

Correspondence on "How Aromatic Are Molecular Nanorings? The Case of a Six-Porphyrin Nanoring"

Jie-Ren Deng,^{[a]†} David Bradley,^{[b]†} Michael Jirásek,^[c] Harry L. Anderson,^{*,[a]} and Martin D. Peeks^{*,[b]}

[a] J.-R. Deng, Prof. H. L. Anderson
Department of Chemistry, University of Oxford, Oxford OX1 3TA, U.K.
E-mail: harry.anderson@chem.ox.ac.uk

[b] D. Bradley, Dr. M. D. Peeks
School of Chemistry, University of New South Wales, Sydney NSW 2052, Australia.
E-mail: m.peek@unsw.edu.au

[c] Dr. M. Jirásek
Laboratory of Organic Chemistry, ETH Zurich, 8093 Zurich, Switzerland.

† These authors contributed equally

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Abstract: A recent Article in this journal by Matito and coworkers claimed that none of the oxidation states of a butadiyne-linked six-porphyrin nanoring exhibit global aromaticity or antiaromaticity. Here we show that this conclusion is incorrect. Experimental data from NMR spectroscopy for a whole family of nanorings provide strong evidence for global ring currents. The NMR data reveal these ring currents directly, without needing analysis by density functional theory (DFT). Furthermore, DFT calculations reproduce the experimental results when a suitable functional is used.

The concept of aromaticity is fundamental to many areas of chemistry, and various criteria have been developed for deciding whether a molecule is aromatic.^[1] These criteria are not always in agreement, which can lead to controversy. Such disagreements are valuable opportunities to refine our understanding of aromaticity. Recently, we published a series of papers demonstrating global aromaticity and antiaromaticity in porphyrin nanorings with Hückel circuits of up to 162 π -electrons.^[2–8] These macrocycles are dramatically larger than previously-reported aromatic rings, and studies on such large macrocycles could shed light on the similarity between aromatic ring currents and persistent currents in non-molecular quantum rings.^[8]

Matito and coworkers^[9] challenged our identification of global ring currents in porphyrin nanorings, based on their DFT calculations. Here we argue that they arrived at a false conclusion because they overlooked three points: (a) that the experimental NMR data indicate global ring currents, even when analyzed directly without using DFT, (b) that DFT simulations reproduce the experimental data and ring currents, when a suitable functional is used (e.g. BLYP35) and (c) that the pattern of NMR shielding in a whole family of 6-porphyrin nanorings (10 different **c-PM[b_xe_y]^Q** species) is fully consistent with Hückel's $4n+2$ rule only if the ring currents are global; it cannot be accounted for by only local porphyrin ring currents.

In our previous work, we analyzed the experimental NMR spectra of porphyrin nanorings (**c-PM[b_xe_y]**, Figure 1) in a range of oxidation states ($Q = -6$ to $+12$) and showed that the ¹H NMR spectra reveal the presence of global aromatic and antiaromatic ring currents in many of these species.^[2,3,5,7,8] ¹³C NMR and ¹⁹F NMR (for **c-P6[b₆]-T6⁰**) chemical shifts, where measured, support the conclusions from ¹H NMR spectra.^[5] Global (anti)aromaticity was also supported by analysis of oxidation potentials and rates of conformational exchange.^[7] It is pertinent to briefly summarize how global (anti)aromaticity is manifest in

the NMR spectra. For simplicity we focus on the four types of experimental NMR data listed for **c-P6[b₆]-T6⁰** in Table 1: $\delta(\alpha_{in}) - \delta(\alpha_{out})$ is the difference in chemical shift between inner and outer *ortho*-aryl protons; $\delta(\text{THS}_{in}) - \delta(\text{THS}_{out})$ is the difference between the chemical shifts of inner and outer Si-CH₂ protons; $\Delta\delta(\alpha)$ is the difference in chemical shift between the α -proton of the template complex and that of the free unbound template, and similarly $\Delta\delta(\beta) = \delta(\beta) - \delta(\beta_{free})$; see Figure 1c for atom labels. An aromatic ring current results in shielding within the ring, and deshielding outside.

