DOI: 10.1002/chem.200600507

On the Lack of Ring-Current Aromaticity of (Heteroatom) [*N*]Radialenes and their Dianions

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Abstract: Current-density maps, calculated at the ab initio RHF//6–31G**/CTOCD-DZ level, show no significant π ring current in planar equilateral geometries of neutral and dianionic [*N*]radialenes, oxocarbons and thiocarbons $C_NY_N^{q-}$ ($Y=CH_2$, O, S; $N=4$, 5, 6; $q=0$ (**1a**–**12a**), 2 (**1b**–**12b**)). Only the $N=3$ deltate dianions $C_3Y_3^{2-}$ ($Y=CH_2$, O, S (**1b**, **5b** and **9b**)) have discernible π ring current, and then with at most 20–25 % of the strength of the standard benzene current. On the magnetic criterion, lack of current is definitive evidence against aromaticity. Pictorial molecular-orbital analysis within the ipsocentric approach shows this to be an inevitable consequence of the nodal structure of the π and π* orbitals of [*N*]radialene-like systems. On grounds of angular-momentum symmetry, spatial distribution, or both, the HOMO–LUMO excitation does not contribute a significant central diamagnetic ring current.

Keywords: ab initio calculations · anions · aromaticity · Hückel theory · radialenes

Introduction

Oxocarbon dianions (**5b**–**8b**, Figure 1) have an extensive chemistry,[1–4] with its beginnings in the early nineteenth century, and they were long considered, following the proposal of West et al,[5–11] to form an aromatic series. More recent work has questioned the aromaticity of the larger dianions[12–14] and of their thio analogues.[15] In one case,[12] only the smallest oxocarbon, the deltate dianion $C_3O_3^{2-}$ (**5b**) is assessed as aromatic. On the magnetic criterion, an aromatic molecule is one that supports a diatropic ring current and so a direct answer to questions of aromaticity can be given by calculation and mapping of the current density induced by a perpendicular external magnetic field. The ipsocentric approach[16,17] gives not only a method for obtaining accurate maps at modest computational cost, but also an interpretation of the sense and strength of induced current in terms of orbital contributions. These contributions obey symmetry-based selection rules and can often be characterised by using little more than a node-counting argument.

We show here that a qualitative orbital model gives a pictorial explanation for the lack of aromaticity in the oxocarbon (**5b**–**8b**) and thiocarbon (**9b**–**12b**) dianion series. This qualitative reasoning is confirmed by systematic ab initio calculations that show no significant π ring current in higher members of the series, and only small currents in deltate (**5b**) and thiodeltate (**9b**) dianions. For comparison, calculations are also carried out for the [*N*]radialenes $C_N(CH_2)_N$ (**1a**–**4a**) and their dianions $C_N(CH_2)_N^{2-}$ (**1b**–**4b**). It turns out that, at least on the magnetic criterion, neither the [*N*]radialenes nor their dianions with $N>3$ are aromatic.

In the ipsocentric approach, the problem of spurious gauge-dependence of calculated magnetic response properties is solved by taking each point in space as its own origin in the calculation of induced current density.[16] This leads to a clear partition of the total current density into easily interpretable orbital contributions. Each occupied molecular orbital makes a contribution that depends on the availability of formal excitations to empty orbitals, and hence is gov-

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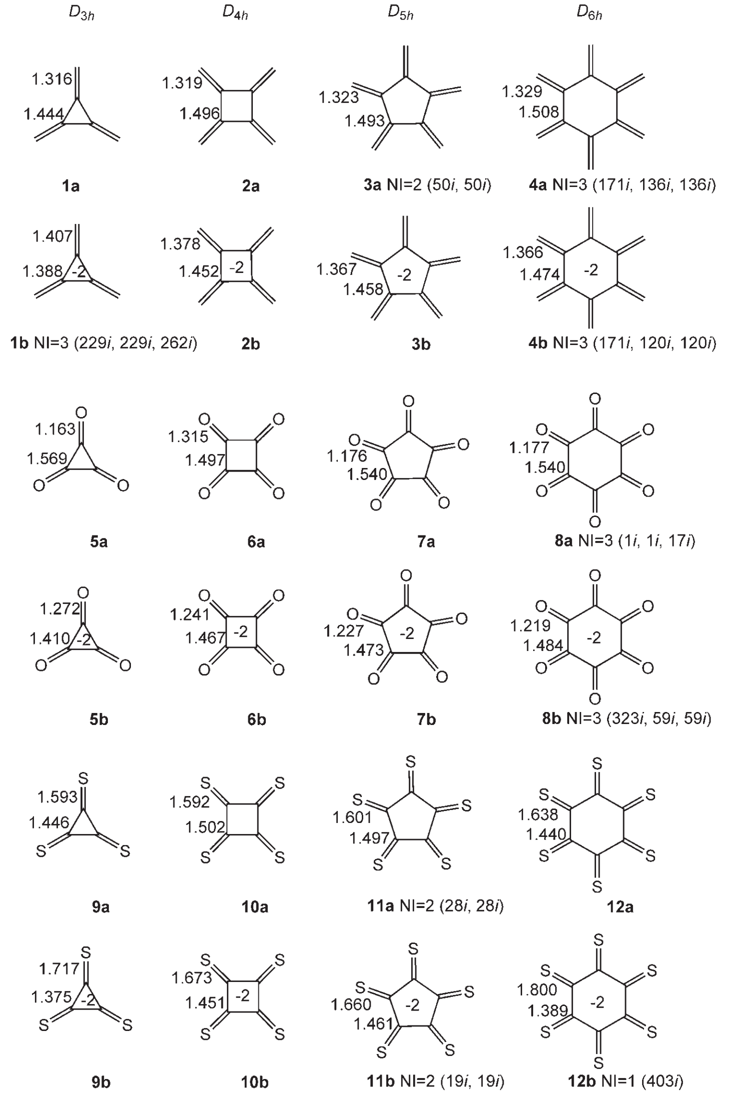


