Aromaticity Reversal Induced by Vibrations in Cyclo[16]carbon

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ABSTRACT: Aromaticity, most commonly defined as the ability to sustain a diatropic ring current, is typically regarded as an intrinsic property of a molecule. It is often correlated with electron delocalization, stability, and other properties. Small variations in the molecular geometry usually result in small changes in aromaticity, in line with Hammond's postulate: for example, introducing bond-length alternation in benzene and square cyclobutadiene gradually decreases the magnitude of their ring currents, making them less aromatic and less antiaromatic, respectively. A sign change in the ring current, corresponding to a reversal of aromaticity, typically requires a significant perturbation such as electronic excitation, addition or removal of two electrons, or a dramatic change in the molecular geometry. Here, we use multireference calculations to show how small changes in bond-length alternation induce a sudden reversal in the ring current of cyclo[16]carbon, C₁₆. This reversal occurs when the two orthogonal π systems of C₁₆ sustain opposing currents. These results are rationalized by a Hückel model which includes bond-length alternation combined with a minimal model accounting for orbital contributions to the ring current. Finally, we successfully describe the electronic structure of C₁₆ with a divide-and-conquer approach suitable for execution on a quantum computer.

Introduction

Aromaticity is one of the most debated concepts in chemistry, and its definition has undergone several revisions over the last few decades.¹⁻⁵ Today, the most commonly used criterion for aromaticity is magnetic,² equating the presence of a diatropic or paratropic ring in an applied magnetic field with aromaticity or antiaromaticity, respectively. In molecules with several π systems, local and/or global currents may be present simultaneously,^{6,7} reinforcing or opposing each other. Aromaticity is a defining characteristic of a molecule, linked with reactivity, stability, HOMO-LUMO⁸ and singlet-triplet gaps,⁹ feasibility for singlet fission,¹⁰ diradical character,¹¹ wavefunction coherence,¹² and other properties.

Cyclo[*N*]carbons are small all-carbon rings with two orthogonal π systems with *N* electrons in each.¹³ In an analogy to annulenes, cyclocarbons with *N* = 4*n*+2 electrons can be hypothesized to be doubly aromatic (with both π systems sustaining a diatropic ring current), while *N* = 4*n* cyclocarbons are expected to be doubly antiaromatic. Many cyclocarbons have been found in the gas phase, but only C₁₀,¹⁴ C₁₄,¹⁴ C₁₆,¹⁵ and C₁₈¹⁶ have been structurally characterized using scanning probe microscopy.

A recent on-surface investigation of C_{16} revealed the presence of strong bond-length alternation (BLA) and confirmed that its ground state is doubly antiaromatic.¹⁵ Here, we investigate the variation of aromaticity with geometry in the two lowest singlets (S_0 and S_1), the lowest

triplet (T₁) and quintet (Q₁) state of C₁₆. We find that the total ring current in the S₁ and T₁ states can be reversed from aromatic to antiaromatic by movement along the Ke-kulé vibration (~2300 cm⁻¹), i.e. by changing the amount of bond-length alternation.¹⁷ These aromaticity reversals require a relatively small amount of energy, in contrast with previous reports which require a change in the electronic state,¹⁸⁻²¹ molecular charge²²⁻²⁴ or composition,^{25, 26} or involve a high-lying transition state^{27, 28} or a highly strained geometry.²⁹

The unique electronic structure of cyclocarbons makes them an interesting testing ground for various theoretical methods.¹³ Quantum algorithms, which strongly benefit from execution on a quantum computer, are a promising avenue for further development of electronic structure methods, but are currently limited by noise and coherence time.^{30,31} Here, we exploit the orthogonality between the two π systems of C₁₆ to effectively increase the active space of the quantum unitary coupled clusters singles doubles (q-UCCSD) method,³² which we solve variationally.³³ This divide-and-conquer approach enables us to obtain highly accurate results which would otherwise not be feasible to compute using near-term quantum devices.

