A Unified Orbital Model of Delocalised and Localised Currents in Monocycles, from Annulenes to Azabora-heterocycles


Abstract: Why are some \((4n+2)\pi\) systems aromatic, and some not? The ipsocentric approach to the calculation of the current density induced in a molecule by an external magnetic field predicts a four-electron diatropic (aromatic) ring current for \((4n+2)\pi\) carbocycles and a two-electron paratropic (antiaromatic) current for \((4n)\pi\) carbocycles. With the inclusion of an electronegativity parameter, an ipsocentric frontier-orbital model also predicts the transition from delocalised currents in carbocycles to nitrogen-localised currents in alternating azabora-heterocycles, which rationalises the differences in (magnetic) aromaticity between these isoelectronic \(\pi\)-conjugated systems. Ab initio valence-bond calculations confirm the localisation predicted by the naive model, and coupled-Hartree–Fock calculations give current-density maps that exhibit the predicted delocalised-to-localised/carbocycle–heterocycle transition.

Keywords: aromaticity · boron · nitrogen heterocycles · ring current · valence bond

Introduction

Planar conjugated carbocyclic compounds show a strong link between \(\pi\)-electron count and molecular properties. Hückel’s long-standing \(4n+2\) rule distinguishes aromatic from antiaromatic monocycles, and correlates the energetics of these systems with their characteristic magnetic properties.[1] However, the periodic table offers wide possibilities for the construction of isoelectronic heterocycles, and for many of them, direct transferability of the implied relationship between aromaticity and electron count is questionable or even counterfactual. The replacement of CC by BN, for example, is known to lead to marked differences in magnetic properties:[2] the strong ring currents of the carbocycle vanish in the isoelectronic azabora-heterocycles, \(B_3N_3H_3, B_3N_2H_4, B_3N_2H_5\) (1–3). Herein we show that a simple frontier-orbital model...
of induced currents can in fact cope with both extremes, predicting the transition from delocalised to localised magnetic behaviour that is found in full ab initio current-density maps.

The ipsocentric model\cite{3–5} gives an accurate account of π ring currents in planar carbocycles in terms of frontier-orbital contributions. The hallmarks of aromaticity and antiaromaticity on the magnetic criterion\cite{6–9} that is, the diatropic currents of 4n+2 systems and the paratropic currents\cite{10} of planar 4n systems are attributed in this model to four and two frontier electrons, respectively.\cite{4} In both cases, the sense of the ring current follows directly from the symmetry properties of the HOMO–LUMO transition, and the predictions of a simple orbital theory are borne out in full ab initio calculations of current-density maps.\cite{3,4} For the 4n+2π heterocycles, borazine and boroxine, however, ab initio maps show only localised circulation of the π electrons around the electronegative nuclei.\cite{22} How does the simple orbital model deal with this dichotomy? In particular, why does it not predict ring currents for all planar 4n and 4n+2 π systems? It is shown here that a generalisation of the pictorial orbital model is able to account for both the presence of global currents in carbocycles, and their absence in boron–nitrogen analogues such as borazine (2) and the eight-membered borazocene (3).

Results and Discussion

The aromaticity analogy: The considerations of magnetic aromaticity have their counterparts in the chemistry of these boron–nitrogen systems. Although 6π-omaticity have their counterparts in the chemistry of these systems are attributed in this model to four and two frontier electrons, respectively.\cite{4} In both cases, the sense of the ring current follows directly from the symmetry properties of the HOMO–LUMO transition, and the predictions of a simple orbital theory are borne out in full ab initio calculations of current-density maps.\cite{3,4} For the 4n+2π heterocycles, borazine and boroxine, however, ab initio maps show only localised circulation of the π electrons around the electronegative nuclei.\cite{22} How does the simple orbital model deal with this dichotomy? In particular, why does it not predict ring currents for all planar 4n and 4n+2 π systems? It is shown here that a generalisation of the pictorial orbital model is able to account for both the presence of global currents in carbocycles, and their absence in boron–nitrogen analogues such as borazine (2) and the eight-membered borazocene (3).

Currents in carbocycles: Current-density maps from ab initio calculations\cite{4} on the archetypal carbocycles, benzene and (planarised\cite{20}) cyclooctatetraene (COT), are shown in Figure 1. For each molecule, the maps show total π and σ contributions to the induced current density. As expected, the currents arising from the π electrons are, respectively, strongly diatropic in benzene and strongly paratropic in COT. The currents are dominated by HOMO contributions in both cases.