Figure 1. Optimised structures of neutral and dianionic [*N*]radialenes (**1a**–**4a** and **1b**–**4b**), oxocarbons (**5a**–**8a** and **5b**–**8b**) and thiocarbons (**9a**–**12a** and **9b**–**12b**). The two independent bond lengths obtained in a D_{Nh}-constrained optimisation at the RHF/6–31G** level are listed (in Å), and numbers (NI) and values of the imaginary frequencies (as wavenumbers, (cm^{-1})) are given for those cases in which the D_{Nh}-constrained structure is not at a local minimum.

erned by the symmetry of the occupied orbital, and the energies and symmetries of the manifold of unoccupied orbitals. The symmetry of the excitation determines the sense of the ring current: in a monocyclic system, diatropic current arises from a translational (electric–dipole allowed, node-increasing) excitation, and paratropic current from a rotational (magnetic–dipole allowed, node-preserving) excitation.[17] Questions of aromaticity can therefore often be resolved by purely pictorial arguments. Here, we will use as a starting point the simplest molecular-orbital method, that is, Hückel theory, to characterise the allowed excitations in [*N*]radialenes (**1a**–**4a**), oxocarbons (**5a**–**8a**), thiocarbons (**9a**–**12a**) and their dianions ((**1b**–**4b**), (**5b**–**8a**b and (**9b**–**12b**), respectively (Figure 1), and hence predict the ring-current behaviour of these systems. The predictions are tested against full ab initio calculations.

Results and Discussion

Hückel model for the [*N*]radialene framework

Orbital energies: The π system of a $C_N(CH_2)_N$ [*N*]radialene (cf. **1a**–**4a**, Figure 1) has a graph that is a connected cycle of *N* vertices each with one pendant neighbour (Figure 2). Molecular orbitals and orbital energies of the [*N*]radialene follow from the eigenvectors and eigenvalues of the adjacency matrix of the graph and can be obtained by an analytical construction directly from those of the central [*N*]annulene monocycle. Each vertex of the [*N*]radialene graph represents an sp^2 carbon atom contributing one π electron.

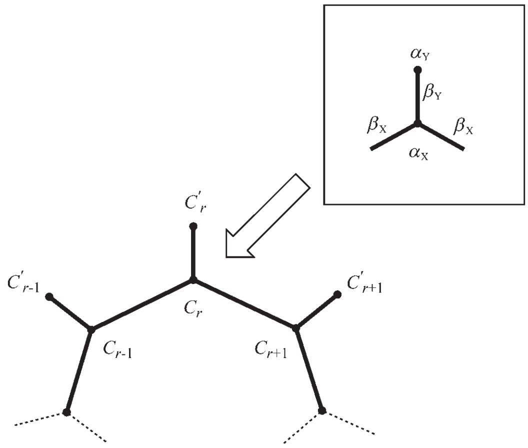


Figure 2. Graph of heavy-atom framework for the [*N*]radialene (**1a**–**4a**), oxocarbon (**5a**–**8a**) and thiocarbon (**9a**–**12a**) series, showing labelling of Hückel parameters and eigenvector coefficients.

