University of Groningen

Periodoannulenes

Fowler, Patrick W.; Havenith, Remco W.A.

Published in:
Journal of Physical Chemistry A

DOI:
[10.1021/acs.jpca.1c03170](https://doi.org/10.1021/acs.jpca.1c03170)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2021

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Fowler, P. W., & Havenith, R. W. A. (2021). Periodoannulenes: A Generalized Annulene-within-an-Annulene Paradigm for Combined σ and π ring Currents. *Journal of Physical Chemistry A*, 125(29), 6374-6383. <https://doi.org/10.1021/acs.jpca.1c03170>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Periodoannulenes: A Generalized Annulene-within-an-Annulene Paradigm for Combined σ and π Ring Currents

Published as part of *The Journal of Physical Chemistry virtual special issue "Alexander Boldyrev Festschrift"*.

Patrick W. Fowler* and Remco W.A. Havenith

Cite This: *J. Phys. Chem. A* 2021, 125, 6374–6383

Read Online

ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Periodoannulene molecules and ions $C_xI_x^q$ in planar geometry offer examples of systems with the potential for outer σ and inner π ring-current double aromaticity, given a sufficient overlap of tangential p_σ -orbital manifolds on the large atoms of the outer cycle. Previous theoretical work indicated concentric diatropic currents in the dication $C_6I_6^{2+}$. Ab initio ipsocentric calculations support an account in terms of frontier-orbital selection rules for current contributions in $C_6I_6^{2+}$ (and radical $C_6I_6^+$, implicated in recent experimental work on the oxidation of *periodobenzene*). A σ/π analogue of the annulene-within-an-annulene model is applied here to *periodo* systems based on cyclooctatetraene. Model species $C_8I_8^q$ with charges $q = 0, +1, +2, +4, -2$ and structures constrained to a planar D_{4h} symmetry exhibit maps with all combinations of σ/π con- and counter-rotation, comprising global σ ring currents on the iodine perimeter and central π ring currents on the carbocycle. All can be rationalized by the separate application of the tropicity selection rules to the two subsystems, whether in singlet or triplet states.

1. INTRODUCTION

Aromaticity in all its manifold variations¹ has engaged the attention of chemists for many decades and has figured prominently in the work of Boldyrev and his collaborators for several of those.^{2–14} “Double aromaticity”¹⁵ is a recurring term in the literature,¹⁶ where it is usually associated with a combination of σ and π aromaticities, as diagnosed by electron counting, delocalization, enhanced stability, or characteristic magnetic properties.¹⁷ The recent full characterization of the hexakis(phenylselenenyl)benzene dication is claimed as the first example of a bench-stable double aromatic.¹⁶ A second example has now appeared.² The present article returns to some systems of earlier interest as possible experimental realizations of double aromaticity. We deal with a theoretical puzzle about aromaticity in substituted benzenes that was apparently solved, then “unsolved” by further experimental evidence. Where there is aromaticity, there is also the possibility of antiaromaticity,¹⁸ and our main focus here is on the possibility of a system that exhibits mixed aromaticity and antiaromaticity. We describe a new application of the annulene-within-an-annulene (AWA) model,^{19–27} which was originally devised for a qualitative description of the electronic structure of polycyclic hydrocarbons, where the carbon skeleton consists of two concentric cycles (an inner “hub” and an outer “rim”) connected by radial bonds (“spokes”). It has been used to discuss the π aromaticity of these and related systems from the perspective of magnetic properties, where it performs with varying degrees of success.^{25–32} One natural question concerns the relative sense of rim and hub ring

currents (if any) in such molecules. A crucial factor in predicting this feature of the current-density map is the strength of the coupling between rim and hub, as supplied by the spoke bonds;^{21,31,32} when this coupling is significant AWA cannot be trusted to give even qualitatively correct results,²¹ as the archetypal examples of coronene and corannulene amply demonstrate.³⁰

An extension of the AWA idea, which does not seem to have been remarked as such, is to systems with “double aromaticity”, where ring currents arise separately in σ and π orbital manifolds. In this case, direct coupling of σ and π systems is ruled out by symmetry, and a prediction of the current direction can be expected to follow established selection rules based on orbital occupancy and nodal character within each manifold. Orthogonality, in the sense of a symmetry separation of the two orbital subsystems,¹⁵ was behind the specific proposals^{33,34} for double aromaticity in *periodobenzene*, but it has an even simpler manifestation in magnetically active single cycles. For example, the systematics of ring currents in bare all-carbon cycles^{35,36} can be seen in the light of AWA, as a hub of p_π orbitals supporting the conventional central π current, and a

Received: April 8, 2021

Revised: June 30, 2021

Published: July 19, 2021

rim of radial p_σ orbitals supporting a σ current around the molecular perimeter. In this case, the two “annulene” rings occupy the same physical space, as there is only one cycle of nuclei, but the two manifolds are by definition orthogonal. Furthermore, calculations indicate that the relative sense of the two currents may be tuned by, for example, donation of electrons from an encapsulated metal center.³⁷ The relative occupancy of the two manifolds is determined by orbital energies, and the current maps for the subsystems are well-described by the separate use of principles developed for conventional annulenes π systems.³⁸ Here, the symmetry-enforced orthogonality provides the factor to weaken the coupling of the two manifolds, giving an ideal situation for an application of the AWA model.²¹ The identification of spatially separated “radial” and “tangential” currents for hypothetical boron toroidal shells is also consistent with an extended AWA-type rationale.³⁹

Another class of systems that has usually been treated in a different way, but for which the AWA analogy also supplies a useful schematic description, consists of *periodobenzene* and its ions (and potentially other [n]annulene analogues). The underlying idea is that the iodine ligands have a poor π overlap with the 2p orbitals of the central carbon atoms and do not interfere with the central π current but have a significant σ tangential overlap around the molecular perimeter through their 5p orbitals, potentially allowing a σ delocalization^{33,34} and σ current¹⁷ (perimeter current⁴⁰) to develop. We first review the checkered history of this idea for the hexaiodobenzene molecule and its ions and then in the main body of the paper extend the calculations to *periodoannulenes* with an antiaromatic core, as instantiated by C_8I_8 and its ions. This leads to a verification of the σ/π AWA rules for (constrained) antiaromatic systems.

The putative double aromaticity of *periodo*[6]annulenes has been studied for several decades. The dication of hexaiodobenzene is often quoted as an example of a molecular system where nonbonding interactions on the outside of a molecule give a σ contribution to aromaticity, over and above the usual π aromaticity of the central carbon ring. The species $C_6I_6^{2+}$ was assigned in early experiments^{33,34} as a reaction product of oxidation of hexaiodobenzene, and it is true that a structure with D_{6h} symmetry corresponds at various levels of theory^{17,34,40–42} to a local minimum on the potential energy surface for this ion.

The hexaiodobenzene dication is predicted by ipsocentric calculations to show concentric rim-and-hub σ and π diatropic ring currents induced by an external magnetic field directed along the principal symmetry axis and, hence, double aromaticity in the magnetic sense.¹⁷ In ipsocentric calculations,^{43–47} the problems associated with the gauge dependence of magnetic properties computed in finite basis sets are sidestepped by taking the origin for a calculation of the current at any point in molecular space as that point itself (or, for points very close to a nucleus, at the nearest nucleus). This approach to current mapping has decisive advantages in terms of economy, accuracy, and interpretability, and it leads to simple selection rules based on an orbital nodal character that predict and rationalize diatropic and paratropic currents.^{38,45} The pattern of distribution of current in the dication is also consistent with calculations in approaches that do not make the breakdown into orbital contributions,⁴⁰ though we would contend that interpretability is always an advantage.