An angular-momentum analysis shows how the symmetry rules account for these features. The Hückel π molecular orbitals of a cycle of N identical atoms in full $D_{n\pi}$ symmetry have well-defined angular-momentum properties with respect to the principal axis. At each successive energy level, the quantum number, $\lambda = n, n+1, \ldots, N/2$, increases by one. In a cycle with $N = 4n+2$ electrons, the HOMO and LUMO correspond to $\lambda = n$ and $n+1$, respectively, whereas for a cycle
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with \( N = 4n \) electrons, in the closed-shell configuration obtained on distortion to \( D_{\text{N}} \), symmetry, the HOMO and LUMO are derived from the splitting of a pair of originally degenerate orbitals with \( \lambda = n \).

The canonical molecular orbitals are the delocalised set \( \{ \psi_{1,\text{c}} \} \), which produce uniform \( \pi \)-charge distribution on all the carbon atoms. Functions \( \psi_{1,\text{c}} \) and \( \psi_{1,\text{a}} \) (degeneracy \( N \)) have coefficients on centre \( r \) equal to \( \sqrt{2d_r/\cos(\lambda \pi r/2)} \) and \( \sqrt{2d_r/\sin(\lambda \pi r/2)} \), respectively.\(^{[21]}\) Unless \( \lambda = 0 \) (or \( N/2 \), if allowed), the two functions share a single, well-defined angular momentum and are degenerate. For \( \lambda = 0 \) and \( N/2 \), the sines/cosines form is simply a choice that gives convenient nodal properties.

When orbitals have well-defined values of \( \lambda \), the symmetry selection rules for occupied-to-unoccupied transitions are reduced to the following:\(^{[19]}\) a diatropic contribution arises from a transition in which \( \Delta \lambda = +1 \) and a paratropic contribution arises from a transition in which \( \Delta \lambda = 0 \). Thus, for a \( 4n+2 \) cycle with maximum symmetry, only the HOMO–LUMO transition is active, and is responsible for the entire (four-electron) diatropic current. For a \( 4n \) cycle with the lower symmetry of the closed shell, two types of transition are active: the HOMO–LUMO transition leads to a two-electron paratropic contribution, and HOMO–1–LUMO and HOMO–LUMO+1 transitions to diatropic contributions. Here, the smaller HOMO–LUMO splitting ensures dominance of the paratropic current. Decomposition of the carbocycle ab initio \( \pi \) maps into orbital contributions confirms the above analysis.\(^{[4]}\)

Figure 1. Maps of the current density induced in benzene (left) and (planar) cyclooctatetraene (right) by a perpendicular external magnetic field. Contributions of the \( \pi \) (top) and \( \sigma \) orbitals (bottom) calculated by the RHF/6-31G** ipsocentric approach are plotted at one bohr above the molecular plane. Anticlockwise circulations are diatropic, clockwise circulations paratropic. ●: Carbon atoms; ○: hydrogenn atoms.

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A model for currents in aza-bora-heterocycles: To adapt the pictorial molecular-orbital analysis to the ipsocentric model for currents in alternating heterocycles such as borazine (2) and homologues 1 and 3, it is sufficient to include one extra feature. To deal with heteroatoms in Hückel theory it is necessary to modify the Coulomb and/or resonance integral parameters: for boron and nitrogen (as zero- and two-electron donors), the recommended parameters are \( a_b = \alpha - \beta \) and \( a_n = \alpha + 1.5\beta \).\(^{[23]}\) Hückel calculations using \( a_b = \alpha - 1.1\beta \) and \( a_n = \alpha + 1.5\beta \) have been reported for 1–3.\(^{[10]}\) In the simplest model of an equilateral \( \text{B}_3\text{N}_3\text{H}_6 \) cycle that allows for the differing electronegativities of boron and nitrogen, symmetrical changes are made to the Coulomb parameters, that is, \( a_b = \alpha - \eta\beta \) and \( a_n = \alpha + \eta\beta \), where \( \eta \) is positive. Variation of the dimensionless quantity \( \eta \) from 0 to \( \approx 1 \) thus gives a one-parameter model to correlate the properties of annulenes and BN cycles.

The implications of this model for six- and eight-membered cycles, as representatives of \( 4n+2 \) and \( 4n \) \( \pi \) systems, respectively, are now investigated in detail. Direct solution of the Hückel problem with modified \( \alpha \) values gives energy levels \( \varepsilon \) and molecular orbitals \( \{ \psi \} \) from which the consequences for ring currents can be deduced. In the limit, \( \eta = 0 \), the canonical molecular orbitals are \( \{ \psi_{1,\text{c}} \} \); when \( \eta \neq 0 \), they are linear combinations of this starting set.