Ipsocentric approach. Before discussing the electronic structure and ring current in C_{16} , we briefly summarize the rules for evaluating orbital contributions to magnetic properties in the ipsocentric approach, as developed by

Steiner and Fowler:³⁴⁻³⁶

1. The current density J_{TOT} induced by a magnetic field (which, when integrated over the ring, gives the ring current strength, usually measured in nA/T) can be expressed as a sum of spin-allowed transitions from occupied (ψ_s) to unoccupied (ψ_t) orbitals. The contribution of each transition (J_{st}) can be written as a sum of a diatropic term (J_{st}^{DIA}), which is positive and associated with aromaticity, and a negative paratropic term (J_{st}^{PARA}) associated with antiaromaticity:

$$J_{\text{TOT}} = \sum_{s} \sum_{t} J_{st} = \sum_{s} \sum_{t} (J_{st}^{\text{DIA}} + J_{st}^{\text{PARA}})$$
(1)

2. The diatropic (aromatic) contribution of a transition from ψ_s to ψ_t to the current density (J_{st}^{DIA}) is determined by the orbital energy difference $\Delta_{\mathcal{E}st}$ and the translational matrix element M_{st}^{T} , which reflects the orbital coupling under the linear momentum operator \hat{p} :³⁵

$$J_{st}^{\text{DIA}} \propto \frac{M_{st}^{\text{T}}}{\Delta \varepsilon_{st}} = \frac{\left\langle \psi_t \left| \hat{p} \right| \psi_s \right\rangle}{\Delta \varepsilon_{st}}$$
(2)

In general, M_{st}^{T} will be large for spatially similar orbitals differing in the number of nodes by two,³⁴ corresponding (in planar monocyclic molecules) to a change in the angular momentum *k* by one. For example, the purely diatropic ring current in benzene can wholly be attributed to translational transitions from k = 1 to k = 2 (Figure 1a left).³⁶ The contribution of an orbital pair to the paratropic cur-

The contribution of an orbital pair to the paratropic current (J_{st}^{PARA}) is also modulated by $\Delta \mathcal{E}_{st}$ and depends on the magnitude of the rotational matrix element M_{st}^{R} , which couples the orbitals under the angular momentum operator $\hat{l}^{:35}$

$$J_{st}^{\text{PARA}} \propto \frac{M_{st}^{\text{R}}}{\Delta \varepsilon_{st}} = \frac{\left\langle \psi_{t} \left| \hat{l} \right| \psi_{s} \right\rangle}{\Delta \varepsilon_{st}}$$
(3)

For planar monocyclic molecules without BLA, M_{st}^{R} will approach unity for orbital pairs related by a rotation, such as A₂ and B₂ in D_{8h} cyclooctatetraene (COT, Figure 1b; A and B correspond to sine and cosine density patterns). Such systems will have open-shell character^{19, 37, 38} and very large paratropic currents. Introducing BLA in planar COT (Figure 1c) lifts the degeneracy between A₂ and B₂, producing a closed-shell singlet, lowering the total energy, and decreasing antiaromaticity.

3. From equations (2) and (3) we can deduce that very few orbitals around the HOMO and LUMO will meaningfully contribute to the ring current. In aromatic annulenes, it is generally sufficient to consider only translational transitions with $\Delta k = 1$, i.e. HOMO \rightarrow LUMO. In antiaromatic annulenes, rotational transitions with $\Delta k = 0$ ($A_2 \leftrightarrow B_2$ in Figure 1b and 1c) are responsible for most of the ring current, with weak contributions from occupied orbitals below the HOMO.³⁶

The ipsocentric approach provides an orbital-based rationalization of Baird's rule, which predicts an aromaticity reversal in the lowest triplet (T₁) state of annulenes compared to the S₀ ground state.³⁹ In benzene (Figure 1a right), promoting one electron to either A₂ or B₂ produces a very strong paratropic current, resulting in an aromaticity reversal in T₁ (and S₁). On the other hand, in planar COT (Figure 1b and 1c) flipping an electron renders the rotational A₂ \leftrightarrow B₂ transitions forbidden, leading to a Baird aromatic T₁ state. Finally, the evaluation of aromaticity in the S₁ (and other excited states) is less straightforward due to a combination of diatropic and paratropic contributions, in agreement with the experimental observation that Baird's rule is weaker for S₁ than for T₁.⁴⁰