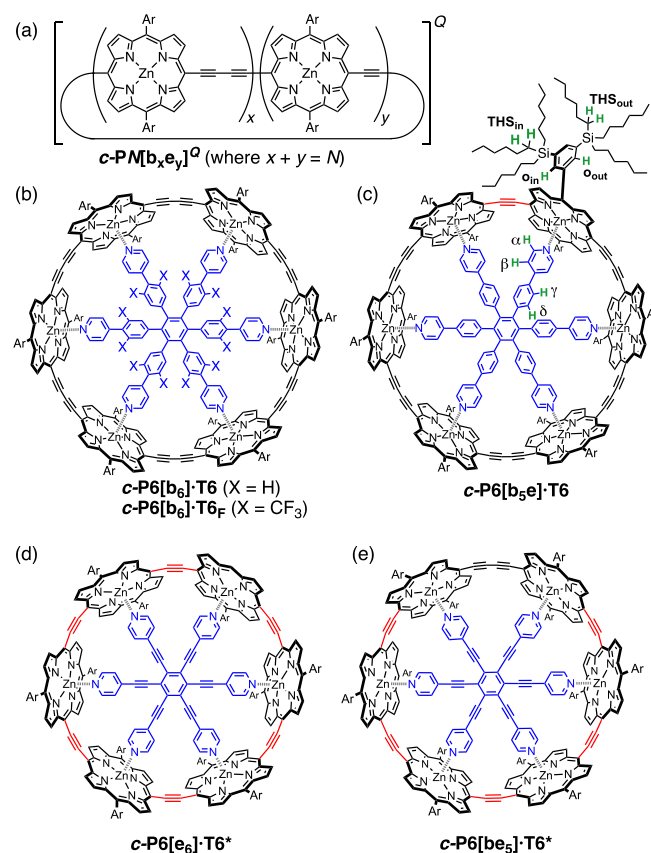


Figure 1. Structures of porphyrin nanorings. (a) General structure for the family of nanorings; Q is the charge (oxidation state); N , x and y are the numbers of porphyrins, butadiynes and ethyne links, respectively. (b)–(e) Structures of six-porphyrin nanoring template complexes. The key ¹H NMR resonances labeled in (c) apply to all the nanoring complexes. All Ar groups are 3,5-bis(trihexylsilyl)phenyl.

Table 1. Selected ^1H -NMR chemical shift differences for **c-P6[b₆]-T6^Q** (in ppm).

Q	method	$\delta(\text{O}_{\text{in}}) - \delta(\text{O}_{\text{out}})$	$\delta(\text{THS}_{\text{in}}) - \delta(\text{THS}_{\text{out}})$	$\Delta\delta(\alpha)$	$\Delta\delta(\beta)$	RMSE ^[a]
0	experimental	0.26	0.00	-6.31	-2.34	—
	CAM-B3LYP ^[b]	0.09	—	-6.34	-2.54	0.15
	B3LYP ^[b]	0.31	—	-5.34	-1.97	0.60
	LC- ω hPBE ^[c]	0.39	—	-5.24	-2.00	0.65
	BLYP35	0.44	—	-5.79	-2.31	0.32
+4	experimental	—	3.93	14.2	12.6	—
	CAM-B3LYP ^[b]	0.41	—	-1.92	-0.44	14.6
	B3LYP ^[b]	36.36	—	60.4	49.1	41.7
	LC- ω hPBE ^[c]	4.27	—	4.80	4.96	8.53
	BLYP35	8.56	—	12.1	10.8	1.93
+6	experimental	-1.87	-0.73	-2.83	-2.06	—
	CAM-B3LYP ^[b]	-0.19	—	-0.97	-0.36	1.74
	B3LYP ^[b]	-7.23	—	-12.3	-9.85	7.71
	LC- ω hPBE ^[c]	-1.03	—	-2.53	-1.54	0.60
	BLYP35	-1.17	—	-1.99	-1.37	0.75
+12	experimental	-0.74	-0.16	2.77	1.50	—
	CAM-B3LYP ^[b]	-0.91	—	1.88	1.13	0.57
	B3LYP ^[b]	-2.67	—	5.63	2.68	2.10
	LC- ω hPBE ^[c]	-2.76	—	5.33	2.67	2.00
	BLYP35	-1.53	—	3.09	1.64	0.50

[a] The root-mean square error (RMSE) values are calculated from the $\Delta\delta$ shown in this table and are with respect to experiment. [b] Data from Matito and coworkers.^[9] [c] $\omega = 0.1$.

