

On the JAP Method for the Indirect Determination of Delocalized Currents from Experimental Chemical Shifts**

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The JAP model (after Jirásek, Anderson, and Peeks) to retrieve global current strengths from experimental ¹H chemical shifts has been tested with DFT computations. Both global and local tropicities are correctly predicted in most cases and the

quantitative agreement is overall fair. An extension of the model is found to give improvement in an exemplary critical case, where the global delocalized current is negligible and the current density map is dominated by local currents.

Introduction

Quantities which are not directly observed, but appear in integrals which define observable quantities are known as subobservables.^[1] The most known of these quantities is the electron density ρ , which determines charge and static multipole moments, as well as diffracted intensities by Fourier transform, but we will focus on the magnetically induced current density \mathcal{J}^B , the tensor field which determines the magnetizabilities and the chemical shifts via suitable integrations.^[2,3] In the case of ρ , the indirect route for its determination is approached optimizing some parameters of a model integrand function; the wealth of experimental data has allowed to adopt more flexible model functions over the years, so that the parameters are not only the positions of the atoms, but also the terms defining the non-sphericity of the atoms.^[4] The indirect route in the case of \mathcal{J}^B is far more challenging, due to the numerically far less abundant experimental data. Something similar to the indirect route for ρ can be recognized in the efforts to model the peculiar values of chemical shifts and magnetizabilities of aromatic compounds in terms of few loops of current, but these models, introduced to estimate the magnetic properties from computed currents,^[5–7] have been rarely used along the reverse indirect route.^[8,9] The availability of good computations of the induced magnetic field^[10] has led to flourish the topic anew: the induced magnetic field, which for a unitary external field is nothing but the well-known nucleus-independent chemical shift (in effect the so-called NICS_{zz}),^[11,12] has given the possibility to explore the indirect approach, starting from computed NICS.^[13–19] The disclosure of

procedures to determine bond and ring current (RC) strength from suitable integration of the first-principle current density,^[20–23] allows for a strong evaluation of the quality of the NICS-based ring currents: not only as effective fitting parameters of the NICS values, but as quantities which give a coarse-grained picture of the current density field itself. This computational endeavor has led to test and assess several ring current models in monocycles.^[24–26] Recently, also for planar polycyclics, NICS values have been related qualitatively^[27] and quantitatively^[28] with bond current strengths. The relationship between the induced magnetic field and ring currents continues to be a matter of interest,^[29] but, even when it will be possible to recover reliable current strengths from NICS in complex three-dimensional systems, the fact remains that these works connect two sets of computed properties, and the motivation to perform the indirect analysis reduces to preference of software.

The much more ambitious goal of recovering a coarse-grained picture of the current density from experimental values has been recently advanced by Jirásek, Anderson and Peeks (JAP), who estimated the global current strength in several macrocycles from the change of their proton chemical shifts recorded in solution over the proton chemical shifts of suitably chosen reference compounds,^[30] according to the simple intercept-free linear equation

$$\Delta\delta_i = \delta_{i,aro} - \delta_{i,ref} = \sigma_{i,ref} - \sigma_{i,aro} = RCGF_i \frac{l}{B} \quad (1)$$

where l is the global current strength induced in linear regime by a magnetic field of modulus B , and, for each magnetic nucleus i , the ring current geometric factor $RCGF_i$, first proposed in ref.^[9] is a function of the geometry of the molecule and of the circuits considered relevant for the non-localized part of the magnetic response. As with NICS-based works, JAP approach comes with an internal validation, the ability of the model to reproduce the experimental $\Delta\delta_i$, but, due to the small number of experimental data (not to say about the far from trivial problem of identifying correct reference compounds) the possibility remains that JAP currents are not in agreement with reliable computations, and their meaning could then be questioned. As JAP approach could be of wide use in the realm

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of magnetic aromaticity, as it comes with a well-documented open-source MATLAB code and has already produced interesting and sometimes unprecedented results on systems of high technological relevance,^[31,32] we deemed it necessary to assess its effectiveness, and we took the task of computing local and global current strengths for the systems considered in Ref. [30]. From this analysis, we excluded cycloporphyrin nanorings, which have been object of a previous study.^[33]