In Hückel theory, molecular-orbital energies are $\varepsilon=\alpha+\lambda\beta$ in which λ is an adjacency eigenvalue, and α and β are the usual coulomb and resonance integrals. For each eigenvalue ν of the monocycle, there are two eigenvalues μ in the adjacency spectrum of the [*N*]radialene, given by the roots of the following quadratic equation [Eq. (1)].

$$\mu^2-\nu\mu-1=0 \tag{1}$$

The proof of this relation is as follows. In the monocycle, number the vertices 1, 2, …, *r*, …*N* so that an adjacency eigenvector will be (c_1, c_2, …, c_r, …c_N). Then the secular equations obeyed by the eigenvector coefficients are given be Equation (2), with the well-known solutions given by Equation (3) and with degeneracies 1 for $k=0$ and 2 for $k>0$. The *N* eigenvectors are sine and cosine waves with argument $2\pi kr/N$ at vertex *r*.

$$
\begin{aligned}
&c_N - \nu c_1 + c_2 = 0\\
&\ldots\\
&c_{r-1} - \nu c_r + c_{r+1} = 0 \qquad (2)\\
&\ldots\\
&c_{N-1} - \nu c_N + c_1 = 0
\end{aligned}
$$

$$\nu = 2\cos(2\pi k/N) \quad k = 0, \ldots (N-1)/2 \text{ or } N/2 \qquad (3)$$

In the $C_N(CH_2)_N$ [*N*]radialenes (**1a**–**4a**), the eigenvector corresponding to eigenvalue μ has coefficients C_r on the inner vertices of the cycle and C'_r on the outer, pendant vertices, with C'_r neighbouring C_r. The typical secular equations become those in Equation (4).

$$
\begin{aligned}
&C'_r + C_{r-1} - \mu C_r + C_{r+1} = 0\\
&C_r - \mu C'_r = 0
\end{aligned}
\qquad (4)
$$

Hence, the inner coefficients satisfy Equation (5) and obey the monocycle Equations (2) with eigenvalues obeying Equation (6); hence, $\mu^2 - \mu\nu - 1 = 0$, proving (1), and incidentally giving a route to determine the coefficients $\{C_1, \ldots C_r, \ldots C_N, C_1, \ldots C_r, \ldots C_N\}$ up to normalisation.

$$C_{r-1} - \left(\mu - \frac{1}{\mu}\right) C_r + C_{r+1} = 0 \qquad (5)$$

$$\mu - \frac{1}{\mu} = \nu \qquad (6)$$

The [*N*]radialene eigenvalues are given by Equation (7) and the corresponding orbital energies by Equation (8).

$$\mu_{\pm}(\nu) = \frac{\nu \pm \sqrt{\nu^2 + 4}}{2} \qquad (7)$$

$$\alpha + \left\{\frac{1}{2}\nu \pm \frac{1}{2}\sqrt{\nu^2 + 4}\right\}\beta \qquad (8)$$

As the eigenvalues ν fall in the range +2 and −2 (with +2 realised for all *N*, but −2 realised only for even *N*), μ lies between $\mu_-(-2) = -(1+\sqrt{2})$ and $\mu_+(+2) = +(1+\sqrt{2})$. As Equation (1) has a non-zero μ-independent term, the $C_N(CH_2)_N$ [*N*]radialene spectrum contains no zero, and consists of two compressed copies of the monocycle spectrum, preserving the order of eigenvalues within each copy, and separated by a gap. The gap is at least $\mu_+(-2) - \mu_-(+2) = 2(\sqrt{2}-1)$. Monotonicity of $\mu(\nu)$ with ν within each stack again follows from Equation (1) when Equation (9) is taken into account.

$$\left(\frac{d\mu}{d\nu}\right) = \frac{\mu}{2\mu - \nu} = \frac{1}{2}\left(1 \pm \frac{\nu}{\sqrt{\nu^2 + 4}}\right) > 0 \qquad (9)$$

The relationship between ν and μ sets of energy levels is illustrated schematically in Figure 3 and gives a basis for the interpretation of electronic configuration and properties of the various neutral and dianionic [*N*]radialene-like systems.

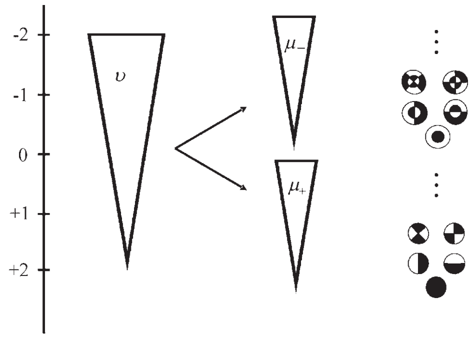


Figure 3. Schematic diagram of the splitting of the monocycle spectrum $\{\nu\}$ into the two branches $\{\mu_+\}$ and $\{\mu_-\}$ of the [*N*]radialene spectrum, with illustrations of the nodal patterns for the first three eigenfunctions of each set. The vertical scale shows the adjacency eigenvalues, with positive (bonding) values at the bottom.