These effects are opposite for an antiaromatic ring. Negative values of $\Delta\delta(\alpha)$ and $\Delta\delta(\beta)$ indicate either a local aromatic ring current in each porphyrin unit, or a global ring current around the whole nanoring. In contrast, the differences $\delta(\text{O}_{\text{in}}) - \delta(\text{O}_{\text{out}})$ and $\delta(\text{THS}_{\text{in}}) - \delta(\text{THS}_{\text{out}})$ are less affected by local ring currents and large negative (or positive) values of these parameters indicate the presence of global (anti)aromatic ring currents. The pattern of shielding in Table 1 indicates that $Q = 0$ has locally aromatic porphyrin units, but no global ring current; $Q = +4$ has a global antiaromatic ring current, $Q = +6$ is globally aromatic and $Q = +12$ is locally antiaromatic. This qualitative interpretation of the experimental data is fully supported by the correlation of $\Delta\delta$ values with ring current geometric factors, from the Biot-Savart law, as discussed below.^[8]

Matito and coworkers^[9] compared our experimental ^1H NMR chemical shifts for **c-P6[b₆]-T6^Q** with those that they calculated using two different functionals, B3LYP and CAM-B3LYP.^[10a,b] The chemical shifts calculated using CAM-B3LYP are closer to the experimental values, and this functional does not predict global (anti)aromaticity. Although the NMR spectra predicted by

CAM-B3LYP are indeed closer to experiment than B3LYP, the agreement is still poor, especially for the chemical shifts most important for aromaticity (Table 1). It is well-known that hybrid density functional approximations (DFAs, often simply referred to as “functionals”) with a low proportion of exact (Hartree-Fock) exchange, like B3LYP, tend to exaggerate the delocalization of electrons owing to the self-interaction error.^[10d,11] Range-separated functionals like CAM-B3LYP and LC- ω hPBE vary the amount of exact exchange as a function of distance and can substantially correct this problem. Table 1 shows that other DFAs — namely BLYP35 and LC- ω hPBE ($\omega = 0.1$)^[10c,d] — predict ^1H NMR chemical shifts that match experimental values better than either B3LYP and CAM-B3LYP. We used the 6-31G* basis set for all of our calculations, as did Matito and coworkers, and we used the Gaussian16 program.^[10e-i] When considering the data in Table 1, we focus on the $Q = +4$ and $+6$ oxidation states, because these are the systems with indications of global ring currents.^[2] In **c-P6[b₆]-T6⁴⁺**, CAM-B3LYP completely fails to reproduce the sign or magnitude of the shifts $\Delta\delta(\alpha)$ and $\Delta\delta(\beta)$, while B3LYP grossly exaggerates these shifts; only BLYP35 predicts shifts that are close to experimental values. Similarly with **c-P6[b₆]-T6⁶⁺**, BLYP35 reproduces the experimental chemical shifts better than CAM-B3LYP or B3LYP. The emerging picture is that whereas B3LYP over-estimates the extent of (anti)aromaticity, CAM-B3LYP goes the other way, and fails to reproduce important features of the experimental data. If we compare all the experimental ^1H NMR resonances (SI Table S3), we again find that BLYP35 gives the best match to experiment. The success of BLYP35 in describing the behavior of partially oxidized nanorings is perhaps not surprising, because this DFA was originally developed to model organic mixed-valence systems.^[10c,12]