Results and Discussion

The systems studied, labeled as in Ref. [30], are reported in Scheme 1. Topologically, they are annulenes (**1,2**), nano hoops decorated by single rings (**3-7,12**) or by small polycycles (**8,10-11**), and a circulene, i.e. a swung-in-plane nanobelt (**9**), sometimes in different charge states. The structures in Scheme 1 come with labelling of their unique rings, following symmetry and the smallest-set-of-smallest-rings (SSSR^[34]). If the continuity equation were fulfilled, the bond current strengths could be equivalently reported as ring current strengths,^[35] which are a more compact way of expressing the current data, and will be commented below. Additionally, a sign can be given to ring current strength I to get the signed ring current strength \bar{I} , which is positive or negative for a paratropic and a diatropic circulation, respectively.^[25,36]

Global and local current strength have been obtained integrating the DFT magnetically induced current density using appropriate contour levels, as shown in the case of 11^{2+} in Figure 1 and in Figures S1 and S2 for all the molecules studied.

It is pleasing to note that the global tropicity, i.e. the sign of the signed^[25,36] global current (negative diatropic, positive paratropic), is always predicted correctly by the JAP model, which is rather effective even on the quantitative level. However, the excellent agreement for annulenes is not always found for more complicated topologies, where the errors

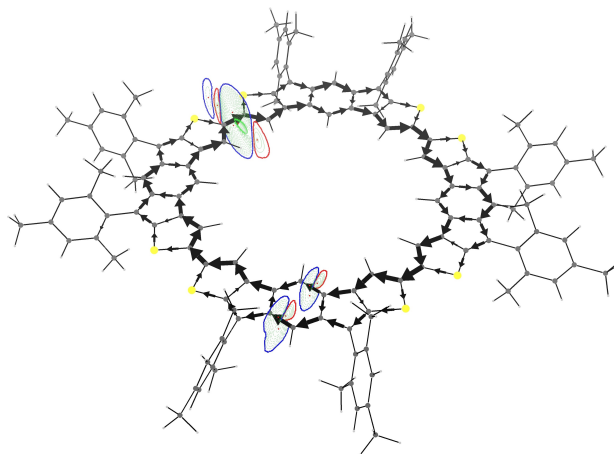


Figure 1. Integration domains used to determine the global ring current strength and the local ring current strength in the case of 11^{2+} (ring D) and arrows whose area is proportional to the ring current strength (more details in the Computational Methods).

amount in several cases to more than a benzene ring current (3^{2+} , 4^{2+} , 9^{2+} , 10^{2+} , 12^{4+} , 11^{2+} , 9^{2-}); in percent terms, they rarely exceed 30%, but sizably larger deviations occur in case of small computed currents (9^{4-} , **11**) and for 12^{4+} . Interestingly, many of the above cases showing large deviations in absolute values could not have been determined by their least-squares R^2 values, which were among the highest. In an effort to understand the sources of the residual disagreement, it is appropriate to consider the basic assumptions of the JAP model.

