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Open-shell spherical aromaticity: the $2N^2 + 2N + 1$ (with $S = N + \frac{1}{2}$) rule†

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$4N$ Baird's rule represented the extension of Hückel's $4N + 2$ rule to triplet state systems. In this work we extend the $2(N + 1)^2$ Hirsch rule for spherical aromatic species to open-shell spherical compounds and we provide evidence that those spherical species having a same-spin half-filled last energy level with the rest of the levels being fully-filled, *i.e.*, those having $2N^2 + 2N + 1$ electrons and $S = N + \frac{1}{2}$, are aromatic.

In 1972, Baird showed that cyclic annulenes which are aromatic in their singlet ground state are antiaromatic in their lowest-lying triplet state and *vice versa* for annulenes that are antiaromatic in the ground state.¹ The identification² of the planar triplet ground states of $C_5H_5^+$ and $C_5Cl_5^+$ as well as a more recent photoelectron spectroscopic study³ of the first singlet and triplet states of $C_5H_5^+$ provided experimental support for $4N$ Baird's rule. This rule was further confirmed through NICS, magnetic susceptibility, and aromatic stabilization energy calculations by Schleyer *et al.*⁴ as well as from the study of ring currents in $4n\pi$ -electron monocycles.⁵ $4N$ Baird's rule represented an extension of the renowned Hückel's $4N + 2$ rule⁶ to open-shell species. Hückel's theory shows that, except for the most stable and unstable π -orbitals, the rest of the molecular orbitals of annulenes with an even number of C atoms are grouped in pairs of degenerate orbitals.⁷ Thus, aromaticity of $(4N + 2)\pi$ -annulenes with D_{nh} symmetry (with $n = 4N + 2$) was interpreted by Hückel as the fulfillment of a closed-shell that provides extra energetic stability, similar to the situation found in noble gas elements. Similarly, one could attribute the aromaticity of the lowest-lying triplet state in the $4N\pi$ -annulenes with D_{nh} symmetry (with $n = 4N$) to the additional stability provided by the same-spin half-filled degenerate highest-occupied molecular orbitals.

Hirsch's $2(N + 1)^2$ rule of aromaticity⁸ for spherical compounds has been considered the spherical analog of the $4N + 2$ rule for the cyclic annulenes. It is based on the fact that the π -electron system of an icosahedral fullerene can be in a first approximation considered as a spherical electron gas surrounding the surface of a sphere. The wave functions of this

electron gas are characterized by the angular momentum quantum number l ($l = 0, 1, 2, \dots$) similar to the situation found for atomic orbitals.^{8a} Each energy level is $2l + 1$ times degenerated, and, therefore, all π -shells are completely filled when we have $2(N + 1)^2$ electrons. Consequently, spherical species with $2(N + 1)^2\pi$ -electrons are aromatic in an analogous way to $(4N + 2)\pi$ -annulenes. According to this rule, icosahedral C_{20}^{2+} , C_{60}^{10+} or C_{80}^{8+} are aromatic fullerenes.⁸

Extension of Baird's rule to spherical compounds leads to the conclusion that spherical systems having a same-spin half-filled last energy level with the rest of the levels being fully filled should be aromatic. This situation is reached for a number of electrons equal to $2N^2 + 2N + 1$ with a spin of $S = N + \frac{1}{2}$. The aim of the present communication is to propose and check the validity of this $2N^2 + 2N + 1$ rule. As for the $2(N + 1)^2$ rule, the $2N^2 + 2N + 1$ (with $S = N + \frac{1}{2}$) rule should be applicable for any conjugated π -system, being or not an organic fullerene, that can be approximated as a collection of nuclei distributed uniformly over a spherical surface.⁹

The validity of the $2(N + 1)^2$ rule has been computationally substantiated with NICS values obtained at the center of the five- and six-membered rings (5- and 6-MRs) and calculations of ³He chemical shifts of fullerenes having He encapsulated inside.^{8a,b} In the present work we provide evidence of the $2N^2 + 2N + 1$ rule using NICS¹⁰ and the electronic multicenter index (MCI)¹¹ as measures of local aromaticity in selected anions and cations of the C_{20} , C_{60} and C_{80} fullerenes with icosahedral symmetry.‡ Among the different NICS variants, we will use the NICS(1)_{zz} that is considered together with NICS(0)_{zz} as the most reliable NICS measure.¹² We have recently shown that MCI is the index of aromaticity that more accurately determines aromaticity.¹³ For the indices used, we have that the more negative the NICS and the higher the MCI values, the more aromatic the rings are. In addition, for those systems having different C–C bond lengths we have collected the bond length alternation (BLA) values, *i.e.*, the bond length difference between the longest and shortest C–C bonds in the fullerene, as an indicator of aromaticity based on molecular structure.