Matito and co-workers supported their choice of functional by noting that the geometry found by B3LYP was significantly different to those calculated using CAM-B3LYP, M06-2X, and LC- ω hPBE ($\omega = 0.2$). Unfortunately, experimental geometries are not available for any of the oxidized nanorings. Matito and coworkers used single-point calculations at the DLPNO-CCSD(T) (domain localized pair natural orbital, coupled-cluster singles doubles and perturbative triplets) level to compare the energies of calculated geometries from different DFAs. Even with this method's excellent scaling behavior, only relatively modest basis sets are affordable for the nanorings (Matito and coworkers used def-SVP/C). Recent studies have suggested that DLPNO-CCSD(T) may struggle to describe systems with unusual electronic delocalization, such as some Möbius expanded porphyrins.^[13] We argue that the DFA is best selected by comparison to an experimental observable that is relevant to the problem at hand — for this problem the most relevant data are NMR chemical shifts, and we are fortunate to have a wealth of experimental results on this family of compounds.

Having shown that the experimental ^1H NMR data are modeled well by BLYP35, the next point to check is whether this DFA predicts global ring currents in **c-P6[b₆]-T6⁴⁺** and **c-P6[b₆]-T6⁶⁺**. One way to answer this question is to compute a grid of NMR shielding around the molecule, known as a NICS grid.^[14] The plots of NICS(0)_{iso} and NICS(0)_{zz} in Figure 2 indicate there is indeed a global paratropic ring current in the $+4$ state and a global diatropic current in the $+6$ state.^[2,5,8]

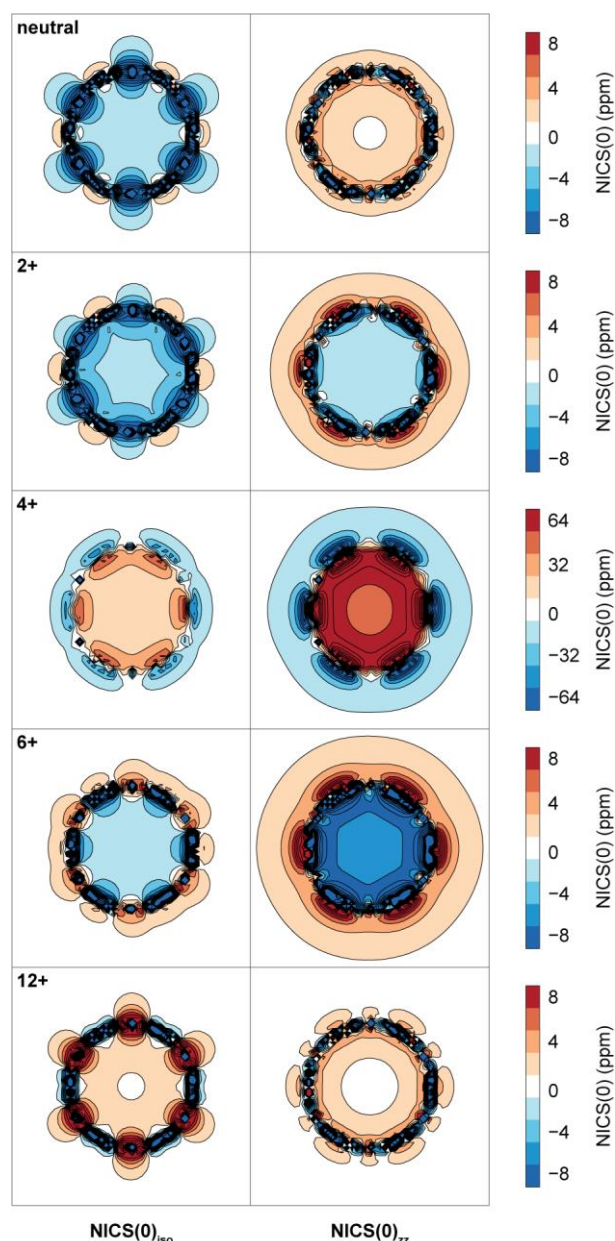


Figure 2. Plots of $\text{NICS}(0)_{\text{iso}}$ and $\text{NICS}(0)_{\text{zz}}$ for $\text{c-P6}[\text{b}_6]^Q$ for $Q = 0, +2, +4, +6$ and $+12$ calculated using the BLYP35 functional. The calculation for $Q = +2$ assumes a symmetry-broken unrestricted singlet-state since this most closely matches the experimental NMR results.^[15]