In the ground state (S₀) of C₁₆, the configuration of both π systems is similar to that in planar COT (Figure 1b,c). Flipping a single electron in C₁₆ will result in a T₁ state with mixed aromaticity, where one π system will be Baird aromatic and the other will remain antiaromatic (norcorrole is a similar example⁴¹). Flipping an electron in both π systems of C₁₆ will result in a doubly Baird aromatic quintet (Q₁) state, as shown by Fowler.⁴² We also investigate the S₁ state, in which an electron moves from one π system to the other, resulting in a pair of oppositely charged doublets.

(a) benzene (D_{6h}) ; $4n + 2 \pi e^{-} (n = 1)$; BLA = 0



Figure 1. Translational (green, labelled *T*) and rotational (purple, labelled *R*) transitions in the lowest singlet (S_0 , left) and triplet (T_1 , right) state for (a) benzene, (b) planar COT with no BLA, and (c) planar COT with BLA. Full and dashed lines show relatively larger and smaller contributions to the ring current, respectively.

 B_2

Results and discussion

To understand how the electronic structure and magnetic properties of C_{16} change with BLA, we use three different approaches: (1) a complete active space self-consistent field (CASSCF) method, (2) density functional theory (DFT), and (3) a minimal tight-binding model model, described in the next section. In CASSCF calculations, all orbitals in a pre-defined active space are optimized, and the wavefunction can be written as a linear combination of many configurations, all of which contribute to the final magnetic properties. In contrast, the DFT wavefunction is only a single determinant, with strictly defined orbital occupations.

Hückel-Heilbronner model. To gain more qualitative insight in the electronic structure of C₁₆, we employ a semiempirical Hückel-Heilbronner model (HHM).⁴³ HHM extends the simple Hückel model by replacing the nearest neighbour interaction energy β with an alternating pattern of $\beta(1 + \delta)$ and $\beta(1 - \delta)$:

$$\begin{bmatrix} \alpha & \beta(1+\delta) & 0 & \cdots & 0 & \beta(1-\delta) \\ \beta(1+\delta) & \alpha & \beta(1-\delta) & \cdots & 0 & 0 \\ 0 & \beta(1-\delta) & \alpha & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & \alpha & \beta(1+\delta) \\ \beta(1-\delta) & 0 & 0 & \cdots & \beta(1+\delta) & \alpha \end{bmatrix}$$
(4)

At $\delta = 0$, HHM reduces to a simple Hückel model. At $0 < \delta < 1$ it describes a system in which the interaction between shorter bonds is given by $\beta(1 + \delta)$, while longer bonds are coupled by $\beta(1 - \delta)$, which was shown to be a good approximation by Stanger.⁴⁴ Using HHM, we can find the π orbital energies of C₁₆ by solving (4) twice (allowing for $\beta'' \neq \beta'$) and offsetting the in-plane orbitals by γ to account for their slightly higher energies (Figure 2a). The total energy $E_{\text{HHM}}^{\text{TOT}}$ can be obtained by adding the sigma contribution $a_{\sigma}\delta^2$ (approximated as a parabola with the minimum at BLA = 0),⁴³ to the energies of the two π systems $(E''_{\pi} \text{ and } E_{\pi}')$:

$$E_{\text{TOT}}^{\text{HHM}} = a_{\sigma}\delta^{2} + E_{\pi}"(\beta",\delta) + E_{\pi}'(\beta',\delta,\gamma)$$
(5)

In C₁₆ without BLA, the frontier out-of-plane orbitals (A₄'' and B₄''; Figure 2a top) are energy degenerate and slightly ($\gamma = 0.1 \text{ eV}$) lower in energy than their in-plane counterparts (A₄' and B₄'), resulting in an unstable double open shell singlet,¹⁵ in analogy to D_{4h} cyclobutadiene⁴⁵ or D_{8h} COT.^{19, 21, 38}