The all-carbon [*N*]radialenes, $C_N(CH_2)_N$ (**1a**–**4a**), have 2*N* π electrons, and thus either a 4*n* or (4*n* + 2) electron count depending on the parity of *N*. In each case the lower stack of the annulene spectrum is filled, with a gap Δ_{H-L} of $\geq 2(\sqrt{2}-1)|\beta|$ to the LUMO. The LUMO is a nondegenerate orbital at adjacency eigenvalue $\mu_-(+2)$ and is formally descended from an antibonding combination of the nodeless functions on inner and outer sets of atoms. In the $C_N(CH_2)_N^{2-}$ (**1b**–**4b**) ions this orbital is also occupied, and the dianion LUMO pair (each with one angular and one radial node) is separated from the HOMO by a gap, Δ^{2-}_{H-L}, that decreases with *N* (i.e., $\Delta^{2-}_{H-L}/|\beta| = 1.204$ ($N=3$), 0.586 ($N=4$), 0.324 ($N=5$), 0.204 ($N=6$), 0.141 ($N=7$)...).

Orbital symmetries and induced currents: As both neutral and dianionic forms of the molecules have closed-shell π-electronic configurations, we can assume that the geometries retain full D_{Nh} symmetry, and so will discuss their orbital symmetries within this point group. The symmetry spanned by the occupied π orbitals of the neutral [*N*]radialene, Γ_{occ}, is equal to that of the full set of π and π* orbitals of the central annulene, $\Gamma_{\pi/\pi*}$, which is itself a product of the representation of the out-of-plane translation, Γ_z, and the permutation representation of the *N* annulene vertices [Eq. (10)]

$$\Gamma_{occ} = \Gamma_{\pi/\pi*} = \Gamma_z \times \Gamma_\sigma \qquad (10)$$

The permutation representation Γ_σ, and hence Γ_{occ}, can be written as an angular-momentum expansion in functions Γ_Λ, in which $\Lambda = 0, 1, \ldots$ is the number of angular nodes. The *N* unoccupied π orbitals of the neutral [*N*]radialene also span Γ_{occ}. Each value of Λ therefore occurs once for an occupied orbital (or pair of orbitals) with no radial nodes and Λ angular nodes, and once for an unoccupied orbital (or pair of orbitals) with one radial node and Λ angular nodes. The radial and angular nodal structures of the various orbitals are sketched at the right-hand side of Figure 3.

In particular, the LUMO of the neutral [*N*]radialene has angular momentum $\Lambda = 0$ (no angular node but one radial node) and hence has symmetry Γ_z. The HOMO has $\Lambda = m$

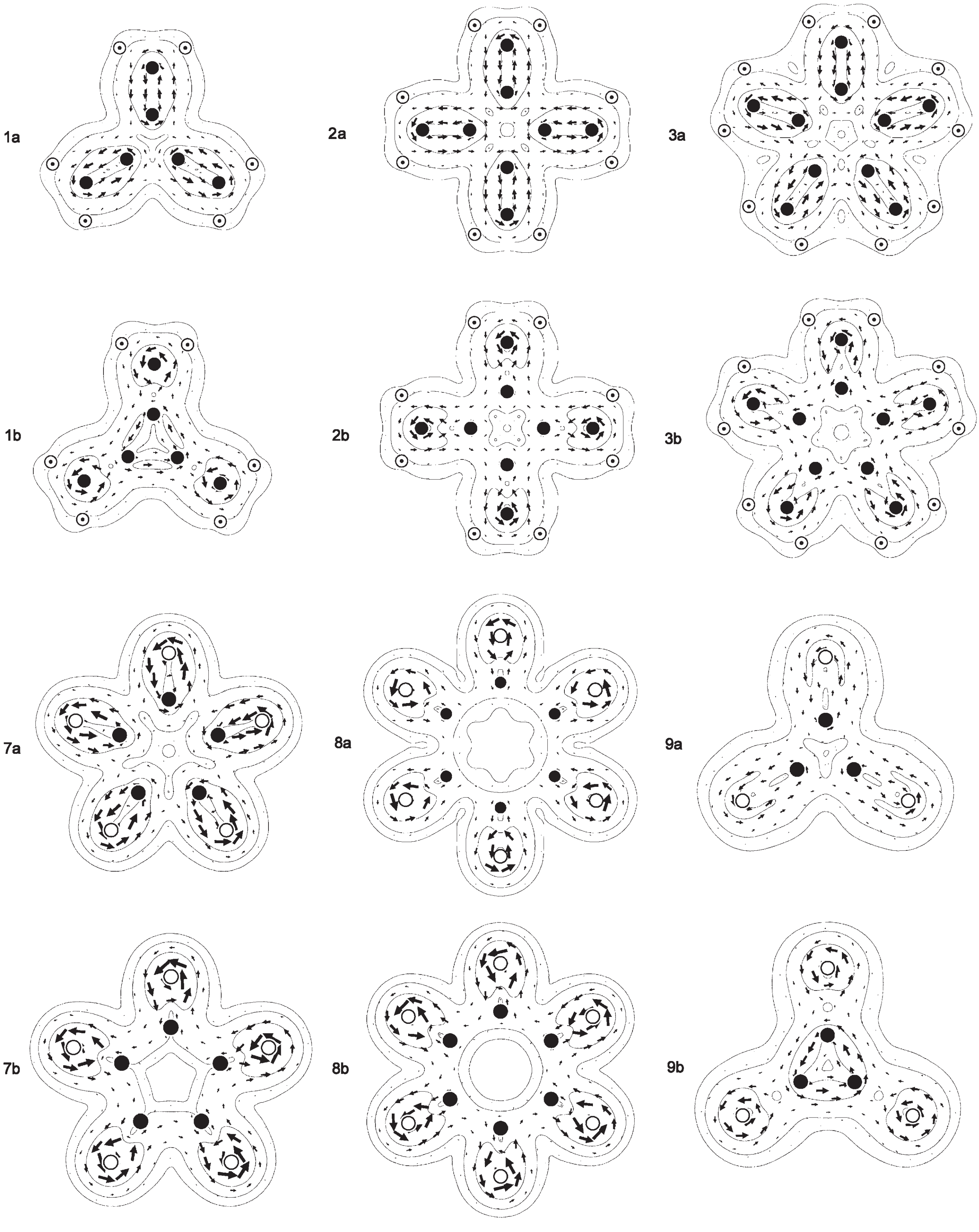
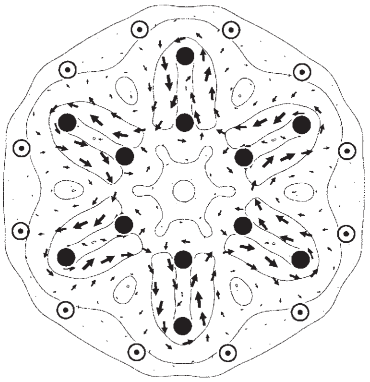
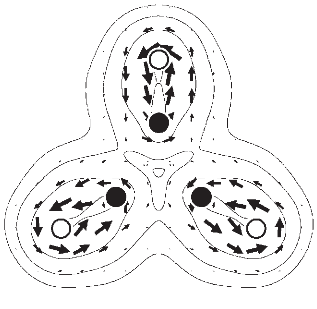


