

## Aromaticity, $\pi$ -electron delocalization, and ring currents\*

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**Abstract:** The magnetic criterion of aromaticity is based on the ability of a cyclic system to support a ring current. If the ring current has the diatropic sense, the system is aromatic; if the sense is paratropic, the system is antiaromatic. Attribution of aromaticity ab initio therefore reduces to the calculation and visualization of induced current density. This can be achieved at modest computational cost within the ipsocentric approach, where current density at any point in space is calculated with that point as origin of vector potential. This choice leads to accurate maps of current density and a uniquely simple interpretation in terms of nonredundant orbital contributions governed by translational and rotational selection rules. For example, four-electron diatropicity and two-electron paratropicity are predicted for delocalized forms of  $[4n+2]$ - and  $[4n]$ -annulenes, respectively. A new application to homoaromatic systems is described. Two model tris-homoaromatics, both neutral molecules, are shown to exhibit a through-space, highest occupied molecular orbital (HOMO)-dominated, four-electron ring current, in a direct analogy with the conventional “aromatic” benzene  $\pi$ -current.

**Keywords:** aromaticity; delocalization; ring current; homoaromaticity; ipsocentric.

### INTRODUCTION

“Aromaticity” is a term that is frequently used in the description and rationalization of stability, properties, and reactivity of unsaturated systems, but it has no universally accepted definition. Electron count, equalization of bond lengths, extra energetic stabilization, exaltation of diamagnetizability, central nuclear shieldings, and various measures of electron delocalization have all been proposed as quantitative criteria [1]. Here, we will adopt a well-established and widely accepted definition of aromaticity, that an aromatic system is a cyclic system with the ability to sustain a diatropic circulation of current in the presence of an external magnetic field. Consequences of the existence of this ring current that are, in principle, detectable in experiment include contributions to the NMR shifts of ring protons [2], exaltation of diamagnetizability [3], and increase in magnetizability anisotropy. Theoretical measures of ring current include predictions of all the above, and also calculation of nucleus-independent chemical shift (NICS) [4]. Clearly, however, the most direct theoretical test of aromaticity on the magnetic criterion is the calculation of induced current density. If this quantity is available, questions of aromaticity

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become questions of visualization: map the current, check for global circulation, and assign aromaticity/antiaromaticity by its sense and strength. It is now straightforward to carry out this procedure *ab initio* using the ipsocentric approach [5–12]. The present paper outlines the background to this approach, its conceptual advantages, and some of its applications. The final section of the paper describes a new application of current-density mapping, to the exploration of the connection between homoaromaticity and ring current.

## THE IPSOCENTRIC METHOD

Calculations of molecular magnetic response properties traditionally suffer from problems of unphysical gauge dependence, which can be traced to the use of a single origin of vector potential in combination with a finite basis set. The use of multiple or distributed origins generally improves matters, and Keith and Bader [5] made the logical inference that, if using several origins is beneficial, use of an infinite number of origins should be best of all. In general, there is a function that chooses, for any point in space where the perturbed wavefunction/density/current density is calculated, a point that is to be taken as the origin of the vector potential. The CSGT (continuous set of gauge transformations) method [5] was given an analytic coupled Hartree–Fock implementation by the Modena group [6–8] under the acronym CTOCD-*DZ* (continuous transformation of origin of current density–diamagnetic zero). In this approach, the simplest possible non-constant choice of origin function is made: the current density at any chosen point in space is calculated with that point itself taken as the origin of vector potential. The physical motivations for this choice and a number of alternatives are described in detail in [8]. To emphasize the special simplifying feature of CSGT or CTOCD-*DZ*, we now refer to the method as *ipsocentric* [9–11].

