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The Influence of Benzene Rings on Aromatic Pathways in the Porphyrins

Rashid R. Valiev*[a,b] and Victor N. Cherepanov[b]

Magnetically induced current density for tetraazaporphyrins (H_2ATP), phthalocyanine (H_2Pc), and tetrabenzoporphyrin (H_2TBP) molecules has been computed. The calculated current strengths for H_2ATP and H_2TBP were found to be close to these of free base porphyrin (27 nA/T). The current strengths appeared to have greater value than the same ones for H_2Pc (21.7 nA/T). The joining of benzene rings to free base porphy- rin and to H_2ATP causes to appear the additional weak ring current densities. The H_2Pc have a degree of aromaticity less than porphyrins according to magnetic criterion. © 2013 Wiley Periodicals, Inc.

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Introduction

The influence of external magnetic field on electrons of aro- matic and antiaromatic molecules is the reason of appearance of diamagnetic and paramagnetic ring currents. The contribu- tion of diamagnetic ring current dominates in aromatic mole- cules and that of paramagnetic dominates in antiaromatic molecules.[1] Therefore, the magnetically induced current of aromatic molecules causes the external magnetic field to be reduced in comparison with antiaromatic molecules. The examples of aromatic molecules are benzenes, porphyrins, and so on. They are stable enough because the diatropic ring cur- rents give them this quality. Generally, the greater diamagnetic ring current is, the more stable the molecule is.[1,2] Therefore, the quantitative determination of the ring current can charac- terize the degree of aromaticity and stability of molecules.

The current can flow within macrocycles in the subrings.[2] There is no way to experimentally determine the values of magnetically induced currents and their pathways. However, carrying out the explicit integration of the magnetically induced ring-current density over the cut plane area, crossing the bonds of interest normally, the ring-current can be deter- mined.[1,2] This technology makes it possible to determine cur- rent pathways in large macrocycles as well.[3–6] Recently, the calculations of the current density for Möbius twisted hexa- phyrins demonstrated that the aromatic and antiaromatic properties of the molecules depend on the geometries and the total number of π electrons.[3–9] In the work of Fliegl et al.,[3] the calculations of the current densities of transpor- phyrins gave some new information about possible current pathways. The results of these calculations show that the cur- rent flow around the macroring has different ways. Recently, in the work of Valiev et al.,[10] the magnetic properties of the iso- phlorins were also investigated. In this work, the calculation of current density confirmed the antiaromatic nature of isophor- ins because the contribution of diamagnetic current dominates in their total ring current. It should be noted that the density functional theory (DFT), where B3LYP exchange-correlation (XC) functional does not depend on the current-density, is used in the works.[3–10] However, in the presence of a mag- netic field, the XC functional also becomes dependent on the current-density, and in such situations, current-DFT (CDFT) is most appropriate.[11–13] At same time, CDFT is still insufficiently developed for application to large-size molecules. Besides, the use of DFT/B3LYP, MCSCF, and CCSD(T) gave similar results.[8,14] Therefore, the application of DFT/B3LYP for the calculation of magnetic current strengths is adequate.

Tetraazaporphyrins (H_2ATP), phthalocyanine (H_2Pc), and tet- rabenzoporphyrin (H_2TBP) are aromatic molecules.[15,16] They have wide application in designing the solar concentrators and sensors as well as in pigments and colorants, drugs, and cata- lysts.[17–19] To create specific devices based on porphyrinoids, the study of an aromatic character of complex multiring mole- cules is important.[20] Therefore, the investigation of physical and chemical properties of H_2Pc and porphyrins is one of the most promising fields of modern chemistry.[21–24]

The ring current can flow by different ways in H_2ATP, Pc, and H_2TBP molecules because they are multiring systems. The determination of the aromaticity degree and the main current pathways for considered molecules gives us a new insight into magnetic properties of aromatic molecules.[25]

The aim of this work is to investigate magnetic properties of H_2ATP, H_2Pc, and H_2TBP molecules using the GIMIC (gauge- including magnetically induced current) code.[5,8]

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Methodology

The equilibrium geometries of H_2ATP, Pc, and H_2TBP molecules were obtained using the DFT with Becke's three-parameter functional (B3LYP)[26,27] and Karlsruhe triple-ζ quality basis sets augmented by polarization functions (def2-TZVP)[28] The prefix def2 is omitted in further consideration. These calculations have been carried out by use of the Turbomole 6.4 code.[29]

An overview of the GIMIC method and its applications are given in Ref. 2]. Here is a quick look at the basic theoretical aspects of computing of magnetically induced current density using GIMIC code.

