Ring-current aromaticity in triplet states of 4n π electron monocycles

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Abstract

The ipsocentric approach to orbital contributions to current density predicts that a triplet state of a 4n π-electron Hückel monocycle should be aromatic, in the sense of supporting a diatropic ring current, and that this current should be carried by just four of the π electrons (three for $n = 1$). The magnetic criterion of aromaticity is thus in agreement with Baird's classic energy-based prediction of aromatic stabilisation for these species.
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1. Introduction

Aromaticity is traditionally diagnosed on a number of more or less mutually consistent energetic, geometric, chemical and magnetic criteria [1–4]. Most definitions compare observables with predictions of a parameterised model in procedures which are therefore subject to some ambiguity [5–9]. Depending on the model used, an aromatic molecule may be one that is more stable, less reactive in some directions, has more nearly equal bond lengths, a greater magnetisability anisotropy, or a more negative central nucleus-inde-

pendent chemical shift (NICS [10]), than is expected. In this respect, the proposal to *define* aromatic systems as exactly those that support a diatropic ring current [11,12] has the advantage that the theoretical determination of whether a system supports a ring current with a given sense is a yes/no decision, even though experimental detection of that current still rests on a model of ^{1}H NMR shifts [13] or magnetic susceptibility [4]. That proposal is followed here.

The concept of aromaticity has been considered mainly in connection with closed-shell systems, and for monocycles is encapsulated by the venerable Hückel 4$n + 2$ rule. Baird [14] argued in a classic paper, however, that aromaticity should also be associated with 4n π-electron monocycles in their triplet states. This argument, based on qualitative calculation of comparative energetics, is supported by the existence of planar triplet ground states of 4π species such as $C_5X_5^+$ (X = H,

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Cl [15,16]). An extensive ab initio study by Gogonea et al. [17] concluded that triplet aromaticity in $4n$ π systems does indeed exist and that is associated with planarisation, bond equalisation, stabilisation, negative NICS, downfield ^{1}H NMR shifts, and significant diamagnetic orbital susceptibility.

The established rules for aromaticity of closed-shell monocyclic molecules on the magnetic criterion are simple, in that cycles with $(4n + 2)$ π electrons are aromatic, as they support diatropic currents, whereas those with $4n$ are anti-aromatic, as they support paratropic ring currents [18]. This distinction between the two types of closed shell takes on a particularly sharp form in the ipsocentric [19,20] approach to calculation of orbital contributions to magnetic response, since there the difference in properties can be ascribed entirely to the difference in the frontier orbitals. It can then be shown by simple angular momentum arguments (reviewed below) that the $(4n + 2)$ π-electron closed-shell singlet should support a *four-electron* diatropic current, and that the closed-shell singlet of the symmetry-broken $4n$ π-electron monocycle should support a *two-electron* paratropic current [20] The opposite sense of the currents in the two cases follows from the different symmetry characteristics of the HOMO–LUMO excitation. The aim of this Letter is to extend these arguments to *open-shell* states of monocycles and hence deduce the sense of their ring currents.

2. The ipsocentric orbital model

The term *ipsocentric* [19] was coined to express the essential feature of the simplest of a family of methods for calculation of magnetic response [21–23] that use a continuous distribution of the origin of vector potential. This special feature is that the current density induced at a point in a molecule is computed with the point itself chosen as the origin of vector potential. Such a choice leads to a specific partition of the total induced current density into physically interpretable orbital contributions [19] in which the traditional division of current density into ground-state diamagnetic and excited-state paramagnetic terms is

replaced by two excited-state sums, each containing *only* transitions from occupied to empty orbitals. It is the exclusion of occupied-to-occupied transitions from these sums that gives the ipsocentric orbital decomposition its special power, as it allows qualitative prediction of the effects of change in electron count, in terms of opening or blocking of excitation channels. The ipsocentric distribution of origin of vector potential is the *only* distribution that gives rise to this clear physical separability of orbital contributions.

In an independent-electron model, the first-order change to a canonical occupied orbital ψ_n of an N-electron system in an external magnetic field $\boldsymbol{B}$ can be expressed in terms of unoccupied orbitals ψ_p and their energies ϵ_p (in atomic units) [20]:

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

where $\boldsymbol{l}$ and $\boldsymbol{p}$ are angular and linear momentum operators, and $\boldsymbol{d}$ is a displacement that will later be set equal to the electron position, $\boldsymbol{r}$. The conventional paramagnetic current for an origin of vector potential at $\boldsymbol{d}$, arises from $\psi_n^{(p)}$, the magnitude of which depends on virtual rotational transitions, and the conventional diamagnetic current for the same origin arises from $\psi_n^{(d)}$, the magnitude of which depends on virtual translational transitions.