Introducing BLA lowers the energies of A₄'' and A₄' by $2\beta''\delta$ and $2\beta'\delta$ (and raises the energies of B₄'' and B₄' by the same value), resulting in a closed-shell doubly antiaromatic configuration. More generally, HHM predicts that the introduction of BLA lowers the π energy of both 4*n* and 4*n*+2 systems, with the effect being smaller in 4*n*+2 than 4*n* systems with equal *n*, and increasing with *n* (details in SI). Therefore, a π -conjugated molecule will have no BLA if its σ contribution outweighs the π contribution, which usually occurs in 4*n*+2 molecules with small *n* (e.g. benzene), in agreement with Shaik's interpretation based on valence-bond theory.⁴⁶

We extend the HHM to excited states by promoting electrons to unoccupied orbitals and adding a state-specific offset E_{xc} to the energy of the newly occupied orbitals, in order to account for orbital relaxation and exchange coupling; in state-averaged fashion, a_{σ} , β'' and β' are kept equal in all states (and at all values of BLA).

Minimal ipsocentric model for C₁₆. To provide a direct relation between aromaticity and orbital energies, we employ a minimal ipsocentric model in which matrix elements in equations (2) and (3) are replaced by orbital-independent parameters, and only few transitions are counted. In this approach, the total ring current of C₁₆ is calculated as the sum of its out-of-plane and in-plane components, which are given by:

$$J'' = \sum_{s''} \sum_{t''} \left(\frac{c_{st}^{\text{DIA}} - c_{st}^{\text{PARA}}}{\Delta \varepsilon_{s''t''}} \right)$$
(6)

$$J' = c' \sum_{s'} \sum_{t'} \left(\frac{c_{st}^{\text{DIA}} - c_{st}^{\text{PARA}}}{\Delta \mathcal{E}_{s't'}} \right)$$
(7)



Figure 2. (a) Frost-Musulin diagrams for C₁₆ in the presence (top) and absence (bottom) of BLA, with the dominant paratropic contributions in the ground state shown in purple. Offset between the out-of-plane (blue) and in-plane (orange) π systems is denoted by γ . (b) Possible translational (*T*, green) and rotational (*R* purple) transitions associated with *k* = 4–5 orbitals in low-lying electronic states of C₁₆.

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In (6) and (7), c_{st}^{DIA} has a constant positive value for all transitions with $\Delta k = 1$ (e.g. $A_4'' \rightarrow A_5''$), while c_{st}^{PARA} has a constant positive value for all $\Delta k = 0$ transitions; both are zero for all other transitions. The third parameter in the model, c', relates the in-plane and the out-of-plane matrix elements (more generally, it relates the currents produced in different π systems by an orbital pair with the same Δc_{st}). c_{st}^{DIA} , c_{st}^{PARA} , and c' are assumed to be independent of BLA and electronic state; for a specific molecule, they reflect how much current is induced by a single transition between orbitals separated by one unit of energy.

Within this minimal model, only orbitals with k = 3-5 contribute to the ring current of C₁₆ (as only $\Delta k = 0$ and $\Delta k = 1$ transitions are counted). For simplicity, we will focus on transitions involving k = 4 and k = 5 orbitals shown in Figure 2b, as the diatropic contribution of $k = 3 \rightarrow k = 4$ transitions changes in the same manner as the contribution from $k = 4 \rightarrow k = 5$ transitions.

CASSCF and HMM results. We now investigate the variation of the ring current with BLA in the S₀, Q₁, T₁, and S₁ states of C₁₆ at a series of eleven D_{8h} geometries with different values of BLA. The considered geometries are interpolated between the ground-state minimum previously found by NEVPT2¹⁵ (BLA = 11.4 pm, ring radius r = 3.33 Å) and the minimum-energy D_{16h} geometry at the same level of theory (BLA = 0 pm, r = 3.32 Å); results for geometries extended to BLA up to 16 pm, which roughly corresponds to the CASSCF minimum at r = 3.32 Å, are given in Figure 7.