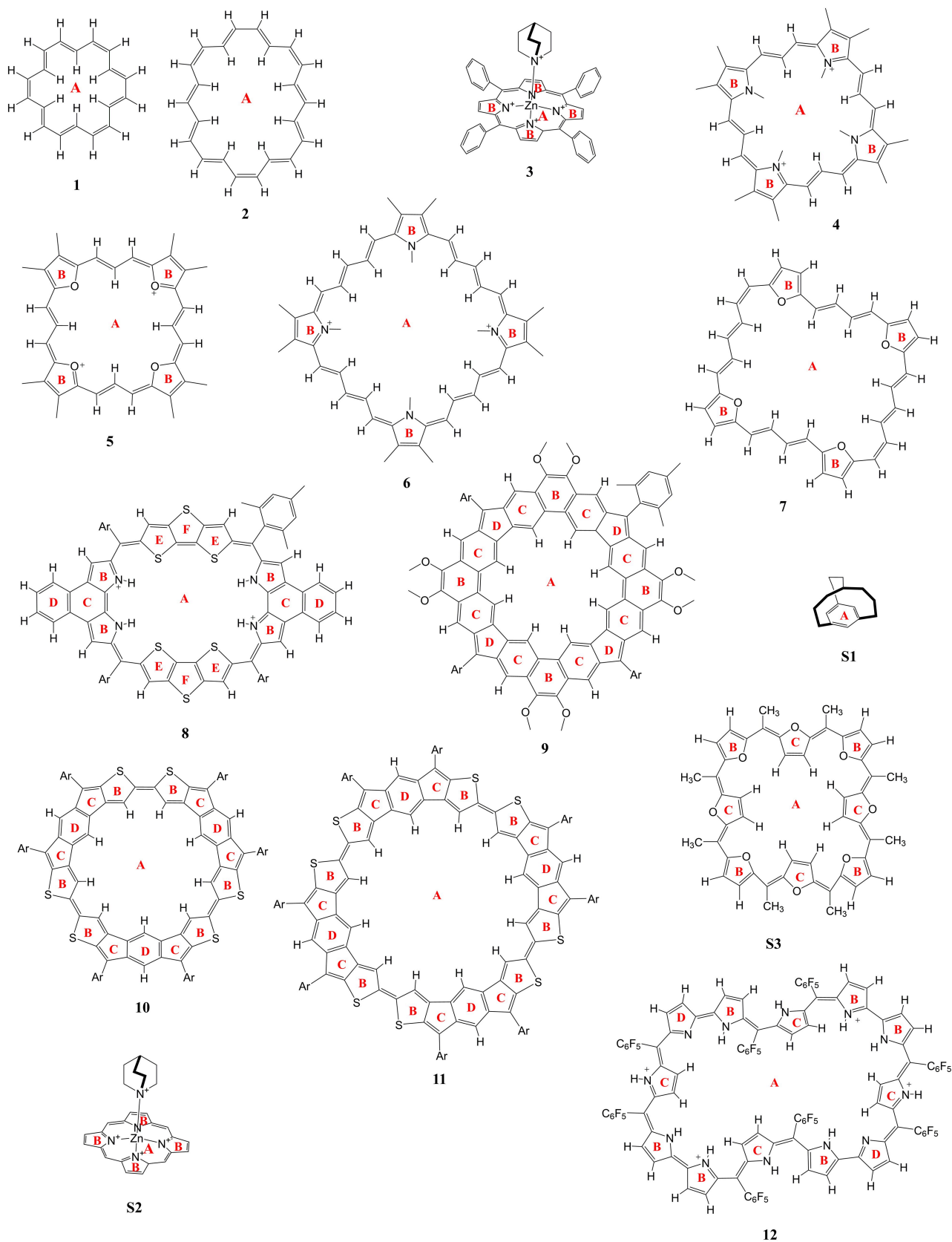
The Biot-Savart law, used to develop the equations of the model, is known to work exactly also in the quantum mechanical domain, provided the correct current density is used.^[38] Therefore, the problems can only come from the inadequate modeling of the current density. In this respect the assumption of the JAP model can be summarized as follows:

- I) The macrocycle is assumed to have a single conformation, built upon gas-phase B3LYP/6-31G* optimization starting from the crystallographic structure,
- II) local currents are preserved passing from the reference compounds to the studied macrocycles,
- III) delocalized currents run along one or few equally weighted piecewise linear pathways running along selected conjugated circuits,
- IV) the shape of the current is that of two infinitely thin homotropic circuits displaced from the average local plane by $\pm 0.7 \text{ \AA}$ (the displacement is in-plane for porphyrins),
- V) the contributions to the shielding of the i -th spectator atom coming from different directions of the external field are weighted by the net projected cross-section area of the circuit along the direction of the applied magnetic field:

$$\text{RCGF}_i = \frac{1}{3} \left(\frac{A_x}{\sqrt{A_x^2 + A_y^2 + A_z^2}} \text{RCGF}_{x,i} + \frac{A_y}{\sqrt{A_x^2 + A_y^2 + A_z^2}} \text{RCGF}_{y,i} + \frac{A_z}{\sqrt{A_x^2 + A_y^2 + A_z^2}} \text{RCGF}_{z,i} \right) \quad (2)$$