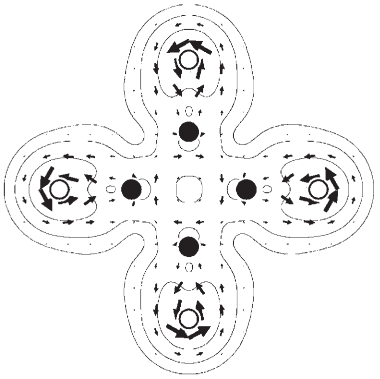
Figure 4. The π current-density maps for planar structures (as shown in Figure 1) of neutral and dianionic [*N*]radialenes (**1a**–**4a** and **1b**–**4b**), oxocarbons (**5a**–**8a** and **5b**–**8b**) and thiocarbons (**9a**–**12a** and **9b**–**12b**).



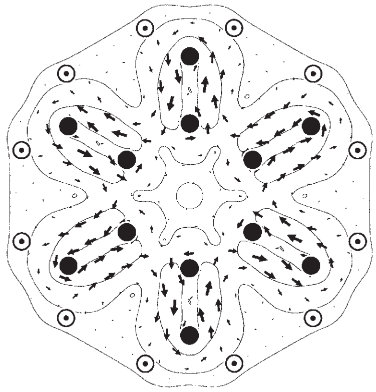
4a



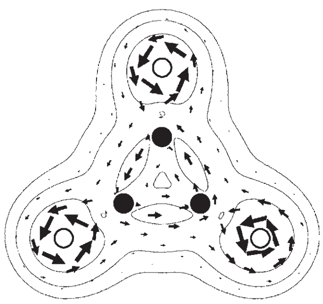
5a



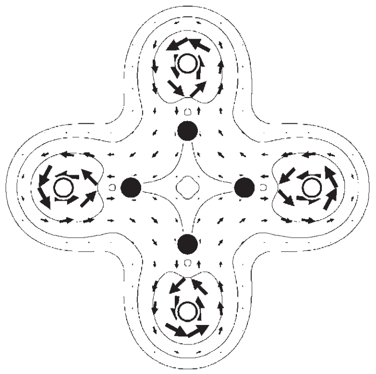
6a



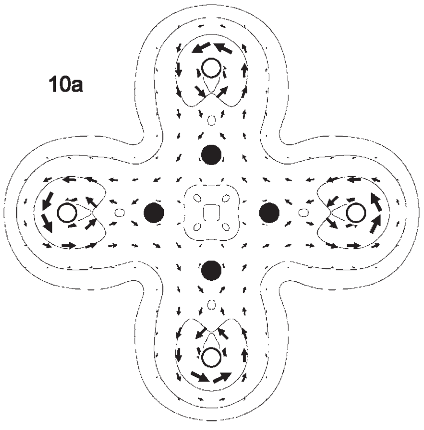
4b



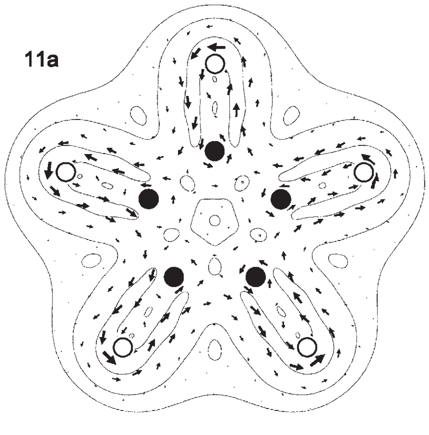
5b



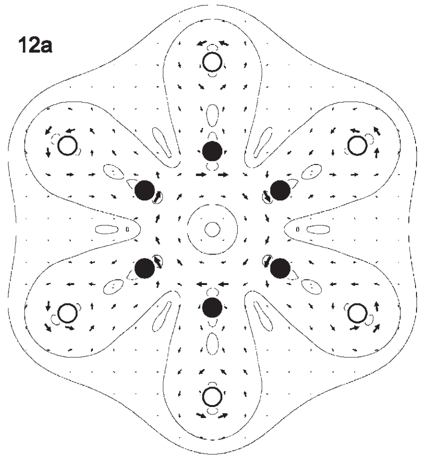
6b



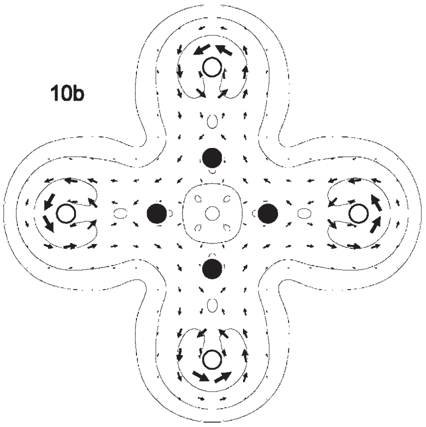
10a



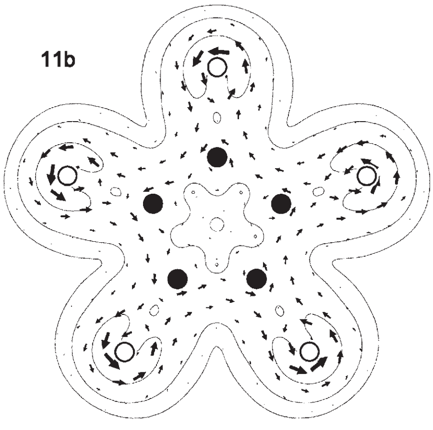
11a



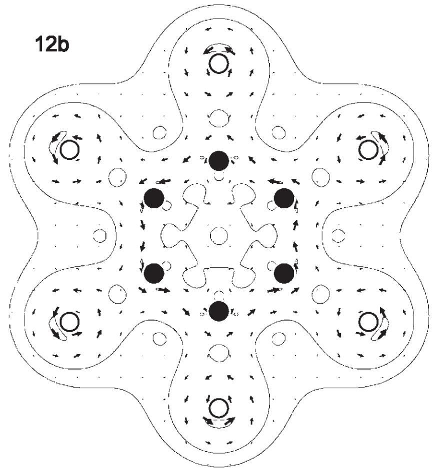
12a



10b



11b



12b

(in which $N=2m$ or $2m+1$), m angular nodes, no radial node and has symmetry $\Gamma_z \times \Gamma_{\Lambda=m}$. The HOMO–LUMO product therefore has symmetry $\Gamma_z \times \Gamma_z \times \Gamma_{\Lambda=m} = \Gamma_{\Lambda=m}$ with $m \geq 1$. In terms of the ipsocentric selection rules,[16,17] the HOMO–LUMO transition is therefore translationally allowed *only* for $N=3$, $\Gamma_{\Lambda=1}$ being the symmetry of the pair of in-plane translations. For all higher N, the HOMO–LUMO transition is translationally forbidden. As the HOMO–LUMO transition involves a change in the value of Λ, it is always rotationally forbidden. Thus, the HOMO–LUMO transition may contribute a diatropic ring current for the neutral $C_3(CH_2)_3$ (**1a**), but neither diatropic nor paratropic currents for $C_N(CH_2)_N$ with $N>3$ (**2a**–**4a**). This leaves only the possibility of local circulations along/within the "arms" of the molecules, which are not addressed in pure Hückel theory (in which all current flow is along paths defined by the existence of σ bonds), though if any such circulations exist they would appear in the full ab initio maps, or in maps from the pseudo-π method,[18] or any other method that takes account of the spatial extent of the π basis functions.