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In this model, as formulated by McWeeny,[23] the ring current, polarisability.[1] benzene LUMO, to mix according to their symmetries in the lower \( D_{3h} \) group, that is, in \( A_1^+ \), \( \lambda = 0 \) mixes with \( \lambda = 3 \), and in \( E^1 \), \( \lambda = 1 \) mixes with \( \lambda = 2 \) (retaining the sine/cosine distinction). As \( \eta \) increases, the degree of mixing increases, and is described by angles \( \mu \) and \( \nu \), where \( \mu = 2\tan 2\mu = 2\tan 2\nu \):

\[
\begin{align*}
\phi_{0,s} &= \cos \mu \psi_{0,s} - \sin \mu \psi_{3,s}, \\
\phi_{1,s} &= \cos \nu \psi_{1,s} - \sin \nu \psi_{2,s}, \\
\phi_{2,s} &= \cos \nu \psi_{1,s} + \sin \nu \psi_{2,s}, \\
\phi_{3,s} &= \sin \mu \psi_{0,s} + \cos \mu \psi_{3,s}.
\end{align*}
\]

When \( \eta = 0 \), \( \mu \) and \( \nu \) are zero; in the limit of a large \( \eta \), the molecular orbitals of the alternating six-membered cycle become exact 50:50 mixtures, with \( |\mu| = |\nu| = 45^\circ \). When \( \eta = 1 \), \( \phi_{1,s} \), still contains 95% of the benzene \( \psi_{0,s} \) (\( |\mu| = 13.3^\circ \)), but the HOMO pair, \( \phi_{1,0,s} \), contains a 15% admixture of the benzene LUMO, \( \psi_{2,s} \) (\( |\nu| = 22.5^\circ \)). Figure 2a shows the correlation of orbitals and energies with \( \eta \) for the six-membered cycle. Hückel \( \pi \) charges reflect this shift with respect to the uniform charge distribution of benzene, with \( 1 \pm \frac{3}{2}(\frac{1}{\sqrt{2}}) \approx 1.62 \) and 0.38 \( \pi \) electrons on the nitrogen and boron atoms when \( \eta = 1 \). As \( \eta \) increases, bonding orbitals concentrate on the electronegative nitrogen atoms, and antibonding orbitals on the electropositive boron atoms, the functions becoming more “localised”.

The mixing has crucial consequences for the predicted currents. When \( \eta = 0 \), the dominant HOMO–LUMO transition responsible for the ring current of the carbocycle is from \( \{\psi_{1,s} \} \) to \( \{\psi_{2,s} \} \) for which \( \Delta \lambda = 1 \); the transition is therefore purely translational and contributes only diatropic current. For all \( \eta > 0 \), as HOMO and LUMO each contain \( \lambda = 1 \) and 2 contributions, the transition includes \( \Delta \lambda = 1 \) and 0 components, and the current gains partial paratropic character. The global diatropic current of benzene therefore weakens as \( \eta \) increases.

A first interpretation of the effect of progressive orbital mixing on the ring current in a 4n+2 cycle can be found by using the simplest approach, the Hückel–London model.[9] In this model, as formulated by McWeeny,[33] the ring current per unit area of a cycle is proportional to the reduced bond current, \( J_n \), where \( p_n \) is the \( \pi \) bond-order between adjacent atoms \( x \) and \( s \) and \( \tau_{m,n} \) is the imaginary bond–bond polarisability.[9]

\[
J_n = (p_n + \beta \tau_{m,n}) |\beta|
\]

In a monocycle, \( J, p \) and \( \pi \) are independent of the choice of adjacent pair. For benzene, \( p = \frac{\gamma}{5} \) and \( \pi = -\frac{5}{2}\beta^{-1} \). For borazine with \( \eta = 1 \), a straightforward calculation gives \( p = \frac{1}{8} \left( \frac{3}{2 \sqrt{5}} \right) \) and \( \pi = -\frac{1}{9} \left( \sqrt{\frac{13}{4}} \right) \beta^{-1} \), from which the borazine:benzene ratio of ring-current intensity, assuming an equal ring area, is \( \left( \frac{3}{8 \sqrt{5}} \right) \approx 0.27 \). This ratio tends to zero as the electronegativity difference parameter \( \eta \) tends to infinity. Thus, this crude model, in which current is constrained to flow along the straight lines between adjacent atoms, predicts that an increase in \( \eta \) leads to diminution and eventual extinction of the global diatropic current.
The picture can be refined by allowing for the spatial extent of the current outside the direct line of centres. The pseudo-π model\(^{[24]}\) includes explicit basis functions, and simulates π ring currents by using a σ model based on the exact symmetry equivalence between the σ orbitals of cyclic \(H_\alpha\) atoms and the π orbitals of the \(N\)-membered carbocycle. It turns out that ipso-centric in-plane currents calculated for the \(H_\alpha\) system with a minimal basis set give an excellent match to the out-of-plane currents of the carbocycle calculated with a large basis set. Figure 3 presents a pseudo-π simulation of the heterocyclic ring in which the boron and nitrogen atoms are modelled by one-electron atoms with nuclear charges of +0.7\(e\) and +1.3\(e\), each carrying STO-3G s and p functions (exponent 1.0\(\rho\)), the charge difference playing the role of the \(\eta\) parameter in the Hückel analysis, and the in-plane p functions giving radial flexibility to charge and current densities. Pure symmetry arguments predicted opposed paramagnetic and diamagnetic currents; the pseudo-π map shows that they occupy different regions of space, with diamagnetic circulation on the outside and paramagnetic circulation on the inside of the ring, the net effect being a set of circulations centred on electronegative atoms. In the graph-theoretical Hückel–London model, this spatial pattern of opposed local currents was expressed as a reduction of the sole available parameter, the bond current. Both models therefore essentially agree on the effect of the electronegativity difference on the ring current.