The current density $\vec{J}$ in the presence of external stationary and uniform magnetic field $(\vec{B})$ may be written as[8]

$$\vec{J}(r) = \frac{i}{2} \int dr_2..dr_n \left(\Psi^* \nabla \Psi - \Psi \nabla \Psi^* - 2i\vec{A}\Psi^*\Psi \right), \qquad (1)$$

where Ψ is the wave function and $\vec{A}$ is the vector potential.[1,2,8] The vector potential $\vec{A}$ describes both the external electric and magnetic fields and the fields arising by nuclei in a molecule. Therefore, the vector potential $(\vec{A})$ is the sum of $\vec{A}^B(\vec{r})$ and $\sum_l^N \vec{A}^{m_l}(\vec{r})$. Here, $\vec{A}^B(\vec{r}) = \frac{1}{2}\vec{B}\times(\vec{r}-\vec{R}_0)$ and $\vec{A}^{m_l} = \alpha^2 \frac{\vec{m}_l \times (\vec{r}-\vec{R}_l)}{|\vec{r}-\vec{R}_l|^3}$, where $\vec{B}$ is the external magnetic field, $\vec{m}_l$ is the magnetic moment of the l-th nucleus, $\vec{R}_l$ is the position of this nucleus, $\vec{R}_0$ is the gauge origin of the magnetic field, and α is the fine-structure constant. Also, the magnetically induced current density $(\vec{J})$ can be obtained using the nuclear magnetic shielding tensor (σ^l) for nucleus I. The σ^l value can be represented as[8]

$$\sigma_{\alpha\beta} = -\left(\frac{\partial^2 E}{\partial m_\alpha^l \partial B_\beta} \right) \begin{matrix} m^l=0 \\ B=0 \end{matrix}. \qquad (2)$$

Here, E is the electronic energy of a molecule:

$$E = \sum_{\mu\nu} h_{\mu\nu} D_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu} g_{\mu\sigma\nu\rho} d_{\mu\sigma\nu\rho}, \qquad (3)$$

where $h_{\mu\nu} = \int d\vec{r} \cdot \chi_\mu^* \hat{h} \cdot \chi_\nu$ is the one-electron interaction integral, $g_{\mu\sigma\nu\rho} = \int d\vec{r}_1 d\vec{r}_2 \chi_\mu^* \chi_\sigma^* r_{12}^{-1} \chi_\nu \chi_\rho$ is the two-electron interaction integral, $D_{\mu\nu}$ and $d_{\mu\sigma\nu\rho}$ are the one- and two-electron density matrices in the atomic-orbital representation, respectively.[8] Note, that χ_i are gauge-origin independent atomic orbitals[8] and $\hat{h}$ is the one-electron Hamiltonian. Consequently, the tensor $\sigma_{\alpha\beta}$ has the form

$$\sigma_{\alpha\beta}^l = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial m_\alpha^l \partial B_\beta} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_\beta} \frac{\partial h_{\mu\nu}}{\partial m_\alpha^l}. \qquad (4)$$

Using the Biot–Savart expression the tensor $\sigma_{\alpha\beta}$ can be represented as well

$$\sigma_{\alpha\beta}^l = -\varepsilon_{\alpha\delta\gamma} \int \frac{(r_\delta - R_{l\delta})}{|\vec{r}-\vec{R}_l|^3} J_\gamma^{B\beta}(\vec{r}) d\vec{r}, \qquad (5)$$

where $\varepsilon_{\alpha\delta\gamma}$ and $J_\gamma^{B\beta}(\vec{r}) = \frac{\partial J_\gamma(\vec{r})}{\partial B_\beta}$ are the Levi-Civita tensor and the tensor elements of the first-order induced current density,

respectively. Then, from Eqs. (4) and (5) the expression for $J_\gamma^{B\beta}$ can be obtained as[5,8]

$$J_\alpha^{B\beta}(\vec{r}) = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial \chi_\mu^*}{\partial B_\beta} \frac{\partial \tilde{h}}{\partial m_\alpha^l} \chi_\nu(\vec{r}) + \sum_{\mu\nu} D_{\mu\nu} \chi_\mu^*(\vec{r}) \frac{\partial \tilde{h}}{\partial m_\alpha^l} \frac{\partial \chi_\nu(\vec{r})}{\partial B_\beta}$$

$$+ \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_\beta} \chi_\mu^*(\vec{r}) \frac{\partial \tilde{h}}{\partial m_\alpha^l} \chi_\nu(\vec{r}) \qquad (6)$$