We next turn to the question posed in the title of Matito and coworkers' article: "How aromatic are molecular nanorings?" Although there is no universally accepted method for quantifying aromaticity, one approach is to estimate the ring current susceptibility (in nA/T, i.e. the magnitude of the ring current (in nA) that would be induced by an external field of 1 T^[8,16] (sometimes called 'ring current strength'^[17]). If we can identify a NMR chemical shift difference, $\Delta\delta$, that is attributable to a ring current effect, then we can estimate the magnitude of that ring current using equation (1)^[8]

$$\Delta\delta = (I/B) \text{RCGF} \quad (1)$$

where I is the current, B is the external magnetic field, I/B is the ring current susceptibility and RCGF is the ring current

geometric factor, which is calculated from the molecular geometry using the Biot-Savart law, and which quantifies the sensitivity of a given point in space to the induced magnetic field of the ring current.^[18] This method allows us to quantify the ring current susceptibility using either experimental or calculated NMR chemical shifts. The consistency between experiment and theory (BLYP35) is illustrated in Figure 3a. We adopt the convention that diatropic ring currents have negative sign, and paratropic positive. The ring current susceptibilities are consistent with global aromaticity in the $Q = +2$ and $+6$, and antiaromaticity in the $Q = +4$, oxidation states of $\text{c-P6}[\text{b}_6] \cdot \text{T6}^Q$, in accord with Hückel's rules. Figure 3b illustrates how the predicted ring-current susceptibility for $\text{c-P6}[\text{b}_6] \cdot \text{T6}^{6+}$ varies with different DFAs and their proportion of Hartree-Fock exchange.