The key features of the ipsocentric approach are revealed by examination of the orbital-by-orbital response of the wavefunction to the applied magnetic field. In an independent-electron model, the first-order change to an occupied orbital  $\psi_n$  of an  $N$ -electron system in an external magnetic field  $\mathbf{B}$  can be expressed in terms of unoccupied orbitals  $\psi_p$  and their energies  $\varepsilon_p$  (in a.u.) as [9]

$$\begin{aligned} \psi_n^{(1)} = \psi_n^{(p)} + \psi_n^{(d)} = & -\frac{1}{2} \sum_{p>N/2} \psi_p \frac{\langle \psi_p | \mathbf{l} | \psi_n \rangle}{\varepsilon_p - \varepsilon_n} \cdot \mathbf{B} \\ & + \frac{1}{2} \mathbf{R} \times \sum_{p>N/2} \psi_p \frac{\langle \psi_p | \mathbf{p} | \psi_n \rangle}{\varepsilon_p - \varepsilon_n} \cdot \mathbf{B} \end{aligned} \quad (1)$$

where  $\mathbf{l}$  and  $\mathbf{p}$  are angular- and linear-momentum operators, respectively, and  $\mathbf{R}$  is the displacement of the origin of vector potential from the origin of coordinates, which will be set equal to  $\mathbf{r}$ , the position of the electron, in the evaluation of current density. In this partitioning of the wavefunction, the conventional paramagnetic/paratropic current arises from  $\psi_n^{(p)}$ , its intensity depending on accessibility of states via rotational transitions, and the diamagnetic/diatropic current arises from  $\psi_n^{(d)}$ , its intensity depending on accessibility of states via translational transitions. The rotations and translations in question when we are discussing ring currents of planar systems are the rotation about the field direction, and the translations in the plane normal to the field. In systems with symmetry, the symmetries of the translational (linear-momentum) and rotational (angular-momentum) operators can be used to derive separate symmetry-based selection rules for the diatropic and paratropic contributions to induced current density.

The form of eq. 1, with its restriction in the sums to occupied–unoccupied transitions, and with orbital-energy differences in the denominators, suggests that, other things being equal, current density will arise from the activity of relatively few electrons near the highest occupied molecular orbital (HOMO) energy, where the gap between occupied and empty orbitals is smallest. Importantly from a conceptual point of view, the restriction to occupied–unoccupied virtual excitations also implies that the

maps can be expressed as sums of the simplest possible orbital contributions—simplest possible in the sense that they involve no nonphysical occupied–occupied remixing terms, so that each contribution will retain a separately attributable significance, and so can be used to construct a chemical interpretation of ring current.

Only the ipsocentric distribution of origins gives rise to this complete absence of occupied–occupied mixing; all other schemes for distribution of origin produce some remixing of occupied orbitals in the presence of the field [12]. We are, of course, free to choose as the starting set of occupied molecular orbitals any orthonormal set that spans the occupied space. For fully delocalized systems, including many classic  $\pi$ -aromatics, it is appropriate to use canonical molecular orbitals, and it is often found then that the current-density contributions are concentrated in the frontier canonical orbitals; more localized systems will show a spread of contributions from a wider range of orbitals, and may be more transparently treated in terms of orbitals that have been localized according to some overlap criterion, as in, e.g., the Pipek–Mezey scheme [13]. Reversing the argument, the number of contributing orbitals and the “open” or “closed” nature of the orbital circulations can be used to give an intrinsic magnetic criterion of localizability of a  $\pi$ - or  $\sigma$ -system [11].

By now, some dozens of systems have been treated in the literature at the CTOCD-*DZ/6-31G\*\*//RHF/6-31G\*\** level, i.e., with optimization of geometry at the RHF/6-31G\*\* level followed by ipsocentric calculation of currents in the same basis set. Current maps derived with the ipsocentric choice of origin are physically realistic, even when these modest basis sets are used for their calculation [14], and are usually insensitive to details of the geometry. Maps are usually plotted with the SYSMO program [15] as projections, in the plane 1 bohr above that of the molecule, of the current density induced by a external magnetic field oriented perpendicular to the ring of interest; decomposition into contributions from  $\sigma$ - and  $\pi$ -subsystems or into more detailed orbital-by-orbital maps are made as appropriate. If required, the orbital contributions can be further analyzed into contributions from individual excitations [16]. We refer to published work for descriptions of current-density maps for various molecules and families of molecules, including [n]-annulenes [10,17], polycyclic hydrocarbons [18–22], heterocycles [23–25], porphyrin macrocycles [26], fullerenes [27] and trannulenes [28], metal clusters [29],  $\sigma$ -aromatics [30], exotic species [31,32], triplets [33], and transition states [34,35]. The following section summarizes the application of the approach in [n]-annulenes, from which many of the principles and advantages of the method are already clear.