The origin of the extra aromaticity in the D_{6h} -symmetric $C_6I_6^{2+}$ molecule is clear in the frontier-orbital model for single annulene rings that derives from an ipsocentric calculation of ring current.³⁸ Just as the central diatropic current around the benzene ring arises from a four-electron virtual excitation from the (e_{1g}) π highest occupied molecular orbital (HOMO) to the (e_{2u}) π lowest unoccupied molecular orbital (LUMO), which increases the number of angular nodes by one, so an outer current in the σ system arises from a four-electron virtual excitation from the (e_{1u}) σ HOMO to the (a_{2g}) σ LUMO, which corresponds to an increase by one in the number of angular nodes and is therefore also diatropic. This latter excitation would be blocked in the neutral species, where the a_{2g} orbital is doubly occupied. It would also be expected to become much less effective in producing a current in the series of dicationic species $C_6X_6^{2+}$, where iodine is replaced by smaller halogen atoms $X = F, Cl, Br$, with a consequent reduction in the σ overlap.

However, recent synthetic work⁴⁸ casts doubt on the experimental identification of $C_6I_6^{2+}$, indicating instead that a vigorous oxidation of hexaiodobenzene produces salts of the radical monocation $C_6I_6^+$. Molski et al. state that “Taken together, our crystallographic and spectroscopic results led us to conclude that the $[C_6I_6]^{2+}$ dication remains an unknown species”.⁴⁸ These authors note that the monocation salts have only very broad electron spin resonance (ESR) signals, so that an apparent lack of the ESR spectrum is not necessarily a reliable indication of a closed-shell species. Interestingly, it is also found^{48,49} that, unlike cognate species $C_6F_6^+$, $C_6Cl_6^+$, and $C_6Br_6^+$, the ion $C_6I_6^+$ does not exhibit a Jahn–Teller distortion in the solid state. This is consistent with calculations. As for the cases of the neutral and the dication, the calculations agree with previous work in indicating a molecular structure for $C_6I_6^+$ that retains the full D_{6h} symmetry,⁴⁸ with half-filling of the (a_{2g}) σ singly occupied molecular orbital (SOMO) that was formerly the dication σ LUMO and the σ HOMO in the neutral. This molecular orbital (MO) is iodine-centered, as expected from relative electronegativities,⁴⁸ and it represents the formally fully antibonding combination of a ring of tangentially overlapping p_σ lone-pair orbitals. The non-degeneracy of the SOMO is consistent with the lack of a Jahn–Teller geometric distortion of the ring. Interestingly, therefore, this open-shell monocationic species should also sustain a diatropic perimeter ring current arising from the same virtual excitation as in the putative dication, although now it would be attributable to only two of the electrons of the $(e_{1u})^4$ set, under the spin selection rule implied by analogy with an ipsocentric ring-current interpretation⁴⁷ of open-shell aromaticity according to Baird’s Rule.⁵⁰ Our orbital explanation fits well with the evidence from a calculation performed by Rauhalahhti et al.,⁴⁰ where “...the ring-current strength of $C_6I_6^+$ in the exterior part of the molecule is only half as strong as the one passing the iodines in $C_6I_6^{2+}$...”; approximate halving is indeed to be expected from the simplest one-electron picture in which orbital currents arise by a virtual excitation from occupied to empty (spin) orbitals (Figure 1). This expectation is borne out by our ipsocentric calculations (not reported here) on the D_{6h} $C_6I_6^+$.

Perhaps ironically, it turns out that the theoretical and computational arguments about double aromaticity of the probably as yet unsynthesized $C_6I_6^{2+}$ species apply equally to the experimentally characterized radical monocation $C_6I_6^+$.

Figure 1. An averaging rule for transitions in neutral, monocation, and dication charge states of species M related by a depletion of a nondegenerate HOMO. All three electron configurations have in common sets of Doubly Occupied and Double Unoccupied Molecular Orbitals (DOMO and DUMO, respectively) and differ only in the occupation of the nondegenerate frontier orbital. Virtual excitations from occupied to empty spin orbitals are shown as green arrows for α and orange for β . In a restricted open-shell calculation where orbital dependence on spin, occupation, and geometry is neglected, the set of transition integrals that produce current in M^+ is exactly the average of those for M and M^{2+} . Analogous reasoning would apply to the depletion of a g -fold degenerate HOMO in the sequence M , M^{g+} , M^{2g+} , where the middle species is high-spin.

However, an experimental verification of ring currents by their effects on NMR spectra is nontrivial for radicals.

An examination of the nodal character of the frontier orbitals in hypothetical species $C_6(EH)_6^{2+}$ ($E = S, Se, Te$)⁴⁰ suggests that a similar mechanism operates in the species with large chalcogen atoms, rationalizing the enhanced (negative) values of nucleus-independent chemical shift (NICS)-related quantities⁵¹ computed in that work. NICS can be a blunt instrument for the detection of details of a complicated magnetic response, as it gives only indirect information about the magnetically induced ring current, whereas current density plots provide a qualitative picture of the entire current flow and a transparent partition into separate σ and π orbital contributions.³⁸ This point has often been noted^{29,52} and has a compelling theoretical justification within ipsocentric theory.⁵³ Nonethe-

less, the observed trend to negative NICS values of a larger absolute value in these molecules is consistent with the presence of conrotatory currents.

The reasoning behind Figure 1 applies to any situation where three species differ solely by changes in the occupancy of a degenerate or nondegenerate HOMO (full, to high-spin half-full, to empty). Note that, in more general cases, predictions based on the reasoning illustrated in Figure 1 are complicated by the need to allow for current from intra-HOMO excitations and Jahn–Teller effects on an electron configuration at intermediate occupancies. An interesting generalization of the Hückel–Baird rules that allows explicitly for situations in which tropicities of α and β spin subsystems differ has been proposed by Mandado et al.⁵⁴

We turn now to a different direction of generalization of the hexaiodobenzene example, moving on from a $[4N+2]$ to a $[4N]$ annulene core based on cyclooctatetraene (COT) to explore some possibilities for reinforcing or conflicting aromaticities of central and perimeter cycles in the σ/π version of the AWA model.