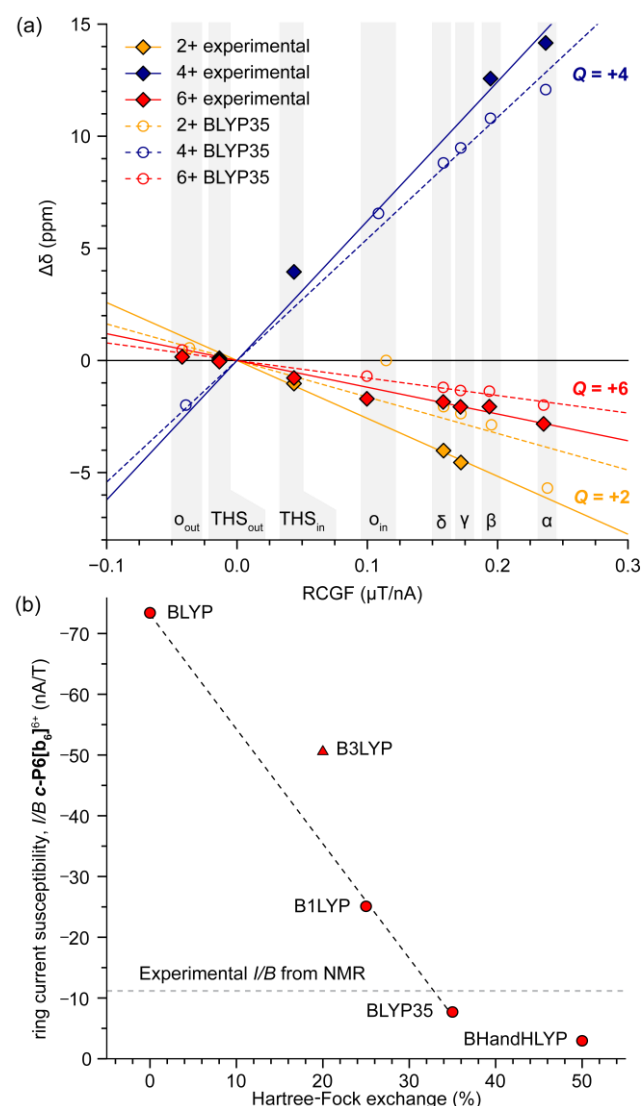


Figure 3. (a) Plot of $\Delta\delta$ vs. RCGF for $\text{c-P6}[\text{b}_6]^Q$ ($Q = +2, +4$ and $+6$) showing experimental points and BLYP35 calculated points. The DFT data for $Q = +2$ show a relatively poor fit to the Biot-Savart model, probably reflecting deficiencies in the DFT treatment of this oxidation state.^[15] (b) Plot of predicted ring current susceptibility (I/B) against the fraction of Hartree-Fock exchange included in the DFA for $\text{c-P6}[\text{b}_6]^{6+}$.

The changes in chemical shift for the other six-porphyrin nanorings, **c-P6[e₆]-T6^{*Q}**, **c-P6[b₆e₅]-T6^{*Q}** and **c-P6[b₅e]-T6^Q** also match well with the predictions from DFT calculations using BLYP35 (see Table 2 and details in Supporting Information). There is a clear alternation between shielding ($\Delta\delta < 0$) of template protons when the Hückel π -electron count is $N_e = 4n + 2$, and deshielding ($\Delta\delta > 0$) when $N_e = 4n$. Adding or removing a C≡C unit changes the electron count by 2 and changes the direction of the global ring current (diatropic vs. paratropic) in agreement with the predictions of Hückel's rule (Table 2 and Figure 4). If each nanoring had six local ring currents, rather than one global ring current, then we could not explain why changing the Hückel electron count by $\Delta N_e = 2$ reverses the shielding pattern for the whole nanoring. The periodicity of the shielding with respect to the Hückel electron count N_e provides the strongest evidence for global ring currents (Figure 4).

Table 2. Experimental (and BLYP35-calculated) changes in chemical shift, in ppm, and ring current susceptibilities I/B in six-porphyrin nanorings.

species	$Q^{[a]}$	$N_e^{[b]}$	$\delta(\alpha_{in}) - \delta(\alpha_{out})$	$\Delta\delta(\alpha)$	$\Delta\delta(\beta)$	I/B (nA/T)
c-P6[e₆]-T6[*]	+2	70	-5.92 (-8.30)	-16.0 (-21.3)	-11.0 (-15.8)	-55 (-76)
	+4	68	— (5.67)	27.3 (8.13)	22.7 (7.02)	111 (35)
	+6	66	-2.43 (-1.03)	-4.40 (-2.13)	-3.13 (-1.89)	-17 (-8.9)
c-P6[b₆e₅]-T6[*]	+4	70	— (-4.57)	-15.2 (-11.3)	-11.1 (-8.72)	-59 (-43)
	+6	68	— (1.06)	2.80 (1.93)	2.68 (1.50)	12 (7.8)
c-P6[b₅e]-T6	+4	78	— (-6.36)	-14.0 (-14.0)	-10.2 (-10.4)	-57 (-54)
	+6	76	— (0.61)	2.17 (1.16)	1.92 (1.20)	9.5 (5.3)
c-P6[b₆]-T6	+2	82	— (-0.56)	— (-5.69)	— (-2.87)	-26 ^[c] (-16)
	+4	80	— (8.56)	14.2 (12.1)	12.6 (10.8)	62 (54)
	+6	78	-1.87 (-1.17)	-2.83 (-1.99)	-2.06 (-1.37)	-12 (-7.8)

[a] Data for the neutral nanorings ($Q = 0$) are not shown here because they only exhibit local ring currents, but their experimental $\Delta\delta$ values are also well reproduced using BLYP35, see SI. [b] N_e is the number of π -electrons in the Hückel circuit around the macrocycle. [c] The experimental I/B for **c-P6[b₆]-T6²⁺** comes from the measured $\Delta\delta(\gamma)$ and $\Delta\delta(\delta)$ values.