## AN EXAMPLE: RING CURRENTS IN [n]-ANNULENES

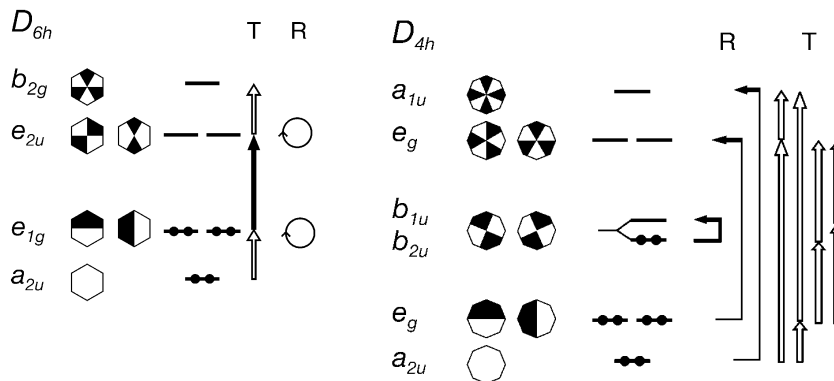
One of the most telling applications of the ipsocentric approach is the archetypal ring-current aromaticity and antiaromaticity of planar [n]-annulenes. The dichotomy between  $4n+2$  aromatic and  $4n$  antiaromatic systems is supported by the maps of ring-current response to an external magnetic field. Ipsocentric calculations on systems such as benzene, cyclopentadienide anion, and tropylium cation [18] lead to maps that show the expected diatropic  $\pi$ -ring currents, whereas calculations on planar-constrained cyclooctatetraene lead to a map with a strong paratropic ring current. Perhaps more surprisingly, the orbital decompositions of these  $\pi$ -maps reveal that only four of the  $4n+2$   $\pi$ -electrons of the aromatic cycles, and only two of the  $4n$   $\pi$ -electrons of the antiaromatic, are making significant contributions to the ring current. In both cases, the ring current is a HOMO-dominated response. The dominance of the HOMO electrons (through their virtual excitation to the lowest unoccupied molecular orbital, LUMO) is readily explained, using only the qualitative features of the  $\pi$ -molecular orbitals that are already apparent in the classical Hückel treatment of an [n]-annulene.

The explanation runs as follows. For the response of planar conjugated  $\pi$ -systems to a perpendicular magnetic field, the relevant operators for the excited-state sums in eq. 1 are  $R_{\parallel}$ , the rotation about the normal to the molecular plane, and  $T_{\perp}$ , the pair of translations within that plane. Contributions to the orbital current density in diatropic and paratropic senses are governed by symmetry-based selection

rules. An occupied-to-virtual transition  $\psi_n \rightarrow \psi_p$  gives a paratropic ring current contribution if, in the point group of the field-free molecule, the product of representations  $\Gamma(\psi_n) \times \Gamma(\psi_p) \times \Gamma(R_{\parallel})$  contains a totally symmetric component, and gives a diatropic ring current if the product  $\Gamma(\psi_n) \times \Gamma(\psi_p) \times \Gamma(T_{\perp})$  contains a totally symmetric component. A transition may be translationally active, rotationally active, both, or neither. These rules have powerful consequences for the [n]-annulenes.