With the aim to provide reference values, Table 1 lists the NICS(1)_{zz} and MCI values of the $4N + 2$ aromatic singlet cyclopentadienyl anion and benzene and $4N$ aromatic triplet cyclopentadienyl cation and benzene dication. As can be seen both NICS and MCI classify these systems as aromatic species with negative NICS and relatively large MCI values.

Table 2 gives the results for the $I_h C_{20}$ derivatives. In accordance with the $2(N + 1)^2$ rule, the singlet $I_h C_{20}^{2+}$ with

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Table 1 NICS(1)_{zz} and MCI values for cyclopentadienyl and benzene systems

| Systems | Symmetry | Ring | NICS(1) _{zz} ^a | MCI ^b | r(C,C) ^c | Spin |
|---|-----------------|------|------------------------------------|------------------|---------------------|-------|
| C ₅ H ₅ ⁻ | D _{5h} | 5-MR | -2.2 | 0.080 | 1.414 | S = 0 |
| C ₅ H ₅ ⁺ | D _{5h} | 5-MR | -3.6 | 0.203 | 1.426 | S = 1 |
| C ₆ H ₆ | D _{6h} | 6-MR | -29.0 | 0.078 | 1.396 | S = 0 |
| C ₆ H ₆ ²⁺ | D _{6h} | 6-MR | -18.9 | 0.162 | 1.433 | S = 1 |

^a Unit is ppm. ^b Unit is electrons. ^c Unit is Å.

Table 2 NICS(1)_{zz} and MCI values for C₂₀ derivatives

| System | Symmetry | NICS(1) _{zz} ^a | MCI ^b | r(C,C) ^c | Spin |
|-------------------------------|-----------------|------------------------------------|------------------|---------------------|---------|
| C ₂₀ ^d | C _{2h} | 0.01–4.16 | 0.011–0.017 | 1.400–1.537 | S = 0 |
| C ₂₀ ²⁺ | I _h | -7.4 | 0.020 | 1.447 | S = 0 |
| C ₂₀ ⁷⁺ | I _h | -4.0 | 0.035 | 1.494 | S = 3/2 |
| C ₂₀ ⁵⁻ | I _h | -18.0 | 0.024 | 1.508 | S = 7/2 |

^a Unit is ppm. ^b Unit is electrons. ^c Unit is Å. ^d Range of values (all positive) for different 5-MRs.

18 electrons is an aromatic fullerene.⁸ This is substantiated by our NICS(1)_{zz} result. The MCI value, although not especially high (it is about that of furan),^{13a} is indicative of a slightly aromatic 5-MR. Interestingly, the open-shell icosahedral C₂₀⁵⁻ with 25 electrons and spin of 7/2 follows the 2N² + 2N + 1 rule and it is somewhat more aromatic than C₂₀²⁺ as indicated by NICS(1)_{zz} and MCI results. On the other hand, the I_h C₂₀⁷⁺ with 13 electrons and S = 5/2 has a similar aromaticity to that of C₂₀²⁺. Finally, the optimized geometry of the C₂₀ neutral system has C_{2h} symmetry and is clearly the less aromatic fullerene among the series analyzed.