2. METHODS AND COMPUTATIONAL DETAILS

For consistency with the previous work, geometry optimizations of C_8I_8 (**1**), $C_8I_8^{2+}$ (1^{2+}), $C_8I_8^{4+}$ (1^{4+}), $C_8I_8^{2-}$ (1^{2-}), and $C_8I_8^+$ (1^+), all initially constrained to the plane in D_{4h} symmetry, were performed first with the Hartree–Fock (HF) method using the 6-311G* basis with GAMESS-UK.⁵⁵ Calculations were performed at the unrestricted Hartree–Fock (UHF) level for the radical species $C_8I_8^+$, as were checks for triplet ground states for the even-electron systems. Stationary points were characterized as saddle points of a higher order by frequency calculations. Unconstrained geometry optimizations at the same level were also performed in order to find the local minima. As expected from the presence of so many modes with an imaginary frequency in D_{4h} symmetry, the final geometries were all far from planar. D_{4h} -constrained optimizations of all species were repeated at the density functional theory (DFT) level, using the B3LYP functional with the same basis. Further calculations to check discordant predictions of the ground-state electron configuration for C_8I_8 (**1**) and $C_8I_8^+$ (1^+) were then performed with several functionals of different types. To check for relativistic effects on ground-state preferences, optimizations for **1** and 1^+ were made with the same sets of functionals in the ZORA

Table 1. Total Energies, C–C/C–I Bond Lengths R , I–I Distances d , and Counts of Imaginary Frequencies $N(\text{imag})$ of D_{4h} -Constrained and Fully Optimized HF Geometries of **1** and Its Ions^a

species	energy (au)	$R(\text{C–C})$ (Å)	$R(\text{C–I})$ (Å)	$d(\text{I–I})$ (Å)	$N(\text{imag})$
C_8I_8 (D_{4h}), S	–55 636.976 157	1.358, 1.574	2.232	3.170, 3.178	5
C_8I_8 (D_{2d}), S	–55 637.341 140	1.326, 1.492	2.117	3.947, 3.743	0
$C_8I_8^+$ (D_{4h}), D	–55 636.953 245	1.350, 1.550	2.198	3.128, 3.136	5
$C_8I_8^{2+}$ (C_1), D	–55 637.241 207	1.340, 1.349, 1.368, 1.415, 1.456, 1.484, 1.491, 1.496	2.069, 2.080, 2.101, 2.104, 2.106, 2.106, 2.110, 2.113	3.962, 3.826, 4.079, 3.714, 3.808, 3.745, 4.029, 3.776	0
$C_8I_8^{2+}$ (D_{4h}), S	–55 636.397 917	1.342, 1.528	2.170	3.092, 3.100	4
$C_8I_8^{2+}$ (C_2), S	–55 636.570 967	1.325, 1.330, 1.426, 1.490, 1.496	2.098, 2.111, 2.113, 2.170, 2.234	3.751, 3.932, 3.597, 2.764, 3.965	0
$C_8I_8^{4+}$ (D_{8h}), S	–55 635.245 544	1.442	2.151	3.088	6
$C_8I_8^{4+}$ (C_1), S	–55 635.406 653	1.346, 1.375, 1.346, 1.432, 1.438, 1.461, 1.467, 1.491	2.016, 2.069, 2.087, 2.119, 2.126, 2.140, 2.145, 2.156	3.758, 3.746, 4.083, 4.061, 3.649, 2.962, 2.889, 3.497	0
$C_8I_8^{2-}$ (D_{8h}), S	–55 637.013 015	1.443	2.278	3.186	5

^aThe optimized neutral species has two distinct C–C bond lengths; for the optimized ions all distinct C–C and C–I bond lengths and I–I distances are quoted. Labels S, D, and T refer to singlet, doublet, and triplet states. Imposition of D_{4h} constraints leads to structures with the higher D_{8h} symmetry in two cases. The dianion undergoes fragmentation on release of the symmetry constraint.

approximation using the Amsterdam AMS2020.101/103 suite.^{56–58} In these calculations, nonrelativistic and relativistic geometries were optimized in D_{4h} symmetry, using the built-in TZP basis (without frozen cores) with each functional. Cartesian coordinates (HF and B3LYP), calculations with multiple functionals, and singlet-triplet energies are reported in Tables S1–S4.

The induced current density for each system in the best planar geometry was calculated and mapped using the ipsocentric CTODD-DZ method for the D_{4h} -constrained geometries at coupled Hartree–Fock and DFT levels (HF/6-311G* and B3LYP/6-311G*) with GAMESS-UK⁵⁵ and SYSMO.⁵⁹ In the maps, the external magnetic field is directed along the normal to the molecular plane. The total ($\sigma + \pi$) induced current density is plotted in a parallel plane $1a_0$ above the molecular plane. This suffices to capture the patterns of out-of-plane π and in-plane σ circulation. Arrows in the plots correspond to the projection in the plotting plane of the induced current per unit external field. For interpretation, total-current maps are partitioned into contributions from subsets of molecular orbitals, following our usual procedure.⁴⁵ In the maps, a counterclockwise (clockwise) circulation about a center corresponds to a diatropic (paratropic) current ring-current, where a global diatropic/paratropic circulation in a monocycle corresponds to aromaticity/antiaromaticity.

3. RESULTS

3.1. Geometries and Electronic Configurations.

3.1.1. Hartree–Fock Calculations. None of the D_{4h} -constrained geometries proved to be minima, as indicated by presence of imaginary frequencies (Table 1). The HF electronic configuration for neutral **1** (Figure 2) is the singlet ($\dots$) $(9b_{2u})^2 (42e_u)^4 (20a_{2g})^2$, which we will call Configuration A. The nearest triplet state found is predicted to lie some 1.6 eV higher in energy (Table S4). In the ion 1^{2+} , two electrons are lost from the $20a_{2g}$ orbital, and on further ionization to 1^{4+} the electrons are lost from $9b_{2u}$, leaving in the singlet state an $(e_u)^4 \sigma$ -HOMO and $(e_g)^4 \pi$ -HOMO. However, the HF ground

Figure 2. Frontier-orbital energy-level diagram for the neutral D_{4h} -constrained C_8I_8 (**1**). Occupation and orbital order are consistent with ground-state electronic configuration A (HF and RS DFT methods). Labels indicate irreducible representation, position in energy order for the given representation, σ/π character, and localization on C or I. Broad arrows show virtual excitations of translational (T) and rotational (R) symmetries, i.e., potential diatropic and paratropic contributions. Excitations are active in configurations where initial and final levels contain an electron and a hole of the same spin.

state for 1^{4+} in D_{4h} symmetry turns out not to be a singlet. A triplet lying 2.3 eV lower was identified in UHF calculations (Table S4), though the fully relaxed structure appears to have a singlet ground state. In the lowest-energy structure of ion 1^{2-} , the $9b_{1u}$ orbital, the LUMO+1 of **1**, is doubly occupied.

In 1^{2+} small reductions are seen in the C–C bond alternation and C–I bond length. For 1^{4+} and 1^{2-} under D_{4h} constraints, the C–C bond lengths equalize, and the symmetry rises to D_{8h} . For comparison with the geometric data in Table 1, bond lengths in C_6I_6 from a crystallographic determination⁶⁰ are 1.402 Å (C–C) and 2.108 Å (C–I) (implying a distance $d(I-I)$ of 3.51 Å). An unconstrained optimization of **1** leads to a D_{2d} -symmetric geometry, with a shortening of all bonds as the symmetry-enforced steric strain of the planar structure is released.

The structure of the minimum energy for 1^{2+} has C_2 symmetry (Figure 3a), and for 1^{4+} it has C_1 symmetry (Figure

Figure 3. HF/6-311G* optimized structures of (a) 1^{2+} and (b) 1^{4+} (singlet configurations). Top-down and side-on views are shown in each case. Bond length annotations are in angstroms.

3b). Clearly, these structures are far from planar. A spin contamination in the UHF wave function is low for the D_{4h} structure of the monocation ($\langle S^2 \rangle = 0.787$). When released from D_{4h} constraints, 1^+ optimizes to a structure with a trivial symmetry. However, the attempted optimization of the dianion led to fragmentation, perhaps unsurprisingly.