Counting of angular nodes indicates the possibility of other diatropic contributions from transitions across wider gaps, for example:

HOMO→LUMO+1 ($N=4, 5$)
HOMO→LUMO+2 ($N=6, 7$)...

HOMO−1→LUMO ($N=4, 5$)
HOMO−1→LUMO+1 ($N=6, 7$)...

There is also the possibility of paratropic contributions from each Γ_Λ of the lower stack to its counterpart in the higher stack. None of these transitions is likely to result in strong ring current, as the product of orbitals has a radial node, leading to cancellation in the integrand, the tendency to low net current being accentuated by the increasingly large orbital energy denominators. The cancellation argument applies to the $N=3$ case also, and so the prediction is of little or no ring current aromaticity for any of the neutral [N]radialenes **1a**–**4a**.

Similar arguments apply to the dianions. The occupied π orbitals of the dianion span the symmetry $\Gamma_z \times (\Gamma_\sigma + \Gamma_0)$. In the [$N$]radialene dianion, the HOMO has $\Lambda=0$ and a single radial node, and the LUMO pair has $\Lambda=1$, and also has one radial node. The HOMO–LUMO transition is thus translationally allowed for all $C_N(CH_2)_N{}^{2-}$ (**1b**–**4b**). However, simple Hückel considerations show that the maximum amplitude of both HOMO and LUMO is on the outer set of atoms, which are not covalently bonded (if all bonds are of equal length, r_{CC}, the outer atoms lie at $r_{CC}\{2\sin(\pi/N)+1\}$ from each other, which is $>1.5\ r_{CC}$ for all $N<13$), and so there is again little likelihood of continuous current flowing between them (none at all in a pure Hückel approach). The ipsocentric model therefore predicts little or no ring-current aromaticity for [N]radialenes, neutral (**1a**–**4a**) or dianionic (**1b**–**4b**).

Heteroatomic systems: Expressions (1)–(9) are straightforwardly generalised to heteroatomic systems such as oxocarbons (**5a**–**8a**) and their thio (**9a**–**12a**) analogues. If the inner cycle of the [N]radialene consists of atoms with coulomb integral α_X joined by bonds with resonance integral β_X and the outer atoms have coulomb integral α_Y, and are joined to their single neighbours by bonds with resonance integral β_Y (see Figure 1), then from the secular equations we get Equation (11).

$$\begin{aligned}(\alpha_X-\varepsilon)C_r+\beta_Y C'_r+\beta_X(C_{r-1}+C_{r+1})&=0\\(\alpha_Y-\varepsilon)C'_r+\beta_Y C_r&=0\end{aligned}\tag{11}$$

The monocycle coefficients are described by the sine/cosine functions of the monocycle, and it follows that the molecular orbital energies ε obey Equations (12)–(14) with ν being a monocycle eigenvalue.

$$\varepsilon^2+A\varepsilon+B=0\tag{12}$$

$$A=-\alpha_X-\alpha_Y-\nu\beta_X\tag{13}$$

$$B=\alpha_X\alpha_Y-\beta_Y{}^2+\nu\alpha_Y\beta_X\tag{14}$$

If we take the atoms of the central cycle to be carbon, and the pendant atoms to be heteroatoms, we can write Equations (15) in which η is an electronegativity parameter.

$$\alpha_X=\alpha;\quad \alpha_Y=\alpha+\eta\beta;\quad \beta_X=\beta;\quad \beta_Y=k\beta\tag{15}$$

For O as a 1π species, values of $\eta \sim 1$ and $k=1$ can be used, whereas for S, a smaller value of η is appropriate.[19] The orbital energies for the heteroatomic [N]radialene are then given by Equation (16).

$$\varepsilon=\alpha+\beta\left\{\frac{1}{2}\eta+\frac{1}{2}\nu\pm\frac{1}{2}\sqrt{(\nu-\eta)^2+4k^2}\right\}\tag{16}$$

The heteroatom systems $C_NO_N{}^{2-}$ (**5b**–**8b**) and $C_NS_N{}^{2-}$ (**9b**–**12b**) show essentially the same pattern of energy levels as the all-carbon systems. All levels drop as η increases. For all reasonable values of η, the two stacks of derived energy levels remain distinct and monotonically related to the [N]annulene levels. Conclusions about ring-current aromaticity are therefore essentially unaffected by the value of the electronegativity parameter η. As the electronegativity of the heteroatoms increases, the concentration of virtual orbitals on the outer set of vertices of the graph becomes less pronounced, so that we could expect (at most) a small ring current in the smaller oxocarbon dianions.