**Currents in the eight-membered cycle:** For the alternating eight-membered cycle, the maximal symmetry is \(D_{\text{ih}}\) (\(\eta \neq 0\)) or \(D_{\text{sh}}\) (\(\eta = 0\)) and the energy levels \(e_i(D_{\text{ih}}/D_{\text{sh}}\) labels, \(d_i = \text{degeneracy}) are:

\[
e_i = \alpha + \sqrt{2 + \eta^2} \beta (A_{2\alpha}/A_{\gamma\beta}), \quad d_i = 1;
\]

\[
e_1 = \alpha + \sqrt{2 + \eta^2} \beta (E_{\gamma\beta}/E_{\delta\gamma}), \quad d_1 = 2;
\]

\[
e_2 = \alpha + \sqrt{2 + \eta^2} \beta (E_\delta/E_{\gamma\beta}), \quad d_2 = 2; \quad e_3 = \alpha - \sqrt{2 + \eta^2} \beta (E_\delta/E_{\gamma\beta}), \quad d_3 = 2;
\]

\[
e_4 = \alpha - \sqrt{4 + \eta^2} \beta (A_{2\alpha}/B_{2\alpha}), \quad d_4 = 1;
\]

In the carbocyclic system with full symmetry, the degeneracy of \(\psi_{1\alpha}\) and \(\psi_{3\alpha}\) leads to an open-shell configuration which can be stabilised in various ways: distortion to \(D_{2a}\) leads to the tub-shaped equilibrium geometry of the free COT molecule; in-plane relaxation to \(D_{\text{sh}}\) yields a geometry similar to those found in “clamped”-substituted COT systems.\(^{[29]}\) In spite of its bond alternation, planar \(D_{\text{sh}}\) COT retains fully delocalised orbitals and the ring current of the equilaterial carbocycle, as Figure 1 shows.\(^{[4,28]}\)

In the heterocyclic system, when \(\eta \neq 0\), with the nitrogen atom as atom 0, \(\psi_{1\alpha}\) as the bonding and \(\psi_{3\alpha}\) the antibonding partner, the assignment of labels \(B_{2\alpha}\) and \(B_{\alpha\beta}\) depends on the setting of \(D_{\text{sh}}\) within \(D_{\text{ih}}\).

For a general value of \(\eta\), the mixing of angular-momentum components is again described by two angles, \(\mu\) and \(\kappa\), with

\[
\eta = 2\tan 2\mu = \sqrt{2}\tan 2\kappa.
\]

\[
\phi_{1\alpha} = \cos \mu \psi_{1\alpha} - \sin \mu \psi_{3\alpha}.
\]

\[
\phi_{3\alpha} = \cos \kappa \psi_{1\alpha} - \sin \kappa \psi_{3\alpha}, \quad \phi_{1\alpha} = \cos \kappa \psi_{1\alpha} + \sin \kappa \psi_{3\alpha}.
\]

\[
\phi_{2\alpha} = \psi_{2\alpha}, \quad \phi_{2\alpha} = \psi_{2\alpha}.
\]

\[
\phi_{3\alpha} = \sin \kappa \psi_{3\alpha} + \cos \kappa \psi_{1\alpha}, \quad \phi_{3\alpha} = -\sin \kappa \psi_{1\alpha} + \cos \kappa \psi_{3\alpha}.
\]

\[
\phi_{4\alpha} = \sin \mu \psi_{1\alpha} + \cos \mu \psi_{3\alpha}.
\]