CASSCF calculations include twelve electrons in twelve orbitals with k = 3-5 in the active space, capturing all $\Delta k = 0$ and $\Delta k = 1$ transitions. These CASSCF(12,12) energies (E_{CAS}) and ring curents (J_{CAS}), calculated from nucleus independent chemical shifts (NICS(2)_{zz}) are used to obtain the optimal parameters for the HHM and the minimal ipsocentric model (E_{HHM} , J_{HHM}). In both cases, J is expressed relative to the benzene ring current ($J_{ref} = 12 \text{ nA/T}$).

Different configurations are named according to the occupancies of their four k = 4 orbitals¹⁵ (Figure 2b bottom), e.g. S₀ at large BLA (Figure 2a bottom) can be written as |20 20>. For each electronic state, the magnetic couplings in the most relevant configuration are described.

The effect of dynamic correlation is evaluated by comparing the CASSCF and QD-NEVPT2⁴⁷ wavefunction composition, as well as by density functional theory (DFT) calculations (ω B97XD/def2-TZVP, Figure S1 in SI).

S₀ **state.** In the ground state, the dominant configuration at virtually all nonzero BLA values is the doubly antiaromatic |20 20> (Figure 3a,d). In this configuration, A₄ orbitals in both π systems are doubly occupied and their B₄ counterparts are doubly unoccupied, leading to A₄" \rightarrow B₄" and A₄' \rightarrow B₄' rotational transitions (Figure 3b).

Decreasing BLA reduces the energy difference between A_4 and B_4 , which rapidly increases antiaromaticity and electronic energy (Figure 3c; we define $E_{rel} = 0$ for BLA = 11.4 pm). Despite a strong multireference character at low BLA

(Figure 3a), HHM reproduces the CASSCF results well (Figure 3c), with mean absolute errors $MAE_E = 0.05 \text{ eV}$ and $MAE_J = 1.0$.

Finally, due to the small separation γ between the two π systems,¹⁵ there is a complete absence of the doubly aromatic |22 00> configuration, even at zero BLA. This is in contrast with single-reference methods and HHM, which incorrectly predict a |2200> ground state for the BLA = 0 configuration.



Figure 3. Aromaticity of C_{16} in the ground (S₀) state. (a) Wavefunction composition at different BLA, as calculated by QD-NEVPT2 (top) and CASSCF (bottom). (b) Translational (green) and rotational (purple) transitions in k = 4-5 orbitals at large and zero BLA in the |20 20> configuration. Full and dashed lines show larger and smaller contributions to the ring current. (c) Total ring current and relative energy at different BLA calculated by CASSCF (circles) and the HHM (dashed lines). (d) In-plane (*J*') and out-of-plane (*J*'') contributions to the total ring current.

Q1 state. The major configuration in the lowest quintet state is ${}^{5}|11\ 11>$, in which the four k = 4 orbitals are singly occupied by four same-spin electrons. This wavefunction composition remains largely unaffected by changes in BLA (Figure 4a). No rotational transitions are allowed, leading to double aromaticity (Figure 4b,d).⁴²

The Q_1 ring current does not change much (~10%) with BLA, as the increase in the energy of A_4 orbitals is offset by a decrease in B_4 energies. At BLA = 0, the energy is

minimized and the ring current is maximized (Figure 4c), which is a complete reversal of the result obtained for the doubly antiaromatic S_0 (cf. Figure 3c and 4c). A very similar result is obtained with DFT (Figure S1b).

HHM reproduces the electronic energies obtained by CASSSCF well (Figure 4b; $MAE_E = 0.12 \text{ eV}$). The ring current fit is of similar accuracy to S₀ (MAE_J = 0.9), but it is limited by the inability of the minimal ipsocentric model to describe variation not driven by changes in orbital energies.