Under the Hückel approximations for a ring of N atoms with equal coulomb parameters  $\alpha$  connected by bonds of equal resonance parameter  $\beta$ , the  $\pi$ -molecular orbitals and their energies are given by the well-known circle construction, where energies correspond to the heights of vertices of an N-gon inscribed point-down in a circle of radius  $2\beta$  drawn about the origin, and the orbitals are sine and cosine combinations associated with an angular momentum quantum number  $k = 0, 1 \dots (N/2)$  (N even),  $\dots (N+1)/2$  (N odd). Closed-shell configurations occur at the  $4n+2$  aromatic counts of 2, 6, 10,  $\dots$   $\pi$ -electrons, and, in the same approximation, open shells with two electrons in two degenerate orbitals at the  $4n$  anti-aromatic counts 4, 8,  $\dots$

In a closed-shell configuration, the occupied orbitals form complete  $k$  shells. Since  $R_{\parallel}$  mixes only orbitals of equal  $k$ , it cannot produce occupied-to-unoccupied transitions. On the other hand,  $T_{\perp}$  operators mix orbitals on adjacent rungs of the Hückel energy ladder, corresponding to orbitals that differ by  $\pm 1$  in  $k$ . The only occupied-to-unoccupied translational transitions in the system are therefore from HOMO to LUMO (see Fig. 1). Hence, in a  $(4n+2)$ -electron monocycle, the ring current is wholly diatropic and arises entirely from the magnetic-field-induced mobility ("strobilism" [36]) of the HOMO electrons. In the general case, the HOMO is doubly degenerate and the system has 4-electron diamagnetism. Bond alternation will allow further mixings, but in small cases the ring current will remain diatropic and dominated by the HOMO/LUMO excitation. In larger annulenes with equilibrium geometries of lower symmetry, the cumulative effect of these new mixings will lead to damping of ring-current aromaticity [17].



**Fig. 1** Virtual excitations contributing to diatropic and paratropic ring currents. Nodal patterns and relative energies of the Hückel orbitals of the hexagonal and octagonal rings are shown. T arrows and R circular/bent arrows denote the symmetry-allowed translational (diatropic) and rotational (paratropic) transitions from occupied to unoccupied orbitals.

The origin of paratropic ring current in monocycles follows by considering the half-filling of the  $\pi$ -system when  $N = 4n$ . In full  $D_{Nh}$  symmetry, the two nonbonding orbitals lead to an open-shell  $e^2$  configuration, but the system can distort to lift this degeneracy, for example, by adopting a bond-alternated  $D_{(N/2)h}$  structure. In the reduced symmetry, the HOMO/LUMO pair splits into nondegenerate components, related by a rotational transition with a small energy denominator. The transition moment numerator remains large, since  $R_{\parallel}$  precisely interchanges HOMO and LUMO in the limit. The HOMO/LUMO term dominates the sum over states, thereby producing a strong 2-electron paratropic

ring current. Additional transitions introduced by the lowering from  $D_{Nh}$  to  $D_{(N/2)h}$  symmetry are relatively unimportant in small ring systems, though they play a more important role in large [4n]-annulenes [17].

Thus, according to the ipso-centric version of magnetic response theory, both aromatic diatropic and antiaromatic paratropic currents in  $\pi$ -monocycles have the same source: both arise from the angular-momentum properties of the HOMO/LUMO transition, which in the diatropic case corresponds to insertion of an additional angular node, and in the paratropic case to a rotation of the existing nodes.