Note that functions \(\psi_{1\alpha}\) and \(\psi_{3\alpha}\) as the HOMO and LUMO, remain unmixed for all values of \(\eta\), separated by a gap that is linear in \(\eta\), that is, \(2\eta\). Each is perfectly localised, the HOMO on the nitrogen atom and the LUMO on the boron atom. In contrast, with increasing values of \(\eta\), the functions \(\phi_{1\alpha}\), \(\phi_{3\alpha}\), \(\phi_{4\alpha}\), \(\phi_{3\alpha}\), and \(\phi_{4\alpha}\) become increasingly localised on the electronegative atoms: when \(\eta = 1\), the nitrogen and boron atoms have Hückel π populations of \(\approx 1.65\) and \(0.35\) electrons, respectively. When \(\eta = 1\), here representing planar \(B_2N_2H_8\), \(\mu = 13.3^\circ\) and \(|\kappa| = 17.6^\circ\) so that \(\phi_{1\alpha}\) contains 5% of \(\psi_{1\alpha}\) and HOMO–1 \(\phi_{4\alpha}\) contains 10% of \(\psi_{3\alpha}\). Figure 2b shows the correlation of or-
bital energies with $\eta$ for the eight-membered cycle.

The symmetry argument for deducing the currents in 4$n$ systems involves several steps. Initially ($\eta \approx 0$), the current is dominated by the HOMO–LUMO transition across a small energy gap. This $\Delta \omega = 0$ transition generates an intense, purely paratropic, ring current. As $\eta$ increases, the HOMO–LUMO gap opens, and the intensity of the current falls but remains paramagnetic. Simultaneously, the separation of the HOMO–1 and the LUMO and that of the HOMO and the LUMO+1 increases, but only slowly; both contribute to $\Delta \omega = \pm \delta$ diatomic contributions to current. Thus, as $\eta$ increases, the original global paratropic (antiaromatic) ring current is subject to intrinsic reduction and increasingly significant cancellation.

In the MeWeeny form of the Hückel–London theory,[23] the ring current of the eight-membered cycle when $\eta$ is small is dominated by the HOMO–LUMO contribution to the imaginary bond–bond polarisability, which is $-\frac{1}{4}\alpha \beta n^2$, and hence falls sharply as $\eta$ increases from the planar-constrained form of COT (where $\eta = 0$) to the heterocycle. When $\eta = 1$, the eight-membered cycle has $\beta = \frac{1}{2}(\alpha + \beta)$ and $\pi = -\frac{1}{3}\alpha^2 - \frac{1}{6}\beta^2 - \alpha - \beta$ from bond currents $J = \frac{1}{\pi \alpha \beta} \pi - 0.105$, which constitute a reduced but still net paratropic circulation. If the ratio of the areas of the six-and eight-membered cycles is 9:16, a ring current of about a sixth of the strength of the (diatropic) benzene current is dominated by the HOMO–LUMO transition across a small $\eta$ transition generates an intense, $\delta$ current that weakens with $\eta$ and is increasingly cancelled by the diatropic current that arises from the transitions across the HOMO–LUMO+1 and HOMO–1–LUMO gaps of $\eta + \sqrt{4 + \eta^2} \beta^2$. In the Hückel–London theory, when $\eta = 1$ the reduced bond current for the four-membered ring remains net paratropic ($J = \frac{1}{\pi \alpha \beta} n^2 - 0.138$) and corresponds to half the current of a benzene ring which has $3/4$ times the area, and again represents the pattern of nitrogen-centred circulations in a more detailed description.

Currents in the four-membered cycle: For the four-membered ring, B$_2$N$_2$H$_4$, the extinction of current with increasing $\eta$ follows the same pattern as that for the eight-membered cycle. The four orbital energies are now $\epsilon_0 = \alpha + \sqrt{4 + \eta^2} \beta$, $\epsilon_1 = \alpha - \sqrt{4 + \eta^2} \beta$ again giving a linear HOMO–LUMO gap of $2\eta$ (see Figure 2c), and yielding a paratropic current that weakens with $\eta$ and is increasingly cancelled by the diatropic current that arises from the transitions across the HOMO–LUMO+1 and HOMO–1–LUMO gaps of $\eta + \sqrt{4 + \eta^2} \beta^2$. In the Hückel–London theory, when $\eta = 1$ the reduced bond current for the four-membered ring remains net paratropic ($J = \frac{1}{\pi \alpha \beta} n^2 - 0.138$) and corresponds to half the current of a benzene ring which has $3/4$ times the area, and again represents the pattern of nitrogen-centred circulations in a more detailed description.