3.1.2. DFT (B3LYP) Calculations. As a routine check, optimizations were rerun under D_{4h} symmetry constraints (Table S2). For C_8I_8 (**1**) and $C_8I_8^+$ (1^+), the predicted singlet ground-state electron configurations differ between HF and B3LYP. For the neutral species, the ground-state electronic configuration with the B3LYP functional was found to be ($\dots$) $(9b_{2u})^2 (42e_u)^4 (23a_{1g})^2$. We call this Configuration B. It differs from A only by a swap in the symmetry of σ HOMO and LUMO. The separation between this singlet and a nearby triplet state is small (0.2 eV, Table S4). Likewise, the ion $C_8I_8^+$ has a doublet configuration corresponding to the loss of a HOMO electron from B. The spin contamination is again low for the D_{4h} structure of 1^+ ($\langle S^2 \rangle = 0.766$). The alternative candidates for the HOMO of **1** (and SOMO of 1^+) differ in both symmetry and orbital composition, though each orbital has a very similar appearance in both HF and DFT

calculations. The $20a_{2g}$ HOMO in A is the fully antibonding combination of tangential $5p_\sigma$ orbitals on iodine centers; the $23a_{1g}$ HOMO in B is instead the out-of-phase combination of separate all-bonding combinations of radial p_σ orbitals on carbon and iodine rings (Figure 1). The difference in orbital composition has consequences for currents, as does the need to consider triplet ground states. HF and B3LYP ground states are in agreement for $C_8I_8^{4+}$ (1^{4+}), where both methods give a triplet ($\cdots$) $(9b_{2u})^2 (42e_u)^2$, indicating an open shell in the iodine-based tangential subsystem (Table S4).

3.1.3. DFT Calculations with Diverse Functionals. As a further check, constrained optimizations were performed for ground-state configurations A and B for **1** and the corresponding doublet open shells for 1^+ (Table S3). Functionals of hybrid type give B as the ground state, but some Range-Separated functionals (LCY-PBE, CAM-B3LYP, wB97) give A as the ground state, in agreement with HF. An inclusion of relativistic effects via ZORA does not alter preferences, except for **1** with CAM-B3LYP, where configurations A and B are almost degenerate in the nonrelativistic approximation. These trends lead us to suspect that the true ground state for D_{4h} **1** is of type A and that the preference for type B shown by B3LYP and similar functionals is an artifact of their known tendency to overestimate delocalization and global aromaticity.^{61,62} It is also known that paratropic currents, which typically arise from virtual excitations across small gaps, as in Jahn–Teller split pairs, can be expected to be sensitive to these features of the functional.^{63,64}

3.2. Current-Density Maps. The keys to the interpretation of computed current maps for planar systems are the ipsocentric selection rules for virtual excitations, as introduced above.^{38,45} In particular, an excitation connects a level containing an electron with another containing a hole of the same spin. The symmetry product of the orbitals in the two levels must then contain the representation of an in-plane translation (for diatropic current) or the in-plane rotation (for paratropic current). For centrosymmetric systems, diatropic and paratropic current contributions obey a mutual exclusion rule. In D_{4h} symmetry, diatropic MO contributions to current can arise *only* from the pairing of a nondegenerate and a degenerate orbital of opposite parity (A or B with E), whereas paratropic MO contributions arise from AA, BB, or EE pairs that preserve parity and degeneracy but swap labels 1 and 2. Moreover, for an excitation to make a contribution to current, initial and final orbitals must have a significant amplitude in the same region of molecular space. Figure 2 indicates the key frontier-orbital transitions that can come into play for D_{4h} -constrained *periodocyclooctatetraenes*. Configuration A of the neutral is illustrated in the figure, but the same selection rules apply to B and other charge/spin states. We will be interested in virtual excitations within conventional p_π and tangential p_σ manifolds, all of which share a degeneracy structure derived from angular-momentum parentage sets and hence have simply related orbital symmetries. In D_{4h} the three sets of p orbitals associated with a ring of eight atoms with two distinct bond lengths span

$$\Gamma(p_\pi) = (A_{2u}) + (E_g) + (B_{1u} + B_{2u}) + (E_g) + (A_{1u})$$

$$\Gamma(p_\sigma, \text{radial}) = (A_{1g}) + (E_u) + (B_{1g} + B_{2g}) + (E_u) + (A_{2g})$$

$$\Gamma(p_\sigma, \text{tangential}) = (A_{2g}) + (E_u) + (B_{1g} + B_{2g}) + (E_u) + (A_{1g})$$

where brackets denote angular-momentum shells, ranked from low to high energy based on angular node counts.

3.2.1. Current-Density Maps for Neutral C_8I_8 . Taking the various charge states in turn, we begin with neutral C_8I_8 , **1**. Figure 4 shows the all-electron total, π -only, and shell

Figure 4. Maps of induced current density for the D_{4h} -constrained neutral, **1**, calculated at the coupled HF level of theory. (a) Total ($\sigma + \pi$) induced current density. (b) Contributions from carbocycle π orbitals. (c) The π -HOMO ($9b_{2u}$) contribution and (d) the contribution from the (σ) HOMO ($20a_{2g}$).

contributions to π current density from the π -HOMO ($9b_{2u}$) and σ -HOMO ($20a_{2g}$) (the system HOMO) in D_{4h} -constrained **1**, calculated with the HF wave function and configuration A. The total ($\sigma + \pi$) induced current density (Figure 4a) shows a complex pattern that includes a paratropic π ring current flowing around the cyclooctatetraene core, local diatropic circulations on C–I bonds, and local paratropic circulations where the $1a_0$ plotting plane slices through the iodine atomic distributions. We will see that this overall picture simplifies for cationic species, for symmetry reasons. The π -only plot (Figure 4b) isolates the paratropic ring current contribution from the occupied π MOs concentrated on the carbon skeleton, and comparison with the orbital contribution from the $9b_{2u}$ orbital (Figure 4c) shows that this π current is dominated by the π -HOMO contribution, dominated in turn by the rotationally allowed $b_{2u} \rightarrow b_{2g}$ virtual excitation (Figure 2). This is the exact analogue of the generation of the paratropic ring current in pristine flat cyclooctatetraene.^{37,43,55} Finally, as shown in Figure 4d, the outermost paratropic flow follows the pattern set in **1** by the orbital contribution of the (σ) -HOMO ($20a_{2g}$), arising from the rotationally allowed $a_{2g} \rightarrow a_{2u}$ virtual excitation (Figure 2). Hence, we have the clear prediction from HF (and, by implication, from DFT with functionals giving configuration A as the ground state) that (flattened) neutral **1** is σ/π doubly antiaromatic.