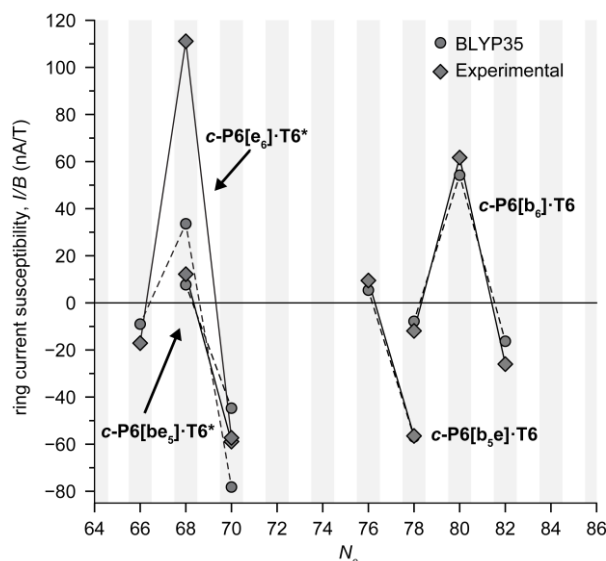


Figure 4. Relationship between ring current susceptibility (I/B) and π -electron count showing calculated points from BLYP35 and values derived from experimental NMR data for the full set of six-porphyrin nanorings from Figure 1 (b)–(e) in various positive non-zero oxidation states.

In conclusion, we have shown that the experimental NMR chemical shift changes, $\Delta\delta$, in six-porphyrin nanorings, in a range of oxidation states, are well reproduced by DFT calculations using hybrid exchange-correlation functionals such as BLYP35. The variation in magnetic shielding as a function of the Hückel electron count N_e across the whole family of nanorings provides compelling evidence for the presence of global ring currents. Although the ring current susceptibilities of **c-P6[b₆]-T6^Q** from both experimental data and BLYP35 are small compared with those from B3LYP, they are still larger than the value for benzene ($I/B \approx 11$ nA/T).^[8,16,17] It would be wrong to say that these species show negligible global aromaticity.

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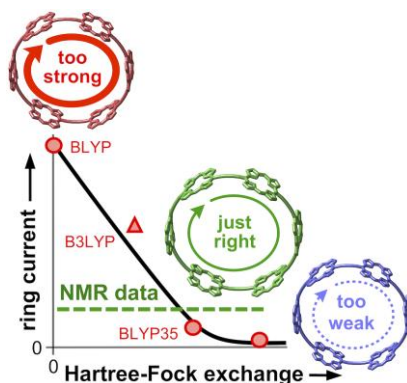
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Keywords: aromaticity • macrocycles • density functional theory • porphyrins • ring current

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- [15] No DFT calculations have been previously reported on the dication, **c-P6[b₆]²⁺**, and species of this type with low values of *Q/N* might be expected to have open-shell character. We found that when we computationally treated **c-P6[b₆]-T6²⁺** in the same way as the other oxidation states, as a closed-shell singlet, BLYP35 dramatically overstated the aromaticity (SI Figure S8). On the other hand, the triplet state resulted in antiaromaticity, consistent with Baird's rule but contrary to experiment. A broken-symmetry unrestricted singlet-state calculation resulted in NMR chemical shift differences in relatively close agreement to experiment (SI Table S12). While this result is useful for connecting experimental observables to computational metrics of aromaticity (e.g. the NICS in Figure 3), we emphasize that our computational study of the dication is limited in scope and completeness, owing to the huge size of the system. Furthermore, the spin state and temperature-dependence of this system has not yet been explored experimentally.
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Entry for the Table of Contents



To be or not to be like benzene? Porphyrin nanoring template complexes provide a wealth of experimental NMR spectroscopy data, which are sensitive to global ring currents and which can be used to answer this question. Both experiment and theory confirm that nanoring cations are globally (anti)aromatic based on magnetic shielding evidence, and consistent with Hückel's rule.

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