Generalisation for 4$n$ and (4$n$+2) $\pi$ BN heterocycles: The results for the four-, six- and eight-membered cycles are generalisations for the 4$n$ and (4$n$+2) $\pi$ BN heterocycles, with separate mechanisms, but equivalent results for the ring current in both cases. Consider an [N]-carbocycle, where N is even. As $\eta$ increases from 0, each bonding (b)/antibonding (a) molecular-orbital pair of the parent biparite carbocycle, with angular momenta $A_b$ and $A_a = N/2 - A_b$, which correspond to equal but opposite eigenvalues, mix to form a bonding/antibonding pair in the [N]-centre BN heterocycle with energies $\epsilon_b = \sqrt{4 \cos^2 \tau_a + \eta^2}$ and $\epsilon_a = -\sqrt{4 \cos^2 \tau_a + \eta^2}$, where $\tau_a = 2\pi/4N$, so that $\epsilon_b = -\epsilon_a$. The rotation describing the mixing is parametrised by the angle $\omega_b = \frac{1}{2\pi} \tan^{-1} (\eta/2 \cos \tau_a)$, where $0 \leq \omega_b \leq \pi/4$.

When $N = 4n+2$, $A_{\text{HOMO}} = n$ and $A_{\text{LUMO}} = n+1$, and the mixing angle $\omega_b$ is maximal for a given value of $\eta$. As we have seen, this leads to a sufficiently large value of $\eta$ to disrupt the global ring current and eventual localisation. When $N = 4n$, $A_{\text{HOMO}} = A_{\text{LUMO}} = n$, the original HOMO and LUMO carbocycle eigenfunctions remain unmix. Disruption of the global paratropic ring current is caused by the widening of the HOMO–LUMO gap, triggering cancellation of the rotational OHO–LUMO and translational HOMO–1–LUMO contributions.

**Ab initio current-density maps in azabora-heterocycles:** To obtain ab initio data on the currents in BN analogues of the 4$n$ and 4$n$+2 carbocycles, calculations were performed on B$_2$N$_2$H$_4$, B$_3$N$_3$H$_6$, and B$_4$N$_4$H$_8$. The geometry of each molecule was optimised at the restricted Hartree–Fock (RHF) level with the 6-31G** basis set and currents were calculated by using the ipsocentric approach at the coupled Hartree–Fock (CHF) level with the same basis set. At this level of theory, B$_3$N$_3$H$_6$ and B$_4$N$_4$H$_8$ have planar structures with $D_h$ and $D_{4h}$ symmetries, respectively, whereas the planar structure of B$_2$N$_2$H$_4$ with $D_{2h}$ symmetry is a transition state (imaginary frequency 116 cm$^{-1}$) that leads to a shallow $C_{2v}$ butterfly optimum, hinged at the BB diagonal, with a direhedral angle of 167°. Current-density maps were computed for both the constrained planar and the fully optimised structures of B$_2$N$_2$H$_4$. An alternative geometry for B$_2$N$_2$H$_4$ is based on the occupation of the corners of a cube[25b] this compact structure is slightly preferred to the planar form, as determined with small basis sets,[25b] but lies 302 kJmol$^{-1}$ above it when calculated at the 6-31G** level. All three planar molecules have uniform BN distances ($R = 1.4432, 1.4258, 1.4254$ Å, respectively).

These geometries are in general agreement with available experimental and theoretical data. The nonplanarity of B$_2$N$_2$H$_4$ has been noted in previous ab initio calculations,[26] which gave a BN distance of 1.457 Å, and although the parent molecule itself has not been synthesised, X-ray structures of five substituted molecules[24b] are known with mean BN distances varying between 1.430 and 1.486 Å, and all are planar apart from the severely hindered tetra-butyl derivative. Borazine has been the subject of many ab initio calculations.[27] The RHF/6-31G**-calculated BN distance of 1.4258 Å in borazine compares with 1.4355 ± 0.0021 Å (gas electron diffraction[26a,b]) and 1.429 Å (X-ray[26b]). No experimental data are available for the parent B$_2$N$_2$H$_4$, but experimental and theoretical structural data on its derivatives have been reviewed by Gilbert and Gallbreath.[29] Calculations at different levels give a planar (B3LYP/6-31G**+) or near-planar (MP2/6-31G**+) structure for B$_2$N$_2$H$_4$ with a BN length of 1.436 Å, intermediate between single and double bonds. Equivalent calculations on the permethylated mono-
cycle show it to adopt a tub structure. X-ray structures for derivatives with bulky substituents are tub-like with alternating BN bonds as in, for example, (tBuN)₄(MeB)₄. Solution ¹H NMR spectra of B₄N₄(CH₂R)₄(Me)₄ show a non-planar eight-membered ring. The current densities induced in (planar) B₄N₄H₈, B₅N₅H₁₀ and B₆N₆H₁₂ by a perpendicular magnetic field are plotted in Figure 4. For each molecule, the maps show HOMO, HOMO−1 and the total π and σ contributions to the induced current density plotted in a plane one bohr above...
that of the nuclei. As Figure 4 shows, all three systems, in contrast to the carbocycles, have multicentre patterns of local diatropic \( \pi \) circulations centred on the nitrogen atoms. In \( \text{B}_2\text{N}_2\text{H}_4 \), the nitrogen-centred \( \pi \) circulations arise entirely from the four electrons of the doubly degenerate HOMO: the total \( \pi \) and HOMO maps are visually indistinguishable, and the contribution of the HOMO–1 is negligible. In \( \text{B}_2\text{N}_2\text{H}_4 \) and \( \text{B}_3\text{N}_3\text{H}_6 \), the nitrogen-centred \( \pi \) circulations arise from a combination of the inner paratropic HOMO and the outer diatropic HOMO–1 currents. As the localised \( \sigma \) and \( \pi \) currents rotate in the same sense, they are reinforced in all three molecules. Maps of total current density (not shown) plotted for the puckered optimum geometry of \( \text{B}_2\text{N}_2\text{H}_4 \) at a height of \( 1 \alpha_0 \) above the nitrogen atoms and parallel to the median nuclear plane show the same general features: the localised nature of the current density is not critically dependent on planarity.