Given the different ground-state configurations in HF and B3LYP treatments, we may expect differences in current maps. Figure 5 shows B3LYP current maps evaluated at the optimum

Figure 5. Maps of induced current density for the D_{4h} -constrained neutral, **1**, calculated at the B3LYP/DFT level of theory (Configuration B). (a) Total ($\sigma + \pi$) induced current density. (b) Contribution from (σ) HOMO ($23a_{1g}$). (c) Contribution from tangential σ MOs $42e_u + 21b_{2g} + 21b_{1g}$.

geometry for ground-state B. Maps of the total current for A and B are different in that the “atomic” circulations of Figure 4a are much weaker in Figure 5a, which presents an appearance of concentric global currents. At the B3LYP level, the central carbocycle ring current is paratropic as before, but with enhanced intensity from the smaller gap characteristic of DFT. The σ -HOMO retains very weak locally paratropic atomic circulations (Figure 5b), but no significant global perimeter current. The perimeter supports a global diatropic current, from the four highest-lying iodine tangential MOs $42e_u + 21b_{2g} + 21b_{1g}$ (Figure 5c).

Symmetry sheds light on this qualitative distinction. To a first approximation, configurations A and B differ by a swap of HOMO and LUMO symmetries, with all other orbitals in common, but spatial distributions of HOMO and LUMO are essentially different, and energy gaps are generally smaller in DFT methods. Orbital symmetry products, on which the selection rules depend, predict that the HOMO–LUMO virtual excitation remains paratropic, virtual excitations from HOMO to ungerade degenerate LUMO+ orbitals remain diatropic, and excitations from lower doubly occupied orbitals to orbitals above the LUMO all retain their individual diatropic/paratropic/atropic character. What does change is that the virtual excitations from the e_u σ HOMO–1 pair to a_{2g} σ LUMO now become allowed and strong, as both are combinations of tangential σ orbitals. Diatropic excitations from the e_u pair (and lower orbitals) now dominate the σ perimeter current. Experience from NICS calculations^{51,65–67} suggests, however, that range-separated (RS) functionals will reverse the B3LYP predictions, bringing current maps back in line with HF predictions.

At present, we do not have a suitable program to test this conjecture by evaluation of ipsocentric current maps with functionals of the RS type. We can say that, for neutral C_8I_8 ,

HF and B3LYP DFT predictions are at odds about the sign of the perimeter current, but at both levels the molecule behaves as a σ/π AWA system obeying ipsocentric selection rules.

3.2.2. Current-Density Maps for Ions of $C_8I_8^q$, $q = +1, +2, +4, -2$. Figure 6 shows current maps for two D_{4h} -constrained

Figure 6. Maps of induced current density for the D_{4h} -constrained dication 1^{2+} and monocation 1^+ , calculated at the coupled HF level of theory. (a) Total ($\sigma + \pi$) induced current for the dication 1^{2+} . (b) Contribution to the induced current in 1^{2+} from the (σ) HOMO shell ($42e_u$). (c) Total ($\sigma + \pi$) induced current for the monocation 1^+ . (d) Carbocycle π current density for 1^+ . (e) Contribution to σ current density in 1^+ from the single α electron of the α -HOMO ($20a_{2g}$). (f) Contribution to σ current density in 1^+ from the two β electrons of the β HOMO–1 shell ($42e_u$).

cations. Figure 6a,b shows, respectively, the total induced current and the σ -HOMO ($42e_u$) shell contribution for 1^{2+} . This dication has well-separated ring currents (Figure 6a), for similar reasons as those for Configuration B. When the two electrons of the $20a_{2g}$ orbital are removed, the translationally allowed $42e_u \rightarrow 20a_{2g}$ virtual transition becomes available (Figure 2), giving rise to a strong diatropic contribution to the σ current arising from a tangential overlap of iodine p_σ orbitals (Figure 6b). The central paratropic π -current is not strongly affected by the removal of two σ electrons. The constrained 1^{2+} cation is therefore predicted to be an example of a system with a double tropicity: σ aromatic but π -antiaromatic. HF and B3LYP maps for 1^{2+} (Figure S1) are in essential agreement, as expected from their agreement on the D_{4h} -constrained ground state.

To complete the connection with the example of periodinated benzenes, Figure 6c–f presents maps for the constrained monocation 1^+ . Simple symmetry considerations for this nondegenerate case (Figure 1) suggest that the maps for frontier-orbital contributions to current should be rationalized as “averages” of those for **1** and 1^{2+} . To be precise, the α electron in the σ SOMO of 1^+ can still access the virtual excitation to the LUMO of the neutral (which gave rise to the σ paratropicity of **1**), but the β electrons of the σ shell immediately below can now access the $e_u \rightarrow a_{2g}$ virtual excitation, which gave rise to the strong diatropic σ current of 1^{2+} . Spin selection rules imply that both currents should persist but with a strength reduced by the halving of virtual excitation channels (Figure 1). The computed maps in Figure 6c–f bear out these expectations, with the system retaining the carbocycle paratropic current (Figure 6d) and with the weak σ current arising from the SOMO (Figure 6e) masked by the still relatively intense diatropic current contributed by two electrons in the next shell (Figure 6f). As expected from the averaging argument, B3LYP calculations also predict a diatropic perimeter current for D_{4h} -constrained monocation 1^+ (Figure S1). The result is that D_{4h} -constrained 1^+ is, like 1^{2+} , predicted to have a conflicting double tropicity: σ aromatic but π -antiaromatic. The analogy here with the relationship between doubly aromatic $C_6I_6^+$ and $C_6I_6^{2+}$ is complete.

Figure 7 shows the total induced current and orbital contributions for D_{4h} -constrained 1^{4+} . At both HF and B3LYP levels, this system has a triplet ground state (Table S4), with a full $9b_{2u}$ π orbital concentrated on the central cycle and a half-full e_u shell concentrated on the iodine perimeter. The HF map of total ($\sigma + \pi$) induced current (Figure 7a) shows a central paratropic π current (Figure 7b) dominated by the 2π virtual excitation characteristic of planar COT and a diatropic σ current on the perimeter. In the α subsystem, a diatropic perimeter current (Figure 7c) arises from the $42e_u \rightarrow 20a_{2g}$ transition (Figure 7d), as in the cation, and in the β subsystem a diatropic perimeter current (Figure 7e) arises from the virtual transition of β electrons to β holes in the highest occupied σ MOs. A modified version of the argument used in Figure 1 predicts that the α current in Figure 7d for 1^{4+} should be similar to the β current in Figure 6f for 1^{1+} and roughly half the combined $\alpha + \beta$ current in Figure 6b for 1^{2+} . Augmentation of the α perimeter current by the β contribution in 1^{4+} (Figure 7f) is in accord with the selection-rule picture. Interestingly, for the lowest singlet state of $C_8I_8^{2+}$ the map (Figure S1) is similar to Figure 7a, but with a reversed the central carbocycle current, again in complete conformity with the orbital model. HF and B3LYP (Figure S2) singlet maps are in essential agreement (Table S4).

Finally, Figure 8 shows the total induced current and orbital contributions for D_{4h} -constrained 1^{2-} . The map of the total current (Figure 8a) shows a superposition of localized and global currents. An addition of two electrons to the π $9b_{1u}$ orbital blocks the paratropic contribution from the $9b_{2u} \rightarrow 9b_{1u}$ virtual excitation (Figure 1) but opens a node-increasing (hence diatropic) HOMO–LUMO excitation from $9b_{1u} \rightarrow 18e_g$, reinforcing the existing $9b_{2u} \rightarrow 18e_g$ and leading to a diatropic π ring current (Figure 8b,c), directly analogous to the ring current of the planarized cyclooctatetraene dianion. The perimeter σ current from the a_{2g} HOMO (Figure 8d) is only weakly perturbed by this addition of π electrons, and 1^{2-} is revealed as a system with an inverted double tropicity: it is σ antiaromatic but π -aromatic. HF and B3LYP maps for the

Figure 7. Maps of induced current density for the D_{4h} -constrained triplet tetracation, 1^{4+} , calculated at the coupled HF level of theory. (a) Total ($\sigma + \pi$) induced current density. (b) Carbocycle π current density. (c) Contribution to current from the occupied α spin orbitals. (d) Contribution to current from the α HOMO ($42e_u$). (e) Contribution to current from the occupied β spin orbitals. (f) Contribution to current from the perimeter β pair, $21b_{1g} + 21b_{2g}$.

singlet are in essential agreement, but as the methods disagree on the nature of the ground state (Table S4) and as the ion dissociates on a release of the constraints, it is probably wise not to attach much importance to this case.