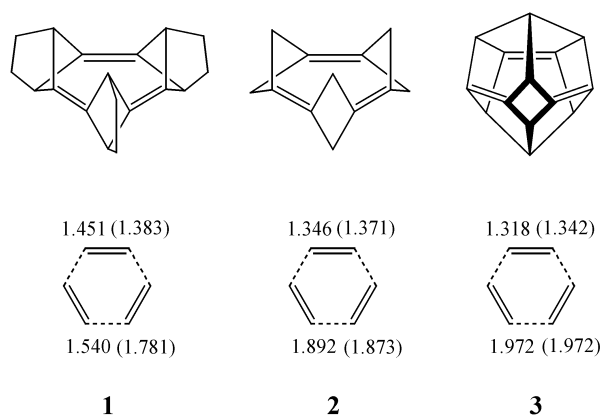
These qualitative predictions from Hückel theory give an excellent description of what is seen in the ab initio computed maps [10,11]. Extensions of the arguments have been used to rationalize ring-current aromaticity of heterocycles [23], suppression and survival of current in clamped benzene and planarized COT [37,38], counter-rotation of rim and hub currents in [n]-circulenes [19] and kekulene [20], lack of ring current in radialenes and oxocarbons [39], and the patterns of current in giant graphitic flakes [40], where the molecular-orbital arguments become arguments about “bands” arising from interaction of Clar sextets. In many cases, the selection rules reduce to node counting, and so survive into situations of low symmetry, where formal statements about products of representations are no longer helpful. The one-to-one correspondence of  $\pi$ -symmetries on an [n]-annulene with those of  $\sigma$ -orbitals of hydrogenic rings, an idea which can be traced back to London’s very early work on ring current [41], has been used to construct a successful “pseudo- $\pi$ ” model version of the ipso-centric calculation [42], which can be used for rapid screening of current patterns of polycyclic hydrocarbons and even three-dimensional carbon clusters [43].

## HOMOAROMATIC RING CURRENTS?

Homoaromaticity (stabilization of a formally disconnected unsaturated system by the continuation of delocalization across saturated linkages [44]), and in particular the possibility of the occurrence of homoaromaticity in neutral molecules, has been the subject of some controversy for over four decades. The subject is reviewed by Williams [45] and a survey of the history of the debate is given by Stahl et al. [46], who use evidence based on magnetic and energetic criteria to argue for the “tris-homoaromaticity” of several members of a family of specially constructed  $6\pi$ -systems based on an “in-plane benzene”. Three systems from this family will be studied in the present paper.

As we have noted earlier, on the widely accepted magnetic criterion for conventional aromaticity, an aromatic system is one that supports an induced diatropic ring current. The natural extension for homoaromatic systems is to propose that a homoaromatic system should support an induced diatropic ring current that jumps the gap(s) made by the saturated linkages [47]. Owing to the different directionality properties of the participating orbitals, we can expect some differences in spatial distribution of the current, but on this criterion we do have a clear test that can be applied to decide attributions of homoaromaticity. It is necessary only to inspect a current-density map: either a current with the desired sense will be seen, or not, and the map will then show *how* the ring current (if any) crosses the gaps in formal conjugation.

We apply our usual approach for the calculation of induced currents to three systems (**1–3** (Scheme 1), identical with **17**, **15**, and **16** of ref. [46], respectively). These systems were designed to test the notion of tris-homoaromaticity in neutral species [46]. They incorporate rigid saturated clamping frameworks that maintain three double bonds in a geometry where end-to-end  $\sigma$ -overlap of the participating p-orbitals should be possible. All three contain a planar array of six carbon atoms, linked pairwise by double bonds that are formally constructed from p-orbitals that lie in this “central” plane. The gap between the nonbonded atoms is different in all three cases, but the three systems all correspond to minima on their respective potential surfaces. As far as we are aware, all three structures remain hypothetical. NICS calculations are interpreted [46] as indicating that systems **1** and **2** support a significant diatropic ring current, but that **3** sustains only a “weak diatropic current”. Indeed, the computed values of NICS(0) for **1** to **3** (e.g.,  $-30.6$  (**1**),  $-21.5$  (**2**), and  $-3.6$  (**3**) at the B3LYP/6-31G\*// B3LYP/6-31G\*