Commenting the above assumptions,

- I) as it is well-known that chemical shifts can be strongly influenced by geometry,^[39,40] which in turn is sensitive to the level of theory,^[41] its accurate determination is a point of attention. In the case of 12^{4+} , we have taken the geometry from the crystal structure and we have optimized it at the BHandHLYP/6-31G* level. The optimized structure, which is marginally less flat than the crystal structure, has very different current density and nuclear magnetic shieldings, and compares definitely worse with the JAP estimate as compared with the frozen structure.
- II) the ring currents of the small rings can undergo significant variations when included in larger molecules. Figure 2 shows the values of the ring currents of pyrrolic and furanic rings in reference systems and in the molecules studied. The non-preservation of the currents of small rings would correspond to an intercept term in Eq. (1). In effect the plots reported in Ref. [30] often show an unbalanced disposition



Scheme 1. Molecules studied in this work.

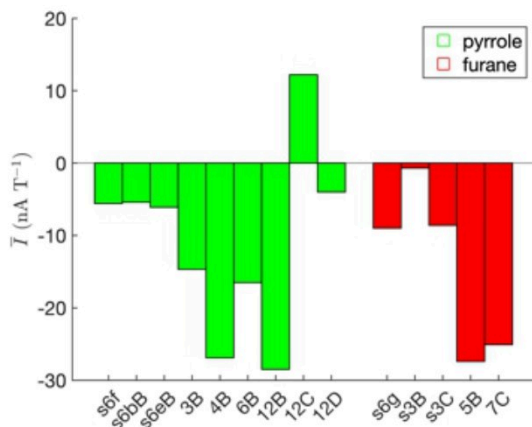


Figure 2. Ring current strength of pyrrolic and furanic rings.

of the data with respect to the best-fit line, suggesting that an intercept is needed.

- III) Identification of the current pathway is a non-trivial theoretical problem, and several methods^[42–44] have been proposed in literature,^[25] besides the quantum-mechanical calculations. The current path proposed in Ref. [30] can be considered as a reduced version of Randić conjugated circuit model, where only pairs of resonance structures leading to global delocalization are considered. However, it is known that in polycyclic systems, small circuits influence more than large ones the final current density.^[45,46] As a matter of fact, considering the current pathways used in the JAP calculation to retrieve local ring currents, it turns out that in the vast majority of cases, with the exception of 9^{4-} , JAP tropicities of individual rings are consistent with DFT values (Table 1 and S1). A more detailed analysis can be done looking at Figures S1 and Table S1. Starting from monocycle-decorated nano hoops, **S2**, **3**, **4**, **5**, **6**, **7**, the procedure outlined in Ref. [30] assumes a half-and-half bifurcation of the current at the monocycles, which means that the RC of the monocycle is half the RC of the central ring. This turns out a reasonable approximation in half of the cases, but not for **4**, **5** and **7**, where the current flowing on the outside is sizably larger than that flowing in the inside. In case of **10**, the pattern proposed is consistent with the calculation on the central benzene D, and qualitatively with the external thiophene A, but the outer DFT current on ring B is roughly half of the current flowing on the inside. Also for **S3**, the JAP pattern of ring current, which can be described by a paratropic and a diatropic flow on rings B and C, is in qualitative disagreement with the DFT computation. The most striking qualitative difference is found for 9^{4-} , where the current pattern is basically localized and has no delocalized current. It is to be noted that the missing current on benzene in the model of reference^[30] was motivated by an “ACID calculation”. In effect, the only computation known to us is found in Ref.

Table 1. Signed current strengths (in nA T^{-1}) retrieved by the JAP method (ref. 30) and by DFT (this work) for the systems sketched in Scheme 1, some of them with different charge. R^2 is the coefficient of determination of the JAP linear model taken from ref. 30. %err is the percent error of the \bar{I}_{JAP} over the \bar{I}_{DFT} values. The fraction of rings whose tropicity is predicted correctly, $\phi_{\text{TROP}}^{\text{ok}}$ is given in the last column.