4. CONCLUSION

The model calculations reported here have shown that it is possible, by tuning the charge, to access the gamut of possible combinations of σ/π aromaticity/antiaromaticity (as diagnosed by magnetic tropicity) in (constrained) planar geometries of $C_8I_8^q$. The AWA paradigm for combined σ and π ring currents accounts for the computed ring-current patterns in systems where the central cyclooctatetraene ring is either formally π antiaromatic or aromatic. This study of planar systems is necessarily a Gedankenexperiment, as a referee has commented, since the antiaromaticity of the C_8 ring and the high charges in some of the examples lead as a matter of course to a preference for nonplanar geometries. Naturally, I–I repulsions exacerbate the tendency of antiaromatic systems to “escape” into nonplanar geometries, where they will first lose their I–I ring current and then⁶⁸ their C–C ring current. Ring currents tend to survive minor departures from planarity,⁶⁹ and diatropic currents have a larger geometric range of persistence,

Figure 8. Maps of the induced current density for the D_{4h} -constrained dianion, I_2^{2-} , calculated at the coupled HF level of theory. (a) Total ($\sigma + \pi$) induced current density. (b) Carbocycle π current density. (c) Contributions from the π -HOMO pair ($9b_{1u} + 9b_{2u}$). (d) Contribution from the (σ)-HOMO ($20a_{2g}$).

but they eventually localize.⁷⁰ It is an interesting irony that the size of the iodine atoms, which leads to the overlap argument for an extra perimeter current, also leads via a steric interaction to the loss of planarity that ultimately disrupts the current. From this point of view, the experimental realization of double aromaticity in a large selenylbenzene cation¹⁶ depended on over-riding steric effects by imposing an even more demanding framework enforcing σ overlap and enabling covalent connection to the framework by moving to the left in the Periodic Table. It may be mentioned that “clamping” strategies have proved effective for suppressing/preserving single diatropic and paratropic π currents^{71,72} and may also be useful in creating analogues of these COT-based double aromatics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c03170>.

Cartesian coordinates of optimized C_8I_8 and its ions (HF and B3LYP), energies of electron configurations A and B for various functionals, Hartree–Fock and B3LYP (TZP) bonding energies (au) for D_{4h} molecules in singlet and triplet states, B3LYP/6-311G** current density maps for $C_8I_8^+$, $C_8I_8^{2+}$, $C_8I_8^{4+}$, and $C_8I_8^{2-}$ (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Patrick W. Fowler — Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.; orcid.org/0000-0003-2106-1104; Email: P.W.Fowler@sheffield.ac.uk

Author

Remco W.A. Havenith — Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, Rijksuniversiteit Groningen, 9747 AG Groningen, The

Netherlands; Ghent Quantum Chemistry Group, Department of Chemistry, Ghent University, B-9000 Gent, Belgium; orcid.org/0000-0003-0038-6030

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.jpca.1c03170>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

R.W.A.H. received funding from the Dutch Research Council (NWO Exact and Natural Sciences) Grant No. 17197 7095 for the use of supercomputer facilities. R.W.A.H. thanks S. Dolas (SURF, NL) for allowing him to perform test calculations on the experimental AMD platform kleurplaat maintained and operated by SURF Open Innovation Lab. R.W.A.H. also thanks the Centre for Information Technology of the University of Groningen for access to the Peregrine High-Performance Computing Cluster.

■ REFERENCES

- (1) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*; John Wiley & Sons: New York, 1994.
- (2) Kulichenko, M.; Fedik, N.; Monfredini, A.; Munoz-Castro, A.; Balestri, D.; Boldyrev, A. I.; Maestri, G. “Bottled” Spiro-doubly Aromatic Trinuclear $[Pd_2Ru]^+$ Complexes. *Chemical Science* **2021**, *12*, 477–86.
- (3) Liu, C.; Popov, I. A.; Chen, Z.; Boldyrev, A. I.; Sun, Z. Aromaticity and Antiaromaticity in Zintl Clusters. *Chem. - Eur. J.* **2018**, *24*, 14583–14597.
- (4) Popov, I. A.; Starikova, A. A.; Steglenko, D. V.; Boldyrev, A. I. Usefulness of the σ -Aromaticity and σ -Antiaromaticity Concepts for Clusters and Solid-State Compounds. *Chem. - Eur. J.* **2018**, *24*, 292–305.
- (5) Mercero, J. M.; Boldyrev, A. I.; Merino, G.; Ugalde, J. M. Recent Developments and Future Prospects of All-metal Aromatic Compounds. *Chem. Soc. Rev.* **2015**, *44*, 6519–6534.
- (6) Ivanov, A. S.; Boldyrev, A. I. Deciphering Aromaticity in Porphyrinoids via Adaptive Natural Density Partitioning. *Org. Biomol. Chem.* **2014**, *12*, 6145–150.
- (7) Sergeeva, A. P.; Piazza, Z. A.; Romanescu, C.; Li, W.-L.; Boldyrev, A. I.; Wang, L.-S. B_{22}^- and B_{23}^- : All-boron Analogues of Anthracene and Phenanthrene. *J. Am. Chem. Soc.* **2012**, *134*, 18065–18073.
- (8) Popov, I. A.; Bozhenko, K. V.; Boldyrev, A. I. Is Graphene Aromatic? *Nano Res.* **2012**, *5*, 117–123.
- (9) Huang, W.; Sergeeva, A. P.; Zhai, H.-J.; Averkiev, B. B.; Wang, L.-S.; Boldyrev, A. I. A Concentric Planar Doubly π -Aromatic B_{19}^- Cluster. *Nat. Chem.* **2010**, *2*, 202.
- (10) Zubarev, D. Y.; Averkiev, B. B.; Zhai, H.-J.; Wang, L.-S.; Boldyrev, A. I. Aromaticity and Antiaromaticity in Transition-metal Systems. *Phys. Chem. Chem. Phys.* **2008**, *10*, 257–267.
- (11) Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H.-J.; Wang, L.-S. All-boron Aromatic Clusters as Potential New Inorganic Ligands and Building Blocks in Chemistry. *Coord. Chem. Rev.* **2006**, *250*, 2811–2866.
- (12) Alexandrova, A. N.; Koyle, E.; Boldyrev, A. I. Theoretical Study of Hydrogenation of the Doubly Aromatic B_7^- Cluster. *J. Mol. Model.* **2006**, *12*, 569–576.
- (13) Boldyrev, A. I.; Wang, L.-S. All-Metal Aromaticity and Antiaromaticity. *Chem. Rev.* **2005**, *105*, 3716–3757.
- (14) Alexandrova, A. N.; Boldyrev, A. I. Arachno, Nido, and Closo Aromatic Isomers of the $Li_6B_6H_6$ Molecule. *Inorg. Chem.* **2004**, *43*, 3588–3592.