$$- \varepsilon_{\alpha\beta\delta} \left[\sum_{\mu\nu} D_{\mu\nu} \chi_\mu^*(\vec{r}) \frac{\partial^2 \tilde{h}}{\partial m_\alpha^l \partial B_\delta} \chi_\nu(\vec{r}) \right],$$

where $\frac{\partial \tilde{h}_{\mu\nu}}{\partial m_\alpha^l}$ and $\frac{\partial^2 \tilde{h}_{\mu\nu}}{\partial m_\alpha^l \partial B_\delta}$ are defined without the denominator $|\vec{r}-\vec{R}_l|^3$.[8] The Eq. (6) makes it possible to calculate the $J_\gamma^{B\beta}(\vec{r})$ in any space point because it is expressed in terms of basis functions, derivatives of basis functions, and the one-electron density matrices.

Equation (6) for $J_\gamma^{B\beta}(\vec{r})$ is represented in the matrix-vector form to simplify the calculations in GIMIC software as[5,8]

$$J_\alpha^{B\beta}(\vec{r}) = v^T P_\beta d_\alpha - b^T D d_\alpha + v^T D q_{\alpha\beta} - \varepsilon_{\alpha\beta\gamma} \frac{1}{2} \left(v^T D v \right) r_\gamma, \qquad (7)$$

where $b_\alpha = \frac{\partial v}{\partial B_\alpha}$, $d_\alpha = \frac{\partial v}{\partial r_\alpha}$, $q_{\alpha\beta} = \frac{\partial^2 v}{\partial r_\alpha \partial B_\beta}$ and v is the vector elements formed by the basis-function values at each grid point $\vec{r}$.[8] The D is the atomic orbitals density matrix, P_α is the density matrices of the perturbed atomic orbitals. These matricies are calculated at DFT/B3LYP level of theory in Turbomole 6.4 software.[29]

Results and Discussion

Molecular structures and chemical shiftings

The optimized structures of H_2ATP, H_2Pc, and H_2TBP molecules are given in the Supporting Information. The received equilibrium structures of the ground electronic state of these molecules show a good agreement with the calculation results of other authors[30,31] and X-ray data.[32,33]

Optimized structures of the molecules were used to calculate values of the nuclear chemical shieldings. The calculated values of the nuclear chemical shieldings for considered molecules are also given in the Supporting Information. Note that the value of the nuclear magnetic shielding for the hydrogens of tetramethylsilane calculated by use the DFT/B3LYP/TZVP level of theory is 31.91 ppm. As a result, the calculated values of chemical shifts of inner hydrogen atoms for H_2ATP, H_2Pc, and H_2TBP are 5.4, 2.7, and 4.6 ppm, respectively. The experimental values of ^{1}HNMR chemical shifts of inner hydrogen atoms are 2.47, 2.17, and 1.9 ppm, accordingly.[34–37] It is evident that the computed and experimental chemical shifts have a well agreement. This agreement confirms the validity of the nuclear magnetic shielding tensor σ^l found for considered molecules.

The magnetic current density

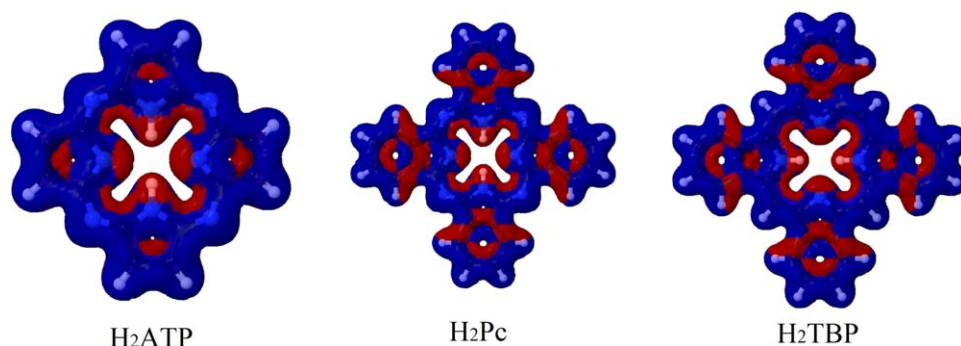The schematic plots of the modulus of current densities of investigated molecules are shown in Figure 1. As seen from

Figure 1. The modulus of the magnetically induced current densities for H_2ATP, H_2Pc, and H_2TBP molecules. Diatropic currents—blue, paratropic currents—red. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Tetraazaporphyrins

The value of the total current strength for H_2ATP is located in the range of 25.7–25.9 nA/T (see Table 1) which is close to the value of the current strength (27 nA/T) of free base porphyrin (H_2P).[3] The computation error of the current strength is about 1–2 nA/T.[2] Therefore, it can be assumed the magnetically induced current densities for

Figure 1, the contribution of the diatropic part into total current density for all considered molecules dominates.