**Localised orbital analysis:** Further analysis using Pipek–Mezey localisation of the canonical molecular orbitals demonstrates the strong generic similarity of all three systems. The localised orbitals of \( \text{B}_3\text{N}_2\text{H}_2 \) are \( N \) core \( 1s \) orbitals on the heavy atoms, \( N/2 \) BN localised \( \sigma \)-bonding orbitals, \( N/2 \) NH and \( N/2 \) BH localised \( \sigma \)-bonding orbitals and \( N/2 \) \( \pi \) orbitals that are essentially nitrogen-localised \( \pi \) lone pairs. In this analysis nitrogen-centred \( \pi \) currents arise naturally as circulations in the lone pairs. The \( \sigma \) currents shown in Figure 4 for \( \text{B}_2\text{N}_2\text{H}_4 \), \( \text{B}_3\text{N}_3\text{H}_6 \) and \( \text{B}_4\text{N}_4\text{H}_8 \) have nodes at the boron sites. In the localised-orbital picture, the prominent “triangular” diatropic circulations around the nitrogen atoms arise from the three bonds meeting at nitrogen, each deltoid constituting a six-electron diatropic circulation. In the carbocycles, the \( \sigma \) currents are more uniformly distributed over all the heavy atoms, but are still spatially localised. The main difference in the magnetic response between carbocycles and azabora-heterocycles is that the \( \pi \) ring currents of one class are absent in the other. This distinction is clear from the computed current-density maps, which are fully compatible with the qualitative analysis based on symmetry and electronegativity. One and the same ipso-centric molecular-orbital picture explains both the current in the carbocycle and the lack of current in the heterocycle.

**Valence-bond calculations on azabora-heterocycles:** As the localisation of density on electronegative nitrogen centres is a key factor in the simple Hückel model of ring-current quenching, it is important to verify this qualitative difference between carbocyclic and azabora-heterocyclic systems by using more sophisticated theoretical methods. Accordingly, ab initio valence-bond configuration-interaction (VBCI) calculations, in which many structures are used, and valence-bond self-consistent field (VBSCF) calculations, in which both orbitals and structure coefficients are optimised, were performed on planar \( \text{B}_2\text{N}_2\text{H}_4 (1) \), \( \text{B}_3\text{N}_3\text{H}_6 (2) \) and \( \text{B}_4\text{N}_4\text{H}_8 (3) \) with the 6-31G** basis set. All were carried out by using TURTLE as implemented in the GAMESS-UK package. The wavefunction in the valence-bond calculations consists of a Hartree–Fock \( \sigma \) core in structures with singly occupied \( \pi \) orbitals. From a chemical point of view, these different structures can be seen as different bonding arrangements. All possible structures that can be generated by using the occupied atomic orbitals were used in the VBCI wavefunction, including chemically irrelevant ones. For \( \text{B}_2\text{N}_2\text{H}_4 \), there are 20 possible structures which arise from the 20 ways of distributing four electrons over four \( \pi \) orbitals to give a singlet. For \( \text{B}_3\text{N}_3\text{H}_6 \), 175 structures are possible, and for \( \text{B}_4\text{N}_4\text{H}_8 \) there are 1764. A VBCI calculation will show which bonding arrangements are preferred.