- (15) Chandrasekhar, J.; Jemmis, E. D.; von Rague Schleyer, P. Double Aromaticity: Aromaticity in Orthogonal Planes. The 3,5-dehydrophenyl cation. *Tetrahedron Lett.* **1979**, *20*, 3707–3710.
- (16) Furukawa, S.; Fujita, M.; Kanatomi, Y.; Minoura, M.; Hatanaka, M.; Morokuma, K.; Ishimura, K.; Saito, M. Double Aromaticity Arising from σ and π -Rings. *Communications Chem.* **2018**, *1*, 60.
- (17) Havenith, R. W. A.; Fowler, P. W.; Fias, S.; Bultinck, P. Evidence from Current-Density Mapping for σ -Delocalisation in the Aromatic Hexaiodobenzene Cation. *Tetrahedron Lett.* **2008**, *49*, 1421–1424.
- (18) Breslow, R. Antiaromaticity. *Acc. Chem. Res.* **1973**, *6*, 393–398.
- (19) Barth, W.; Lawton, R. G. Dibenzo[ghi,mno]fluoranthene. *J. Am. Chem. Soc.* **1966**, *88*, 380–381.
- (20) Barth, W.; Lawton, R. G. Synthesis of Corannulene. *J. Am. Chem. Soc.* **1971**, *93*, 1730–1745.
- (21) Ege, G.; Vogler, H. Zur Konjugation in makrocyclischen Bindungssystemen XX. Charakterordnung, magnetische Suszeptibilitäten und chemische Verschiebungen von Corannulenen. Paramagnetischer Suszeptibilitätsanteil im Innern von Corannulenen. *Theor. Chim. Acta* **1972**, *26*, 55–65.
- (22) Diederich, F.; Staab, H. A. Conjugation in Macrocyclic systems 27. Benzenoid versus Annulene Aromaticity – Synthesis and Properties of Kekulene. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 372–374.
- (23) Baumgarten, M.; Gherghel, L.; Wagner, M.; Weitz, A.; Rabinovitz, M.; Cheng, P. C.; Scott, L. T. Corannulene Reduction: Spectroscopic Detection of All Anionic Oxidation States. *J. Am. Chem. Soc.* **1995**, *117*, 6254–6257.
- (24) Benschafut, R.; Shabtai, E.; Rabinovitz, M.; Scott, L. T. π -Conjugated Anions: From Carbon-Rich Anions to Charged Carbon Allotropes. *Eur. J. Org. Chem.* **2000**, *2000*, 1091–1106.
- (25) Dickens, T. K.; Mallion, R. B. An Analysis of Topological Ring-Currents and their Use in Assessing the Annulene-Within-an-Annulene Model for Super-Ring Conjugated Systems. *Croat. Chem. Acta* **2013**, *86*, 387–406.
- (26) Dickens, T. K.; Mallion, R. B. The Regular $[r, s]$ -Coronenes and the “Annulene-Within-an-Annulene” Rule. *RSC Adv.* **2013**, *3*, 15585.
- (27) Aihara, J.-I. Validity and Limitations of the Annulene-Within-an-Annulene (AWA) Model for Macrocyclic π -Systems. *RSC Adv.* **2014**, *4*, 7256–7265.
- (28) Monaco, G.; Fowler, P. W.; Lillington, M.; Zanasi, R. Designing Paramagnetic Circulenes. *Angew. Chem., Int. Ed.* **2007**, *46*, 1889–1892.
- (29) Monaco, G.; Zanasi, R. Assessment of Ring Current Models for Monocycles. *J. Phys. Chem. A* **2014**, *118*, 1673–1683.
- (30) Steiner, E.; Fowler, P. W.; Jenneskens, L. W. Counter-Rotating Ring Currents in Coronene and Corannulene. *Angew. Chem., Int. Ed.* **2001**, *40*, 362–366.
- (31) Acocella, A.; Havenith, R. W. A.; Steiner, E.; Fowler, P. W.; Jenneskens, L. W. A Simple Model for Counter-Rotating Ring Currents in $[n]$ Circulenes. *Chem. Phys. Lett.* **2002**, *363*, 64–72.
- (32) Steiner, E.; Fowler, P. W.; Jenneskens, L. W.; Acocella, A. Visualisation of Counter-Rotating Ring Currents in Kekulene. *Chem. Commun.* **2001**, 659–660.
- (33) Sagl, D. J.; Martin, J. C. The Stable Singlet Ground State Dication of Hexaiodobenzene: Possibly a σ -Delocalized Dication. *J. Am. Chem. Soc.* **1988**, *110*, 5827–5833.
- (34) Martin, J. C.; Schaad, L. J. Sigma-Delocalized Aromatic Species Formed from Cyclic Arrays of Hypervalent Main-group Element Species. *Pure Appl. Chem.* **1990**, *62*, 547–550.
- (35) Fowler, P. W.; Mizoguchi, N.; Bean, D. E.; Havenith, R. W. A. Double Aromaticity and Ring Currents in All-Carbon Rings. *Chem. - Eur. J.* **2009**, *15*, 6964–6972.
- (36) Bean, D. E.; Fowler, P. W.; Soncini, A. Double Aromaticity and Ring currents in Open-Shell Systems. *Chem. Phys. Lett.* **2009**, *483*, 193–197.
- (37) Jiang, Y.; Wu, Y.; Deng, J.; Wang, Z. Antiaromaticity–Aromaticity Transition of Cyclo[16]carbon upon Metal Encapsulation. *Phys. Chem. Chem. Phys.* **2021**, *23*, 8817–8824.
- (38) Steiner, E.; Fowler, P. W. Four- and Two-Electron Rules for Diatropic and Paratropic Ring Currents in Monocyclic π Systems. *Chem. Commun.* **2001**, 2220–2221.
- (39) Bean, D. E.; Fowler, P. W. Double Aromaticity in “Boron Toroids”. *J. Phys. Chem. C* **2009**, *113*, 155753.
- (40) Rauhalahhti, M.; Taubert, S.; Sundholm, D.; Liégeois, V. Calculations of Current Densities for Neutral and Doubly Charged Persubstituted Benzenes Using Effective Core Potentials. *Phys. Chem. Chem. Phys.* **2017**, *19*, 7124–7131.
- (41) Ciofini, I.; Laine, P. P.; Adamo, C. Quantifying Electron Delocalization in Orthogonal Channels: Theoretical Investigation of σ and π Aromaticity in $[C_6I_6]^{2+}$ and in $[C_6Cl_6]^{2+}$. *Chem. Phys. Lett.* **2007**, *435*, 171–175.
- (42) Hatanaka, M.; Saito, M.; Fujita, M.; Morokuma, K. σ -Aromaticity in Hexa-Group 16 Atom-Substituted Benzene Dications: A Theoretical Study. *J. Org. Chem.* **2014**, *79*, 2640–2646.
- (43) Keith, T. A.; Bader, R. F. W. Calculation of Magnetic Response Properties Using a Continuous Set of Gauge Transformations. *Chem. Phys. Lett.* **1993**, *210*, 223–231.
- (44) Coriani, S.; Lazzeretti, P.; Malagoli, M.; Zanasi, R. On CHF Calculations of 2nd-Order Magnetic Properties Using the Method of Continuous Transformation of Origin of the Current Density. *Theor. Chim. Acta* **1994**, *89*, 181–192.
- (45) Steiner, E.; Fowler, P. W. Patterns of Ring Currents in Conjugated Molecules: A few-electron Model Based on Orbital Contributions. *J. Phys. Chem. A* **2001**, *105*, 9553–9562.
- (46) Havenith, R. W. A.; Fowler, P. W. Ipsocentric Ring Currents in Density Functional Theory. *Chem. Phys. Lett.* **2007**, *449*, 347–353.
- (47) Soncini, A.; Fowler, P. W. Ring-current Aromaticity in Open-Shell Systems. *Chem. Phys. Lett.* **2008**, *450*, 431–436.
- (48) Molski, M.; Mollenhauer, D.; Gohr, S.; Paulus, B.; Khanfar, M. A.; Shorafa, H.; Strauss, S. H.; Seppelt, K. Halogenated Benzene Cation Radicals. *Chem. - Eur. J.* **2012**, *18*, 6644–6654.
- (49) Molski, M. J.; Khanfar, M. A.; Shorafa, H.; Seppelt, K. Halogenated Benzene Cation Radicals. *Eur. J. Org. Chem.* **2013**, *2013*, 3131–3136.
- (50) Baird, N. C. Quantum Organic Photochemistry. II. Resonance and Aromaticity in the Lowest $3\pi\pi^*$ State of Cyclic Hydrocarbons. *J. Am. Chem. Soc.* **1972**, *94*, 4941–4948.
- (51) Schleyer, P.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; van Eikema Hommes, N. J. R. Nucleus-independent Chemical Shifts: A Simple and Efficient Aromaticity Probe. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
- (52) Deb, D.; Duley, S.; Radenković, S.; Bultinck, P.; Chattaraj, P. K.; Bhattacharjee, M. Heterotrimetallic Compounds containing Mo–M–Li [$M = K, Rb$ and Cs] Clusters: Synthesis, Structure, Bonding, Aromaticity and Theoretical investigations of Li_2M_2 [$M = K$ and Rb] and Cs_4 Rings. *Phys. Chem. Chem. Phys.* **2012**, *14*, 15579–15592.
- (53) Steiner, E.; Fowler, P. W. On the orbital Analysis of Magnetic Properties. *Phys. Chem. Chem. Phys.* **2004**, *6*, 261–272.
- (54) Mandado, M.; Graña, A. M.; Pérez-Juste, I. Aromaticity in Spin-Polarized Systems: Can Rings be Simultaneously Alpha Aromatic and Beta Antiaromatic? *J. Chem. Phys.* **2008**, *129*, 164114.
- (55) Guest, M. F.; Bush, I. J.; van Dam, H. J. J.; Sherwood, P.; Thomas, J. M. H.; van Lenthe, J. H.; Havenith, R. W. A.; Kendrick, J. The GAMESS-UK Electronic Structure Package: Algorithms, Developments and Applications. *Mol. Phys.* **2005**, *103*, 719–747.
- (56) Baerends, E. J. *ADF2020.01, SCM, Theoretical Chemistry*; Vrije Universiteit: Amsterdam, The Netherlands, <http://www.scm.com>, 2020.
- (57) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. Towards an Order-N DFT Method. *Theor. Chem. Acc.* **1998**, *99*, 391–403.
- (58) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22*, 931–967.