Figure 4. Aromaticity of C_{16} in the lowest quintet (Q_1) state. (a) Wavefunction composition at different BLA, as calculated by QD-NEVPT2 (top) and CASSCF (bottom). (b) Translational (green) and rotational (purple) transitions in k = 4-5 orbitals at large and zero BLA in the |11 11> configuration. Full and dashed lines show larger and smaller contributions to the ring current. (c) Total ring current and relative energy at different BLA calculated by CASSCF (circles) and the HHM (dashed lines). (d) In-plane (J') and out-of-plane (J'') contributions to the total ring current.

T₁ **state.** In a naïve single-reference picture, the lowest lying triplet state (T₁) might be obtained by changing the spin of a single electron in the S₀ |20 20> configuration. For example, flipping an electron in the out-of-plane π system results in the |11 20> configuration, which is predicted by both CASSCF and NEVPT2 to have the largest contribution to the multireference wavefunction (Figure 5a).

In $|11\ 20\rangle$, the out-of-plane $|11\rangle\pi$ system produces a diatropic current which does not depend much on the BLA (analogously to Q₁; Figure 5b left), while the paratropic current produced by the in-plane $|20\rangle\pi$ system strongly increases with decreasing BLA (analogously to S₀; Figure 5b right). As a result, at large BLA the total current is diatropic, quickly reversing as BLA is decreased. CASSCF predicts the crossing point at BLA = 8 pm and coinciding with the local minimum (Figure 5b). At this point, very small changes in energy (e.g. 50 meV in either direction) result in drastic changes in the ring current (from +0.8 to -2.2 relative to benzene).

HHM qualitatively recovers the variation of energy with BLA, and reproduces the ring current changes with relatively high accuracy (Figure 5c; $MAE_E = 0.09 \text{ eV}$; $MAE_J = 0.3$). The contribution of other notable configurations, such as $|20\ 11>$ (in which an in-plane electron was flipped), is analogous to $|11\ 20>$, with a combination of paratropic and diatropic contributions. This is demonstrated by DFT, which predicts similar variation *J* with BLA for both cases (Figure S1c), in qualitative agreement with CASSCF.



Figure 5. Aromaticity of C_{16} in the lowest triplet (T_1) state. (a) Wavefunction composition at different BLA, as calculated by QD-NEVPT2 (top) and CASSCF (bottom). (b) Translational (green) and rotational (purple) transitions in k = 4-5 orbitals at large and zero BLA in the |11 20> configuration. Full and dashed lines show larger and smaller contributions to the ring current. (c) Total ring current and relative energy at different BLA calculated by CASSCF (circles) and the HHM (dashed lines). (d) In-plane (J') and out-of-plane (J'') contributions to the total ring current.

S₁ state. Unlike all previously considered states, the first excited singlet (S₁) is antisymmetric with respect to the reflection about the molecular plane. This means it consists of configurations with an odd number of electrons in both π systems, and can be described as a pair of doublets, with e.g. 17"+15' or 15"+17' electrons.

At nonzero BLA, both CASSCF and NEVPT2 predict $|21\ 10\rangle$, which has 17"+15' electrons, as the dominant configuration (Figure 6a). In $|21\ 10\rangle$, a combination of rotational and translational transitions is present both π systems (Figure 6b), resulting in mixed aromaticity (Figure 6d). At large BLA (> 9.1 pm), translational contributions are stronger, resulting in an overall diatropic current. At smaller (< 9.1 pm) BLA, the energy difference between A₄ and B₄ orbitals sufficiently shrinks to induce a reversal of the ring current (Figure 6c).

The similarity in the variation of energy and ring current in the T₁ (Figure 5) and S₁ (Figure 6) states can be rationalized by noting that their energies are approximately related by $E_{S1} = E_{T1} + \gamma - E_{EX}$, where γ is the offset between the inplane and out-of-plane orbitals and E_{EX} is the exchange interaction. Analogously, ring currents in T₁ and S₁ are similar because the number of diatropic and paratropic transitions in both is equal (cf. Figure 5b and 6b). At BLA = 9.1, the ring current in S₁ is slightly more sensitive to small changes in energy, with a 50 meV variation in either direction changing *J* from +0.8 to -2.5.