Note that the plots (Fig. 1) of the modulus of current densities for H_2ATP are similar to free base porphyrin.[3] Also, the signed modulus of current densities for H_2Pc and H_2TBP molecules are very similar. However, the information about quantitative differences between the magnetically induced current densities for H_2Pc and H_2TBP molecules can be obtained by the current strength calculation.

The calculated magnetically induced current strengths measured in nA/T[3] (nano ampere per tesla) of H_2ATP, H_2Pc, H_2TBP molecules are given in Tables (1–3) and the aromatic pathways of the considered molecules are shown in Figure 2.

both molecules to be close as well. As seen from the Table 1, the values of the current strengths of all pathways of H_2ATP are also close to those of H_2P. Besides, the positive signs of the current strengths for all pathways have confirmed aromatic nature of H_2ATP molecule.

Phthalocyanine

The calculated total ring current strength for H_2Pc is equal to 21.7 nA/T (see Table 2). The found value is less than 25.9 nA/T

Table 2. The calculated current strengths (I_1, I_2, I_3, and I_4 in nA/T) for selected bonds of H_2Pc H_2ATP (refer to Figs. 1–3).

Ring	Total current	I_1	I_2	I_3	I_4
A	21.7	13.7	1.7	12.0	9.7
B	21.7	12.1	5.2	7.3	14.4

Table 1. The calculated current strengths (I_1 and I_2 in nA/T) for selected bonds of H_2ATP (refer to Figs. 1–3).

Ring	Total current	I_1	I_2
A	25.9	15.9 19.4[a]	10.0 7.8[a]
B	25.7	9.4 12.3[a]	16.3 15.2[a]

[a] The current strengths for free base porphyrins are taken from Ref. [3].

Table 3. The calculated current strengths (I_1, I_2, I_3, and I_4 in nA/T) for selected bonds of H_2TBP H_2ATP (refer to Figs. 1–3).

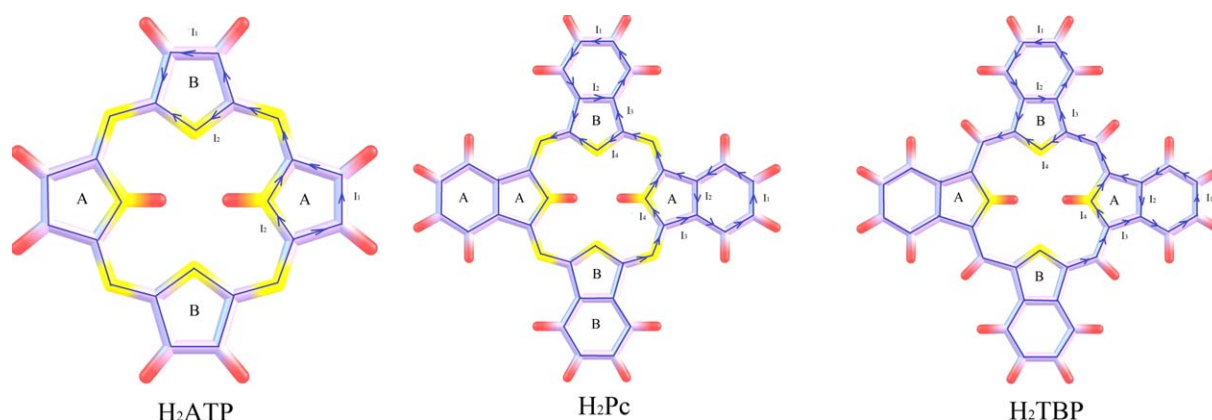| Ring	Total current	I_1	I_2	I_3	I_4
A	25.2	14.7	1.1	13.2	11.6
B	24.9	12.5	2.1	10.3	14.5