	R^2	\bar{I}_{JAP}	\bar{I}_{DFT}	%err	$\phi_{\text{TROP}}^{\text{ok}}$
1	0.97	−13.3	−13.3	0	1/1
2	0.97	−10.1	−8.4	20	1/1
3	0.98	−38.0	−25.1	51	2/2
4^{2+}	0.99	−25.9	−38.5	−33	2/2
5^{2+}	0.98	−26.6	−33.8	−21	2/2
6^{2+}	0.99	−33.4	−25.2	33	2/2
7^{2+}	0.96	−28.3	−27.6	3	2/2
8^{2+}	0.97	−29.3	−25.1	17	3/6
9^{2+}	0.91	−22.7	−36.9	−38	3/4
10^{2+}	0.99	−20.1	−32.6	−38	3/4
11^{2+}	0.99	−26.7	−43.1	−38	3/4
12^{4+}	0.94	−33.0	−6.9	3787	1/4
12^{4+} [a]			−34.5	2	1/4
9^{2-}	0.84	−12.9	−28.1	−54	3/4
9^{4-}	0.23	5.0	1.8	178	1/4
10	0.88	8.6	11.8	−27	2/4
11	0.96	7.0	3.1	126	2/4
S1	0.96	−11.2	−9.3	20	1/1
S2	0.99	−29.8	−26.7	12	2/2
S3	0.94	5.1	2.1	50	2/3

[a] Non-optimized geometry taken from the crystal structure of Ref. [37].

[31], where a current flowing on the benzenoid ring computed by the ACID software^[47] is clearly visible.

- IV) The shape of the current, borrowed from the shape of the π current in monocycles,^[25] is not always the one found in computations. The sketches reported in the SI show that in several cases the current is reminiscent of in-plane σ currents, although these are cases where the currents have low intensity. A more significant problem has already been discussed in the case of cycloporphyrin nanorings, where the in-plane currents can be contra-rotating heterotropic.^[33] This can substantially change the values modeled in a coarse-grained approach, because the nuclei can feel a sizable current, because one of the two heterotropic loops is closer to them, even if the overall current is very small.
- V) Weighing by the net projected cross-section area, Eq. 2, gives the exact response for a planar monocycle or polycyclic not oriented along a principal axis, as the cross sections are proportional to the same cosine needed to project the perpendicular external field along the three Cartesian axes. The application of this scheme for non-planar rings does not come with the same theoretical justification. As a matter of fact, in several trials we have made on the molecules studied in this paper, we get no significant advantage in using Eq. 2, over the simpler

$$\text{RCGF}_i = \frac{1}{3} \text{RCGF}_{\perp,i} \quad (3)$$

where $\text{RCGF}_{\perp,i}$ is the ring-current geometric factor stemming from a magnetic field perpendicular to the average plane of the ring.

The above potential sources of error could be further addressed for future improvements of JAP's model. We have explored a small extension of JAP model to consider the presence of non-equally weighted circuits. We took the SSSR as a starting set of circuits, but we experienced many problems: the ring currents often turn out highly correlated and have large fit errors. Restriction to models of rings with directly attached protons was generally beneficial, but often results were poorer than the starting JAP model. In some cases a better performance has been obtained considering in the set of circuits the largest macrocyclic ring, rather than the smallest one chosen by the SSSR approach. We focus here on 9^{4-} , which is known to be dominated by local currents.^[31] The fit of all 4 independent rings of the SSSR (Figure 3b) allowed for an improvement of the chemical shift calculation over JAP method (Figure 3a), but gave unphysical values for the currents, which is likely a side-effect of the strong correlation of the parameters. A restricted two-parameters and one-parameter model (Figure 3c and 3d) gave acceptable values of the currents, while still improving the calculation of chemical shift over JAP model. According to the original investigation^[31] and to the DFT calculation reported here (Figure S2 and TOC graphics), the correct model of currents is not an annulene-within-an-annulene model (c), but rather a sum of localized ring currents, like those in (b), which have however wrong magnitudes. The correct order of magnitude of the ring current is obtained in model (d), with forced equality of ring currents. However, model (d) has a smaller R^2 value than model (c), which is incorrect, as stated above.