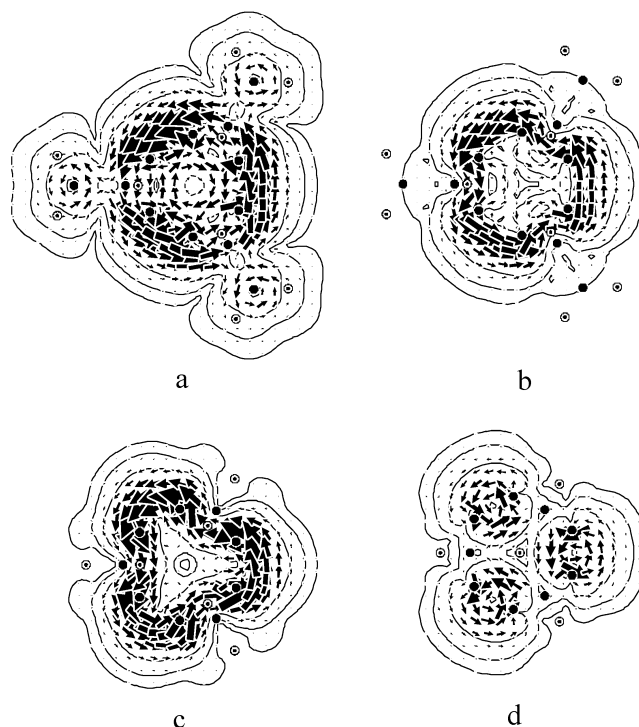


**Scheme 1** Molecular structures of potentially homoaromatic systems, showing CC distances (in Å) for the central array of six carbon nuclei (RHF/6-31G\*\* (present work) and (in brackets) B3LYP/6-31G\*\* [46]). Optimization of **1** at the B3LYP/6-31G\*\* level (present work) gives 1.751 and 1.393 Å, respectively, for long and short CC distances.

level [46]) would, even when reduced for non-“ $\pi$ ” effects, indicate very large ring currents in the first two species.

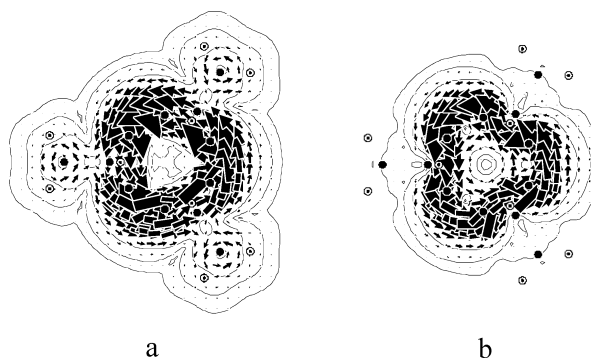
In the present study, the molecular geometries are reoptimized at the RHF/6-31G\*\* level and the current induced by an external magnetic field perpendicular to the central plane is then calculated at the CTOCD-*DZ* (ipsocentric) level, with the same basis set. When exploring conventional  $\pi$ -aromaticity, it is useful to plot the current at a height of  $1 a_0$  above the molecular plane. Here, we expect the ring current arising from homoaromaticity, if any, to flow in the “central” plane itself, where there will be visual interference from localized core and bond currents, and so for clarity we use a slightly shifted plotting plane, at a height of  $0.5 a_0$ . A height profile of the current can be obtained by taking a stack of plotting planes, or a plotting plane at right angles to the original first, retaining the direction of the external magnetic field. We will be interested in orbital contributions to the maps: in the  $D_{3h}$  point group appropriate to these systems, the three in-plane “ $\pi$ ”-orbitals of the ring have symmetries  $A_1'$  and  $E'$ : the  $E'$  pair is the HOMO and the  $A_1'$  MO lies at the top of the stack of  $A_1'$  orbitals.

Figure 2 shows current-density maps for a height of  $0.5 a_0$  above the central plane in **1–3**, and illustrates a clear distinction between **1** and **2** on the one hand, and **3** on the other. The current density arising from all electrons in **1** (Fig. 2a) shows a global, diatropic circulation associated with the six central carbon atoms and crossing the three gaps between the formally double-bonded pairs, i.e., a definite homoaromatic ring current. This ring current is attributable to the four electrons of the  $E'$  HOMO (Fig. 2b), in direct analogy with the HOMO-dominated classical ring current of benzene itself. As Fig. 2c shows, **2** has a similar homoaromatic ring current arising from the contribution of the HOMO electrons. In contrast, the in-plane “ $\pi$ ”-system of **3** contributes three localized circulations, as would be expected for separated double bonds, and has no global HOMO circulation (Fig. 2d).