Figure 2. The directions of the current pathways for H_2ATP, H_2Pc, and H_2TBP molecules are indicated with the blue lines and arrows. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
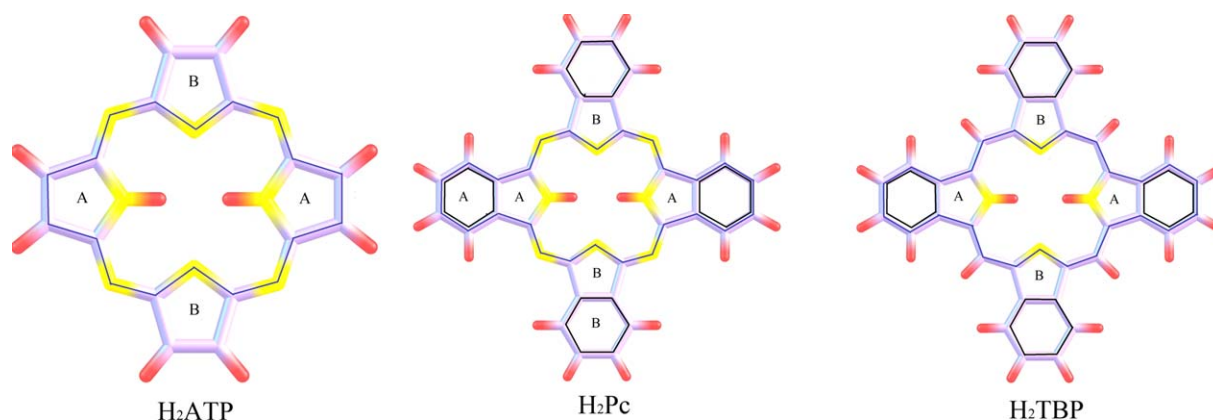
Figure 3. The main current pathways for H₂ATP, H₂Pc, and H₂ATP are indicated by the blue line. The small current rings are shown with the black line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for H₂ATP and 27 nA/T for H₂P. Therefore, H₂Pc molecule has the degree of aromaticity less than one for H₂ATP and H₂P molecules according the magnetic criterion.[1] As seen from Table 2 and Figure 2, the dominant current flows throw pathway crossing the C—N—C bonds of pyrrole (ring B) and C=C bonds (ring A) of benzene molecules. The aromatic pathways of C—N—C with hydrogen have electrical resistance more than C—N—C without hydrogen.[3] This is the reason of the small current strength (I_4) for pyrrole rings (A) of H₂Pc molecule in comparison with the current strength (I_2) of pyrrole rings (B) for H₂ATP and H₂P molecules accordingly Ohm's law.

The main difference of magnetic properties of H₂Pc from H₂ATP and H₂P is the appearance of backward current (I_2, see Table 2) in H₂Pc molecule. This situation can occur when the molecular system has many subrings.[21] Note, that the calculated I_1 current strength is equal to the sum of $I_2 + I_3$ for both rings A and B. This result agrees with Kirchhoff's law for electric chains.

Tetrabenzoporphyrin

As evident from Table 3 and from Figure 2, the total ring current strength in H₂TBP lies in the range of 24.9–25.2 nA/T. The calculated value is very close to 27.0 nA/T for H₂P[3] and 25.7–25.9 nA/T for H₂ATP molecules (the error of calculation is 1–2 nA/T[3]). Therefore, the joining of benzene rings to pyrrole rings of free base porphyrin influences on the total ring current density of porphyrins weakly.

Note, the dominant current density takes the same routes as in the case of H₂Pc molecule. Also, the I_2 currents flow in opposite direction in comparison with I_1, I_3 and I_4 for H₂TBP like the case of H₂Pc. Therefore, the main difference of magnetic properties between H₂Pc and H₂TBP consists in the total current strength (see Tables 2 and 3).

Summary and Conclusions

In this work, the magnetically induced current densities were calculated for H₂ATP, H₂Pc, and H₂TBP molecules by application of GIMIC software. The calculations show that the joining of benzene rings to the free base porphyrin affects the total

ring current density weakly. Therefore, it can be assumed the total ring current strength of extended benzene porphyrins to have the value near 27 nA/T. However, the additional ring currents occur when joining the benzene rings to the porphyrins and the azaporphyrins. The main current pathways for H₂ATP, H₂Pc, and H₂ATP molecules are shown in Figure 3. As may be seen from Figure 3, the additional benzene ring currents are induced in the presence of the external magnetic field. These currents generate the weak additional magnetic field in the benzene parts of the molecules which influences protons of benzene rings.

The computed current strength for H₂Pc molecule is less than that for porphyrins (H₂P, H₂ATP, and H₂TBP). Therefore, it can be assumed that the same takes place with the degree of aromaticity for the H₂Pc and the porphyrins.[8] And it does occur, the H₂Pc are less stable than porphyrins.[37] Thus, the calculation of current pathways and current strengths has given a new understanding of magnetic phenomena and the aromatic character for the classes of H₂Pc and azaporphyrins.

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