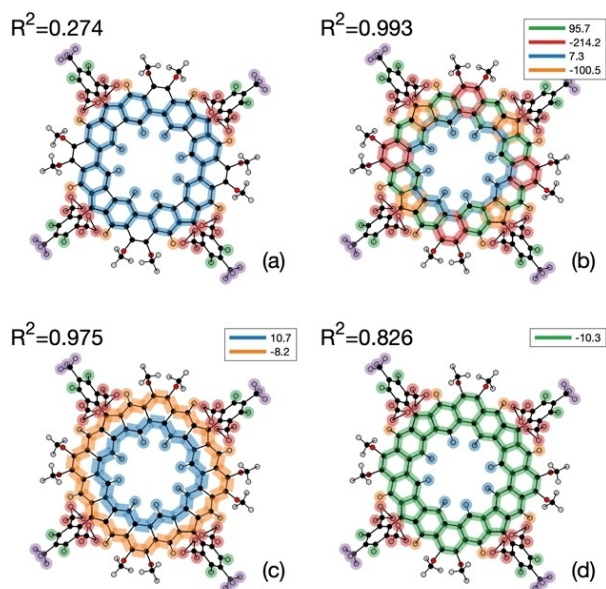


Figure 3. Ring current maps (values in nAT^{-1}) obtained fitting the chemical shift of the highlighted proton atoms of 9^{4-} according to (a) 2^6 equally weighted delocalized circuits, consistently with JAP, (b) all four rings of the SSSR, (c) two concentric annulenes, (d) all small rings with equal ring current.

Conclusions

In conclusion, we have performed a check of the ability of JAP model to recover DFT ring currents, which can be nowadays computed with user friendly automated software.^[48] The model is effective in recovering global and local tropicities, but errors of the order of a full benzene ring current can occur. In percent term, the largest error has been reported for a calculation on 12^{4+} and for 9^{4-} , a system with a negligible global ring current, dominated by local currents. Extension of the model to fit more than a ring current revealed cumbersome, due to heavy correlation of the fit parameters, but good results were obtained in the case of 9^{4-} . The application of a similar approach to other system will be non-trivial, not only because of the strong correlation of the parameters, but also because choosing the proper reference system can be complicated, especially in bent systems,^[49] so that presently the indirect route of retrieving the current density from few experimental chemical shifts should still be considered a rough and bumpy challenging road.

Computational Details

Magnetically induced currents have been obtained by SYSMOIC^[48] starting from wavefunction files (.wfx) obtained by Gaussian16^[50] run at the BHandHLYP/6-31G* level on geometries optimized at the same level. The functional used is one of the best for the calculation of the magnetic response, according to gradings based on magnetizabilities^[51] and hypervirial relationships.^[52] Global current strengths have been computed integrating the current crossing a plane bisecting a C–C bond up to 10^{-3} atomic units (at this level the reference benzene ring current is -12.2 nAT^{-1} , see Figure 1 and the TOC graphics, for an additional example on 9^{4-}). Numerical results are collected in Table 1. Accurate determination of local currents is less straightforward, because the large areas associated to small integration thresholds can include contribution associated to different bonds and a criterion is needed to assign contributions to individual bonds. In this work local currents have been first obtained at the less demanding $2 \cdot 10^{-2}$ atomic units level (the reference benzene ring current reduces to -10.3 nAT^{-1} ; percent values are reported in Figures S1 and S2, with or without the sketch of the integration domains, which are useful to grasp the shape of the currents). Current in percent units of the benzene current strength are only approximately preserved when different integration thresholds are used, so that global current strengths reported in Table 1 and S1 can differ by several nAT^{-1} . As a correction for this error, best values of local signed current strength, e.g. for ring B, have been obtained as

$$\bar{I}_{\text{corr},B} = \bar{I}_{\text{global}}^{(10^{-3})} \frac{\sqrt{(2 \cdot 10^{-2})}}{\sqrt{(2 \cdot 10^{-2})}} \quad (4)$$

Corrected results are also given in Table S1.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aromaticity · current density · proton chemical shift · DFT computations · nanorings

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