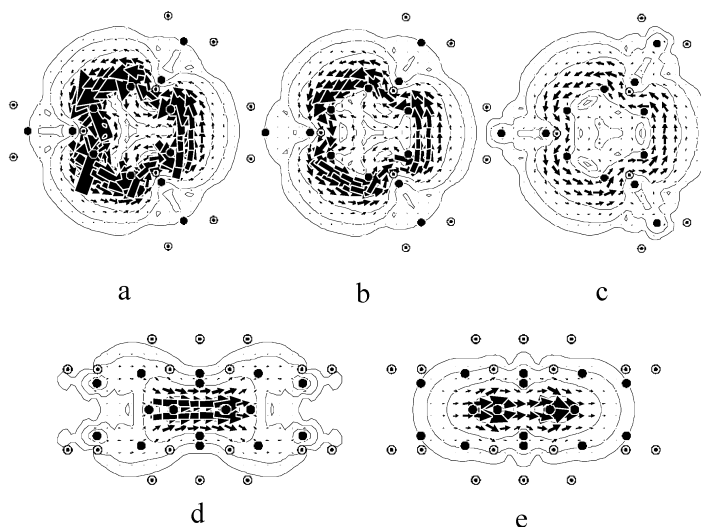
**Fig. 2** Current-density maps calculated at the CTOCD-DZ/6-31G\*\*//RHF/6-31G\*\* level in a plotting plane  $0.5 a_0$  above the plane of the central array of six carbon nuclei, for (a) **1** (contribution of all electrons), (b) **1** (contribution of  $13E$  HOMO), (c) **2** (contribution of  $9E$  HOMO), (d) **3** (contribution of  $9E$  HOMO).

On the magnetic definition, therefore, **1** and **2** are confirmed as homoaromatic whereas **3** is non-homoaromatic. This conclusion is robust against changes in geometry. For example, the optimal geometries of **1** at RHF/6-31G\*\* and B3LYP/6-31G\*\* differ significantly in the predicted “gap distance” (Scheme 1), but lead to essentially identical predictions for the current-density map. Figure 3 shows the all-electron and HOMO-electron maps for the B3LYP/6-31G\*\* geometry of **1**; the arrows are a little larger, as would be expected from the smaller HOMO/LUMO gap, but the patterns are the same as in Figs. 2a and 2b where the RHF/6-31G\*\* geometry was used.



**Fig. 3** Current-density maps calculated at the CTOCD-DZ/6-31G\*\*//B3LYP/6-31G\*\* level in a plotting plane  $0.5 a_0$  above the plane of the central array of six carbon nuclei, for (a) **1** (contribution of all electrons), (b) **1** (contribution of  $13E$  HOMO). Compare with Figs. 2a and 2b.

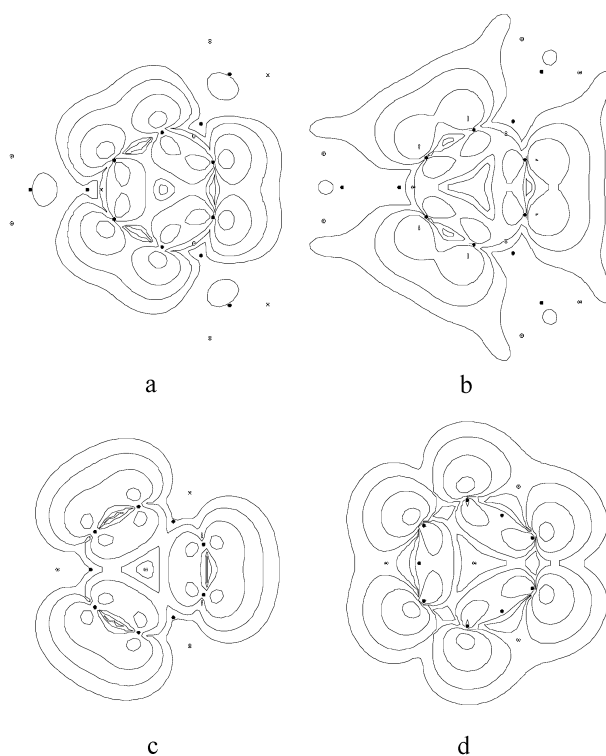
We can check that the current in **1** is maximal in the plane of the six participating carbon centers, as would be expected for a homoaromatic ring current that has its origins in orbitals of  $\sigma$ -symmetry. The current dies away with height from the central plane (Figs. 4a–c) and flows essentially parallel to the central plane, both in the region of a formal double bond (Fig. 4d) and in the gap (Fig. 4e), and so it is a true through-space flow of current across the interruption to conjugation.