In the description of the response of planar conjugated π systems to a perpendicular magnetic field, the relevant operators have the symmetries of (i) the rotation about the field direction, $R_\parallel$, and (ii) the two translations within the molecular plane, $T_\perp$. Given the presence of energy denominators, orbital contributions are also seen to be subject to an *energy* selection rule, so that, other things being equal, the contributions of frontier orbitals will dominate the sum [19,20].

Use of these selection rules allows us to derive, without computation, relationships between electron count and ring current (and hence aromaticity). The case of the closed-shell monocycle is especially straightforward [20], but it is useful to

summarise the argument again here, as it can be extended easily to cover open shells. Using the Hückel approximations for a ring of M atoms, the π molecular orbitals can be taken as sine and cosine combinations associated with an unsigned angular momentum quantum number $\Lambda = 0, 1, \ldots (M/2)$ (M even), $(M-1)/2$ (M odd), or complex functions associated with the signed components $\pm\Lambda$.

Closed-shell configurations occur at the aromatic counts of 2, 6, 10 ... $4n + 2$ π-electrons, where either all orbitals with given Λ are occupied, or all are empty. As $R_\parallel$ mixes only orbitals of equal Λ, it cannot produce occupied-to-empty transitions. On the other hand, $T_\perp$ operators mix orbitals that differ in Λ by ± 1 and therefore, within the Hückel molecular-orbital picture, the *sole* contribution to the ring current of a $(4n + 2)$ π-electron monocycle arises from the HOMO–LUMO transition. As a jump of +1 in axial angular momentum, from $\Lambda_{\text{HOMO}} = n$, $\Lambda_{\text{LUMO}} = n + 1$ (Fig. 1), this transition is translationally allowed and hence gives a diatropic current contribution.

On the other hand, in the $4n$ monocycle, the HOMO–LUMO transition is between two levels of equal $\Lambda(\Lambda_{\text{HOMO}} = \Lambda_{\text{LUMO}} = n)$ which would be
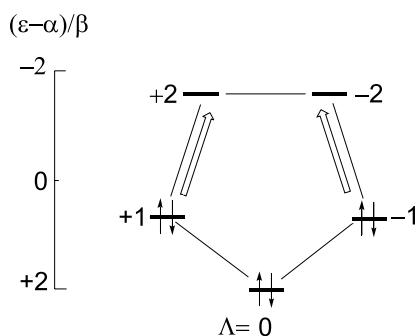

Fig. 1. Orbital contributions to induced current density in a closed-shell $4n + 2$ π-electron monocycle. In the π configuration $(a_2'')^2(e_1'')^4(e_2'')^0$ of D_{5h} $C_5H_5^-$, the only translationally allowed (diatropic ring-current inducing) transitions between occupied and empty orbitals are those from HOMO to LUMO, indicated by open arrows. The scale shows the Hückel orbital energies, and each pair of π orbitals is labelled with the values of $\pm\Lambda$, the components of orbital angular momentum along the principal axis.

degenerate in the absence of Jahn–Teller splitting, and it is therefore rotationally allowed. The match in shape of the two rotational partners, and the small energy gap between them, lead to an intense paratropic ring current, dominated by two electrons. Other transitions with $\Delta\Lambda = \pm 1$ into, and out of, this split pair are translationally allowed, but are disfavoured by larger energy differences; they lead only to small diatropic corrections to the main current.

The only exceptions to the $(4n + 2)$-diatropic, $(4n)$-paratropic rule are those where the π manifold is completely filled, i.e., when $n = (M-1)/2$ for an odd ring; or $n = M/2$ for an even ring. Having no empty π^* orbitals, these physically unlikely $C_M H_M^{M-}$ systems would have no significant π ring current.

3. Predictions for triplet states

Turning now to the predictions of the ipsocentric model for the magnetic behaviour of triplet states of $4n$ monocycles, we find several differences from the closed-shell problem. The triplet state has a magnetic moment arising from the unpaired spins. We assume that spin and orbital effects can be separated in lowest order of treatment, so that the spin moment of the triplet state gives rise to the first-order magnetic energy, and the induced orbital current density independently gives rise to the second-order energy. This assumption was previously used in the computational study of orbital magnetic properties of triplet states by Gogonea et al. [17] and corresponds to a possible, though perhaps difficult, experimental separation of effects. The ipsocentric orbital model can predict the sense of induced ring current in such a system, if we note that the excitations are now one-electron transitions from occupied to unoccupied *spin*-orbitals, without change in spin quantum number, but obeying translational and rotational selection rules as before.

