19	-0.03
6-31+G*	-7.53	-10.40	-10.01	0.38	-10.21	2.68	-0.04
6-311++G**	-7.14	-10.33	-9.92	0.42	-10.13	2.99	-0.04

b) Only results for nonplanar geometry, showing the corresponding splitting, are given

4. Conclusion

The DFT studies on planarity of ZnPc structure and aromaticity of its ring subunits were performed. The structure of free ZnPc molecule, as well as in the presence of water, modeled by PCM method, was calculated using Pople-type basis sets, containing different numbers of polarization and diffuse functions.

The non-specific interaction with water resulted in structures with zinc ion displaced from the ligand plane by about 0.2 to 0.4 Å. The displacement of zinc ion calculated with M06-2X functional, in comparison to B3LYP, was typically larger by about 0.1 to 0.15 Å.

The NICS indexes, calculated with B3LYP and M06-2X density functionals, indicate high aromaticity of A and C subunits in ZnPc for all basis set used. However, the five-membered ring B shows a significantly lower aromaticity in comparison to free pyrrole. No significant impact of polar solvent (water) on aromaticity was observed.

Different values of NICS(-1) and NICS(1) indexes support the idea of stronger perturbation of aromaticity due to dominating distortion of structural planarity for a ring A, directly attached to zinc ion. This kind of magnetic splitting could

be an additional, and important source of theoretical information about the status of an aromatic molecule.

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