Comparison with ab initio results: The qualitative model is clear in its predictions that the [N]radialene systems and their analogues should not show aromaticity according to the ring-current criterion. How do these qualitative predictions compare with the results of more sophisticated calculations? To check this, maps of current density were obtained at the standard CTOCD-DZ/6–31G** ipsocentric level for the six series: $C_N(CH_2)_N$ (**1a**–**4a**), $C_N(CH_2)_N^{2-}$ (**1b**–**4b**), C_NO_N (**5a**–**8a**), $C_NO_N^{2-}$ (**5b**–**8b**), C_NS_N (**9a**–**12a**) and $C_NS_N^{2-}$ (**9b**–**12b**), with $N=3$, 4, 5, 6.

Geometries were optimised subject to planar D_{Nh} constraints at the RHF/6–31G** level with the results illustrated in Figure 1. The constrained structures are not all minima. It is known, for example, that $C_6O_6^{2-}$ (**8b**) adopts a C_2 structure,[13,20] and here it is found to have imaginary-frequency modes in D_{6h} symmetry. The details of the dianion potential surfaces are sensitive to method, and the energy gain on loss of D_{Nh} symmetry for the oxocarbon dianions, for example, is in any case small.[13,20] Even when the D_{Nh} geometry is a local minimum, the neutral oxocarbons (**5a**–**8a**), all have a strongly exothermic dissociation to CO monomers.[13,21] Typically, the earlier members of the various series correspond to planar local optima and the later members to stationary points with one or more imaginary frequencies for out-of-plane distortion modes (an exception is $C_3(CH_2)_3^{2-}$ (**1b**), see also reference [22]). In general, dianions are typically formally unbound in vacuo, though stabilised by crystal-field and solvation effects, and calculation of their properties in basis sets of moderate size relies on a standard approximation that Sommerfeld[23] terms Basis Set Confinement, in which properties are take to represent those of the bound form. This approach works well for geometry[24] and can be expected to perform well for ring current as calculated in the well-converged[16] ipsocentric approach; other properties, such as polarisability, may well be more sensitive to basis size and type.[25]

Here we wish to make a comparative exploration of the potential for aromaticity across all these related series, and so we took the planar, high-symmetry geometry as a model, even in those cases in which further relaxation was possible. For each constrained and optimal planar structure, the current density induced in the π system by a perpendicular magnetic field was computed and is displayed in the usual map form in Figure 4. The π system is taken to include all occupied orbitals of π symmetry. Maps represent the current density per unit inducing magnetic field, projected into the plotting plane at $1a_0$ above the plane of the nuclei (arrows representing the in-plane component, and contours the magnitude of the total current). Anticlockwise circulations represent diatropic currents, clockwise circulations paratropic ones.

The ab initio current maps for all 24 systems show a striking uniformity: no large [N]radialene, oxocarbon or thiocarbon, charged or neutral, shows significant ring current. Only the [3]radialene($C_3(CH_2)_3^{2-}$ (**1b**)), deltate ($C_3O_3^{2-}$ (**5b**)) and thiodeltate ($C_3S_3^{2-}$ (**9b**)) ions show a weak diatropic circulation in the central ring. These have respective values of 0.014, 0.018 and 0.019 a.u., for j_{CC}, the in-plane component of the contribution of all electrons in orbitals of π symmetry to induced current per unit of applied field at a point $1a_0$ above the geometric centre of one of the edges of the CCC triangle; the corresponding value for the total π current in benzene (the maximum in the $1a_0$ plotting plane) is 0.080 a.u. Even these values may be overestimates, as the circulation is "patchy" and much lower strengths would be obtained if the reference point were over an atom, for example. Unlike the current in benzene and other $4n+2$ aromatics, the current in the three systems **1b**, **5b** and **9b** would essentially be a two-electron rather than four-electron[17] diatropic current. Some evidence for partial aromatic status can also be adduced from the computed geometries: we note that only for $N=3$ do the systems C_3X_3 (**1a**, **5a** and **9a**) show a large contraction in the ring CC bond on addition of the extra two π electrons. The status of the deltate and thiodeltate dianions is in line with the indirect[26,27] measure of ring current afforded by NICS(1), which suggests decreasing aromaticity in the oxocarbon series $3>4>5>6$;[13] the evidence from the current-density maps themselves is that even the most negative NICS(1) value here does not correspond to an appreciably aromatic species.

Conclusion

In view of the orbital analysis of ring current, provided by the ipsocentric approach, even the qualitative Hückel model proves to be sufficient to predict and explain the lack of aromaticity of the oxocarbon series. It follows directly from the nodal structure and symmetry of HOMO and LUMO in these and related systems that there are no suitable virtual excitations available to supply an intense global ring current. On the magnetic criterion, these systems are all nonaromatic. This is consistent with the tendency to nonplanarity in the larger systems and suggests that electron counting alone does not provide a sufficient guide to aromaticity. In an orbital model, it is not simply the number of electrons, but also the symmetries and energies of the frontier orbitals that determine aromaticity.

Acknowledgements

P.W.F. acknowledges financial support from the Royal Society/Wolfson Research Merit Award Scheme.

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Received: April 10, 2006