The HHM fit to CASSCF energies and ring current is comparable to other states (MAE_{*E*} = 0.06 eV; MAE_{*J*} = 0.6), indicating that the HHM and the minimal ipsocentric approach can be extended to excited states.



Figure 6. Aromaticity of C16 in the first excited singlet (S1) state. (a) Wavefunction composition at different BLA, as calculated by QD-NEVPT2 (top) and CASSCF (bottom). (b) Translational (green) and rotational (purple) transitions in k = 4-5 orbitals at large and zero BLA in the |21 10> configuration. Full and dashed lines show larger and smaller contributions to the ring current. (c) Total ring current and relative energy at different BLA calculated by CASSCF (circles) and the HHM (dashed lines). (d) In-plane (J') and out-of-plane (J'') contributions to the total ring current.

Qualitative modelling. The state-averaged HHM is successful in describing the variation of energy with BLA in the four lowest-lying electronic states of C₁₆ (Figure 7a), with a mean absolute error (MAE) of 0.09 eV. The HHM orbital separation γ is 0.2 eV, in good agreement with the $\gamma = 0.1$ eV value previously found by DFT.¹⁵ We also obtain a ~38% stronger Hückel coupling between the out-of-plane ($\beta'' = 6.1$ eV) than the in-plane ($\beta'' = 4.4$ eV) orbitals, indicating stronger overlap in the out-of-plane π system.



Figure 7. Comparison between (a) energies and (b) ring current strengths (b) predicted by CASSCF (large symbols) and the HHM (dotted lines). Circles correspond to the S_0 state, hollow triangles to S_1 , full triangles to T_1 , and pentagons to Q_1 . Aromatic and antiaromatic ring currents are shown in green and purple, respectively.

The frontier orbital ipsocentric approach accurately reproduces the aromaticity switching predicted by CASSCF, remaining remarkably robust through a large range of ring current strengths (Figure 7b), with a mean relative error of 11.9%. Its success validates the approximation that the variation in the magnetic response can be recovered purely through the change in frontier orbital energies. The coupling constants we obtain are $c^{\text{DIA}} = 6.05 J_{\text{ref}}/\text{eV}$ and $c^{\text{PARA}} = 8.05 J_{\text{ref}}/\text{eV}$, providing a simple, direct link between orbital energy and aromaticity through equations (6) and (7). In agreement with previous work,^{18, 42, 48} our minimal ipsocentric approach finds a weaker magnetic coupling in the inplane π system (c' = 0.55) relative to the out-of-plane system. Further details on the HHM and the minimal ipsocentric approach are given in the SI.

While we have only been focused on the effect of BLA, aromaticity reversals may occur with any distortion which causes a stronger response in the orbital energies than in their spatial overlap. For example, bond-angle alternation (BAA) could be described by adding a $\beta_{BAA}(1 \pm \delta_{BAA})$ term to the in-plane π system. Also, in cases where no significant open-shell character is present, the minimal ipsocentric approach could employ orbital energies calculated by DFT.

The addition of dynamic correlation does not seem to have a significant effect on the ring currents: DFT also predicts an aromaticity reversal in T_1 (Figure S1c), and perturbatively including coupling with unoccupied orbitals outside the active space (QD-NEVPT2) does not significantly change the composition (Figures 3a-6a) of the CASSCF wavefunction.