However, the VBCI wavefunction, owing to its fixed atomic orbital basis set, does not present a compact description of the wavefunction as orbital optimisation and correlation effects are intermixed. Therefore the most important structures in the VBCI calculations were used to construct a VBSCF wavefunction without imposing restrictions on the orbitals. From the coefficients in the VBCI wavefunctions the weights, and thus the importance of each structure, may be derived. For 1–3, the most important structure types are shown in Figure 5 with their respective weights. From these weights it appears that several structures contribute to the total wavefunction.

Subsequently, for \( \text{B}_2\text{N}_2\text{H}_4 \), the sets of structures of each kind were separately optimised in VBSCF calculations with-

![Figure 4](image-url)
out imposing any restrictions on the orbitals. The resulting energies of the first (1a: $-160.722209 E_h$) and the second (1b: $-160.721245 E_h$) were very similar, with the first structure, having two different orbitals on each nitrogen atom (see Figure 6), slightly more favourable.

A VBCI calculation was then performed on the first two sets of structures (1a+1b), each with their own optimised orbitals. This calculation gave the same energy as the single structure VBSCF calculation (1a), whereas the overlap between set one (1a) and set two (1b) was over 99.9%. This means that the VBSCF calculations converge to the same wavefunction, which is most aptly described as nitrogen atoms, each with a correlated pair of $p$ electrons. The conclusion is that there is no resonance energy and thus no resonance.

Similar results were obtained for B$_3$N$_3$H$_6$ (2) and B$_4$N$_4$H$_8$ (3). These calculations show the same tendency as both the H/C252ckel and the ring current calculations, that is, localisation of electrons on the nitrogen atoms. In fact, the valence-bond results show that the ground states of B$_2$N$_2$H$_4$ (1), B$_3$N$_3$H$_6$ (2) and B$_4$N$_4$H$_8$ (3) correspond to the structures 1a, 2a, and 3a, respectively.

Conclusions

Given the success of the simple one-parameter model in pointing out qualitative differences in current patterns between carbo- and azabora-cycles, it is natural to ask about its predictions for other systems, for example, X$_3$Y$_3$H$_6$—where does the borderline between “aromatic” and “nonaromatic” occur in this picture? The crudest form of the model shows a change from global circulation to localised currents by a strong reduction in the magnitude of ring current from $\eta = 0$ to $\eta = 1$; this variation is sigmoidal (Figure 7) with a point of inflexion, where current will be most sensitive to variation in $\eta$, at $\eta \approx 0.5$, where $\eta$ represents the deviation from the average electronegativity, that is, $|\alpha_X - \alpha_Y|/2|\beta|$. A rule of thumb is that $\alpha_X$ varies with the difference in electronegativity between X and C: $(\alpha_X - \alpha_C)/|\beta| = \chi_X - \chi_C$ for X as a one-electron donor and $(\alpha_X - \alpha_C)/|\beta| = 1 + \chi_X - \chi_C$ as a two-electron donor.[22a] Inflexion at $\eta = 0.5$ is consistent with indications for X$_3$Y$_3$ 6 systems from ring-current maps[2] and NICS calculations,[27c] systems in which the electronegativity/coulomb-parameter difference between X and Y is 1 or more on the Pauling scale lack ring currents (B$_3$O$_3$H$_3$,[2,27c] B$_4$N$_4$H$_8$,[2,27c] Al$_3$N$_3$H$_6$,[27c] and Al$_4$P$_4$H$_{12}$[27f]), whereas those with differences of half a unit or less may (C$_3$N$_3$H$_6$,[2,27c] and B$_3$P$_3$H$_6$[27c]) or may not (B$_3$S$_3$H$_6$[27c]) show global currents. This uniform trend lends support to the expectation that orbital-based models should be able to account for the subtleties of ring current in the range of aromatic, nonaromatic and antiaromatic heterocycles, and is a strong argument for using methods in which the orbital contributions themselves have a clear physical basis.

Figure 6. The singly occupied $p$ orbitals of B$_2$N$_2$H$_4$ (1), B$_3$N$_3$H$_6$ (2) and B$_4$N$_4$H$_8$ (3), respectively, which correspond to the structures 1a, 2a and 3a (see Figure 5). Orbitals from the left and right of the picture together form the correlated lone pair on the nitrogen atom.

Figure 7. Variation of ring current, $j$, with electronegativity parameter, $\eta$, in the Hückel–London treatment of the X$_3$Y$_3$ cycle. $j(\eta)$ is the ring current for a regular hexagonal cycle with alternating coulomb parameters $\alpha \pm \beta$ as a percentage of the current for the same cycle with $\eta = 0$. The inset curve (not to scale) shows the variation of the first derivative $d(j(\eta))/d\eta$ near $\eta = 0.5$.
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