**Fig. 4** Variation of the homoaromatic ring current of **1** with height about the plane of the central array of six carbon nuclei, seen from above (a) in the plane, (b) at a height of  $0.5 a_0$ , (c) at a height of  $1 a_0$ . Height profile of the homoaromatic ring current of **1**, seen as height profiles (d) at a height of  $1 a_0$  outside a formal double bond, (e) at  $0.5 a_0$  outside the “gap” between formally nonbonded carbon centers. Each panel shows a view from the outside of the ring of the current induced by a vertical external magnetic field and plotted in a vertical plane. Diatropic flow is anticlockwise when seen from above, from left to right when seen from the side. Other conventions are as in Fig. 2.

The spatial distribution of the ring current in **1** (and **2**) is also interesting in that current flows on the outside of the formal double bonds but on the inner side of the gaps. This distribution, and the differences between these systems and **3**, are easily rationalized by inspection of the participating orbitals. In the  $E'$  HOMO of **3** (Fig. 5c), the three formal double bonds retain their identity, and overlap across the gaps is small. Instead, in the HOMO of **1**, (Fig. 5a) where the gaps are smaller, there is a significant interaction between the p-orbitals of the double bonds. The in-plane p-orbitals rotate, simultaneously increasing their intra-bond overlap on the outer side of the double bond, and their intra-bond overlap across the inside of the gap. These orbital plots also illustrate the explanation of the ring current of **1** (and **2**). The HOMO and LUMO of the in-plane “ $\pi$ ”-system differ by one in the numbers of their angular nodes, and hence, according to the ipsocentric theory, the orbitals are connected by a translationally allowed virtual excitation, in direct analogy with the HOMO/LUMO excitation of benzene itself.





**Fig. 5** Contour plots for the HOMO and LUMO pairs, (a)  $13E'$  HOMO of **1**, (b)  $14E'$  LUMO of **1**, (c)  $9E'$  HOMO of **3**, (d)  $10E'$  LUMO of **3** showing charge density in the plane of the central array of six carbon nuclei. **1** shows greater density than **3** in the gap between the formally nonbonded atoms.

Current that “jumps across a gap” in this way has also been predicted in current-density calculations in a different context [35]: in the pericyclic transition state for the formation of benzene from three ethyne molecules, where the mutual orientation of the in-plane p-orbital systems is the same as that forced by the clamping superstructures in **1–3**. The prediction for the trimeric system is that as the reactants approach along the intrinsic reaction coordinate, a diatropic  $\sigma$ -ring current connecting the three reactant moieties grows in. This current is fully formed by the transition state. As the reaction moves on downhill toward benzene, the character of the current map continues to change, with the formation of new  $\sigma$ -bonds and eventually the appearance of the normal strong diatropic  $\pi$ -ring current of benzene.

In the present study, the conclusion that **1** and **2** are tris-homoaromatic systems on the magnetic criteria, but that **3** is not, is in essential agreement with the statements made on the basis of NICS and magnetizability calculations in [46]. The non-homoaromaticity of **3** is perhaps to be expected, given the large gap distance and poor orbital overlap in this structure.

Current-density mapping has given an explicit picture of the homoaromatic ring current in **1** and **2**, its distribution in space and its rationalization in terms of electronic structure. As with the currents associated with conventional aromaticity, the existence, sense, and strength of the homoaromatic ring current are seen to have a clear dependence on orbital directionality, symmetry, and energy. The ipso-centric approach promises to be useful in the exploration of further links between current and extended concepts of aromaticity.

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