Divide-and-conquer approach. Due to their orthogonality, the two π systems in cyclocarbons are usually considered separately.^{18, 42, 48} This suggests that one could approximate a 12,12 active space, which is used throughout this work, with a combination of in-plane and out-of-plane 6,6 active spaces. Here, we compute the energy of the two 6,6 subspaces (E'_{qUCCSD} and E''_{qUCCSD}) using the q-UCCSD* method, which includes all single and double excitations between all spin-orbitals in the active space (further details are given in the SI). The total energy is calculated according to:

$$E_{\text{qUCCSD}}^{\text{total}} = E_{\text{inactive}(12,12)} + E'_{\text{qUCCSD}(6,6)} + E''_{\text{qUCCSD}(6,6)}$$
(8)

where $E_{inactive(12,12)}$ is the complete active space configuration interaction inactive energy, which can be obtained efficiently without solving the entire active space. It should be noted that in each of the two q-UCCSD(6,6) calculations, the correlated π -system feels the static orbitals of the noncorrelated π -system, i.e. the two π -system systems remain coupled at a mean-field level.

In the S₀ state, this divide-and-conquer q-UCCSD approach works well for a wide range of nonzero BLA (Figure 8, MAE = 0.16 eV relative to CASSCF), producing results very similar to canonical CCSD and CCSD(T) methods. Around zero BLA, both q-UCCSD and canonical coupled clusters are limited by the poor quality of the underlying HF determinant, although q-UCCSD appears to be more robust in case of BLA \approx 1 pm. In these cases, the performance of q-UCCSD may be further improved by starting from a better reference (e.g. CASSCF) or by using a flavour which includes orbital optimisation.⁴⁹ q-UCCSD calculations for the T₁ and Q₁ states are of similar quality to S₀ (see SI), illustrating a way for applying the q-UCCSD method for systems with many strongly correlated electrons (other possible use cases may be a complex with two weakly coupled transition metals, or a dye with two chromophores connected with sigma bonds).



Figure 8. Energies of ground-state C_{16} at different amounts of BLA calculated using CASSCF (grey circles), CCSD (blue hollow triangles), CCSD(T) (green hollow triangles), and divide-and-conquer q-UCCSD (red rectangles), all obtained with the cc-pVDZ basis set. Note the two breaks on the y axis.

Conclusion

Using CASSCF, qualitative modelling, and DFT, we have demonstrated that the ring current in C_{16} can be reversed with small changes in bond-length alternation. This reversal of aromaticity (according to the ring-current criterion²) is unique as it is not associated by any notable change in the electronic structure, but only with a small change in energy. It occurs in electronic states displaying mixed aromaticity, which can be characterized by the presence of both diatropic and paratropic currents (Table 1).

Table 1. Ring Current of C16 in Low-lying ElectronicStates at Different Amounts of Bond-length Alternation.

state	electronic structure	net ring current	
		BLA >> 0	BLA ≈ 0
S ₀	doubly antiaromatic	paratropic	paratropic
Q1	doubly Baird aromatic	diatropic	diatropic
T 1	Baird aromatic + antiaromatic	diatropic	paratropic
S ₁	doubly mixed	diatropic	paratropic

Magnetic couplings between the C_{16} orbitals are successfully described using a minimal ipsocentric model. This model provides a direct link between aromaticity and orbital energy, thus offering a simple avenue for rationalizing commonly observed correlations between aromaticity and various molecular properties.^{8,9 10,11}

Aromaticity reversals may also be interpreted in terms of antiaromaticity relief.^{28, 50} The doubly aromatic Q_1 state maximizes its aromaticity, while the doubly antiaromatic S_0

minimizes its antiaromaticity as much as the σ system allows. The mixed aromatic T₁ and S₁ states have approximately nonaromatic D_{8h} minima, revealing their aromatic and antiaromatic nature by movement along one and the other direction of the Kekulé vibration.

We also demonstrate that the applicability of quantum algorithms such as q-UCCSD can be improved by partitioning the active space and calculating the correlation energy of each subspace separately. In case of C_{16} , this divide-andconquer approach is particularly successful, approaching the accuracy of fully self-consistent multireference calculations. Finally, as quantum devices have direct access to the wavefunction, it is straightforward to compute the expectation value of any observable. This suggests that the ipsocentric approach could be combined with virtually any quantum ansatz.

ASSOCIATED CONTENT

Supporting Information includes molecular geometries, DFT results for the S_0 , T_1 , and Q_1 states, and MATLAB code used for the HHM.

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