A $4n$ π-electron monocycle in a triplet state has two electrons in two orbitals forming a half-open shell, which is compatible with retention of the full symmetry of the equilateral monocycle. The two frontier orbitals share the same angular
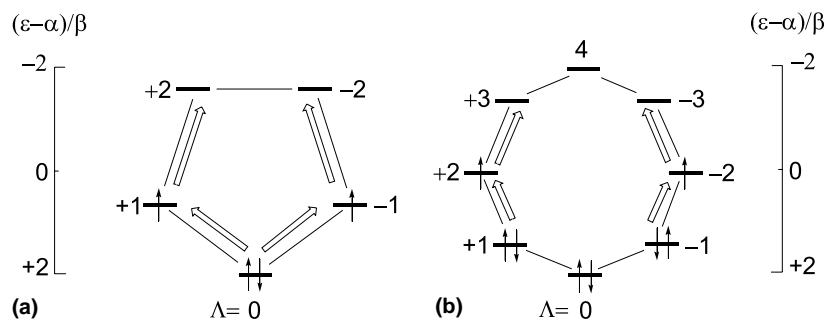
Fig. 2. Orbital contributions to induced current density in two planar [17] triplet states of $4n$ π-electron monocycles (a) D_{5h} $C_5H_5^+$, π configuration $(a_2'')^2(e_1'')^2(e_2'')^0$, and (b) D_{8h} C_8H_8, π configuration $(a_{2u})^2(e_{1g})^4(e_{2u})^2(e_{3g})^0(b_{2u})^0$. The scales show the Hückel orbital energies, and the open arrows indicate the translationally allowed (diatropic ring-current inducing) transitions between spin–orbitals. Each pair of π spin–orbitals is labelled with the values of $\pm\Lambda$, the components of orbital angular momentum along the principal axis.

momentum quantum number, $\Lambda = n$. Triplet $4n$ π-electron species with (computed [17]) planar geometries include C_4H_4, $C_5H_5^+$, $C_7H_7^-$ and C_8H_8. The allowed spin–orbital transitions (illustrated in Fig. 2 for two of these species) are therefore:

(i) (spin-α, $+n$) HOMO
$$\rightarrow (\text{spin-}\alpha, +(n+1)) \text{ LUMO},$$
(ii) (spin-α, $-n$) HOMO
$$\rightarrow (\text{spin-}\alpha, -(n+1)) \text{ LUMO},$$
(iii) (spin-β, $+(n-1)$) HOMO -1
$$\rightarrow (\text{spin-}\beta, +n) \text{ HOMO},$$
(iv) (spin-β, $-(n-1)$) HOMO -1
$$\rightarrow (\text{spin-}\beta, -n) \text{ HOMO}.$$

(If $n = 1$, transitions (iii) and (iv) involve the same electron.) Internal transitions within the open shell are ruled out by the exclusion of occupied-occupied transitions. Transitions (i)–(iv) are all translationally allowed, and hence lead to diatropic ring current, and by the magnetic criterion [11,12], to aromaticity.

Thus, the aromatic $4n$ π-electron triplet system with $n = 1$ has three, and the system with $n > 1$ has four magnetically active electrons in the Hückel picture. The triplet has therefore 3π- or 2π-electron diatropicity. The isoelectronic closed-shell singlet has, in contrast, 2π-electron paratropicity. In more sophisticated treatments of the electronic structure, this result survives as a statement about the major orbital contributions to the induced current density.

4. Conclusion

There has been much discussion in the literature of the degree to which the magnetic and energetic criteria of aromaticity agree [5–9]. In monocycles, open- and closed-shells, the two criteria evidently run in parallel: the aromaticity of triplet states of the $4n$ π-electron monocycle was predicted by Baird many years ago [14], and the magnetic aromaticity of such systems was later predicted computationally by calculation of nucleus-independent chemical shifts [17]. The present work confirms this parallel and gives a simple orbital explanation of the sense and physical origin of the currents that lead on integration to the global magnetic properties.

A special advantage of the orbital formulation is its capacity for easy extension to other electronic configurations. Removal of an electron from the HOMO of a $4n$ π-electron system, for example, leads to a doublet state. If the HOMO–LUMO gap remains small, and the molecule remains planar, that doublet state is predicted to have a paratropic orbital ring current. The current will be reduced with respect to that of the closed-shell $4n$ cycle, as it stems from one rather than two π electrons. The orbital model also explains the 'double aromaticity' of species such as the bare C_{12} cycle in its quintet state [24] where orthogonal (in- and out-of plane) π systems each have $4n$ electrons, and translationally allowed transitions lead to diatropicity in each sub-system. Similar reasoning

would also apply to aromaticity in triplet states of the trannulenes [25].

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