- (59) Lazzeretti, P.; Zanasi, R. *SYSMO Package*; University of Modena, 1980. With additional routines for evaluation and plotting of current density by Steiner, E.; Fowler, P. W.; Havenith, R. W. A.; Soncini, A.
- (60) Ghosh, S.; Reddy, C. M.; Desiraju, G. R. Hexaiodobenzene: a Redetermination at 100 K. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2007**, *63*, o910–o911.
- (61) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Insights into Current Limitations of Density Functional Theory. *Science* **2008**, *321*, 792–794.
- (62) Henderson, T. M.; Izmaylov, A. F.; Scalmani, G.; Scuseria, G. E. Can Short-Range Hybrids Describe long-range-dependent Properties? *J. Chem. Phys.* **2009**, *131*, 044108.
- (63) Teale, A. M.; Helgaker, T.; De Proft, F.; Tozer, D. J.; Soncini, A. Maps of Current Density Using Density-functional Methods. *J. Chem. Phys.* **2008**, *129*, 074101.
- (64) Havenith, R. W. A.; Meijer, A. J. H. M.; Irving, B. J.; Fowler, P. W. Comparison of Ring Currents Evaluated Consistently at Density Functional and Hartree–Fock Levels. *Mol. Phys.* **2009**, *107*, 2591–2600.
- (65) Jirásek, M.; Rickhaus, M.; Tejerina, L.; Anderson, H. L. Experimental and Theoretical Evidence for Aromatic Stabilization Energy in Large Macrocycles. *J. Am. Chem. Soc.* **2021**, *143*, 2403–2412.
- (66) Peeks, M. D.; Gong, J. Q.; McLoughlin, K.; Kobatake, T.; Haver, R.; Herz, L. M.; Anderson, H. L. Aromaticity and Antiaromaticity in the Excited States of Porphyrin Nanorings. *J. Phys. Chem. Lett.* **2019**, *10*, 2017–2022.
- (67) Rickhaus, M.; Jirasek, M.; Tejerina, L.; Gottfredsen, H.; Peeks, M. D.; Haver, R.; Jiang, H.-W.; Claridge, T. D. W.; Anderson, H. L. Global Aromaticity at the Nanoscale. *Nat. Chem.* **2020**, *12*, 236–241.
- (68) Havenith, R. W. A.; Fowler, P. W.; Jenneskens, L. J. Persistence of Paratropic Ring currents in Nonplanar, Tub-Shaped Geometries of 1,3,5,7-cyclooctatetraene. *Org. Lett.* **2006**, *8*, 1255–1258.
- (69) Soncini, A.; Steiner, E.; Fowler, P. W.; Havenith, R. W. A.; Jenneskens, L. W. Perimeter Effects on Ring Currents in Large Alternant Polycyclic Aromatic Hydrocarbons: Circumcoronene and Two Symmetrical Hexabenzocoronenes. *Chem. - Eur. J.* **2003**, *9*, 2974–2981.
- (70) Bean, D. E.; Fowler, P. W. The Effect on Ring Current of the Kekulé Vibration in Aromatic and Anti-aromatic Rings. *J. Phys. Chem. A* **2011**, *115*, 13649–13656.
- (71) Fowler, P. W.; Havenith, R. W. A.; Jenneskens, L. W.; Soncini, A.; Steiner, E. Survival and Extinction of Delocalised Ring Currents in Clamped Benzenes. *Chem. Commun.* **2001**, 2386–2387.
- (72) Fowler, P. W.; Havenith, R. W. A.; Jenneskens, L. W.; Soncini, A.; Steiner, E. Paratropic Delocalised Ring Currents in Flattened Cyclooctatetraene Systems with Bond Alternation. *Angew. Chem., Int. Ed.* **2002**, *41*, 1558–1560.