Next, we have analyzed the results of C₆₀ and three of its anions and cations. The question whether C₆₀ must be

Table 3 NICS(1)_{zz} and MCI values for C₆₀ derivatives

| Systems | Symmetry | Ring | NICS(1) _{zz} ^a | MCI ^b | r(C ₆ ,C ₆) ^c | r(C ₆ ,C ₅) ^c | BLA ^c | Spin |
|--------------------------------|----------------|------|------------------------------------|------------------|---|---|------------------|----------|
| C ₆₀ | I _h | 6-MR | 0.8 | 0.018 | 1.395 | 1.453 | 0.058 | S = 0 |
| | | 5-MR | 21.5 | 0.011 | | | | |
| C ₆₀ ¹⁻ | I _h | 6-MR | -1.4 | 0.017 | 1.438 | 1.440 | 0.002 | S = 11/2 |
| | | 5-MR | -19.9 | 0.049 | | | | |
| C ₆₀ ¹⁹⁺ | I _h | 6-MR | -14.9 | 0.019 | 1.510 | 1.523 | 0.013 | S = 9/2 |
| | | 5-MR | -25.3 | 0.041 | | | | |
| C ₆₀ ¹⁰⁺ | I _h | 6-MR | -18.6 | 0.011 | 1.431 | 1.460 | 0.030 | S = 0 |
| | | 5-MR | -29.5 | 0.017 | | | | |

^a Unit is ppm. ^b Unit is electrons. ^c Unit is Å.

Table 4 NICS(1)_{zz} and MCI values for C₈₀ derivatives

| Systems | Symmetry | Ring | NICS(1) _{zz} ^a | MCI ^b | r(C ₆ ,C ₆) ^c | r(C ₆ ,C ₅) ^c | BLA ^c | Spin |
|--------------------------------|----------------|------|------------------------------------|------------------|---|---|------------------|----------|
| C ₈₀ | S ₆ | 5-MR | 10.7 | 0.019 | 1.418 | 1.454 | 0.025 | S = 0 |
| | | 6-MR | -5.2 | 0.012 | | | | |
| | | 5-MR | 26.3 | 0.018 | | | | |
| | | 6-MR | 11.3 | 0.014 | | | | |
| | | 6-MR | -5.1 | 0.012 | | | | |
| C ₈₀ ⁸⁺ | I _h | 6-MR | -7.2 | 0.011 | 1.430 | 1.446 | 0.015 | S = 0 |
| | | 5-MR | -4.0 | 0.017 | | | | |
| C ₈₀ ^{5-d} | I _h | 6-MR | -20.8 | 0.019 | 1.437 | 1.449 | 0.012 | S = 13/2 |
| | | 5-MR | -5.5 | 0.034 | | | | |

^a Unit is ppm. ^b Unit is electrons. ^c Unit is Å. ^d Geometry optimization with non-totally converged gradients for technical reasons (the largest gradient, however, is only 0.006 a.u. with the displacements being converged).

considered as a fully aromatic molecule or not has been controversial ever since their discovery (for a review see ref. 14). It is generally accepted that fullerenes have an ambiguous aromatic character,^{14,15} with some properties that support the aromatic view of these systems and others that do not. Our NICS(1)_{zz} and MCI calculations in Table 3 for I_h C₆₀ reflect a non-aromatic or slightly aromatic situation. The BLA value of 0.058 Å also points in the same direction. Interestingly, the singlet I_h C₆₀¹⁰⁺ species that obeys the 2(N + 1)² rule is found to be more aromatic than C₆₀ with large negative NICS values and a smaller BLA value. The MCI results do not distinguish between the aromaticity of C₆₀¹⁰⁺ and C₆₀, they only show that when going from C₆₀ to C₆₀¹⁰⁺ the local aromaticity of the 6-MRs decreases and that of the 5-MRs increases. On the other hand, the C₆₀¹⁹⁺ and C₆₀¹⁻ fullerenes with S = 9/2 and 11/2, respectively, that follow the 2N² + 2N + 1 rule are more aromatic than both C₆₀ and C₆₀¹⁰⁺ according to larger and more negative NICS(1)_{zz}, greater MCI values (especially for the 5-MR), and smaller BLAs. It is remarkable that the BLA of C₆₀¹⁻ fullerene is close to zero.

After that we have calculated the singlet C₈₀ and C₈₀⁸⁺ and the C₈₀⁵⁻ species with S = 13/2. C₈₀⁸⁺ follows the Hirsch rule, whereas C₈₀⁵⁻ the 2N² + 2N + 1 rule. From Table 4, the values of NICS(1)_{zz} and MCI for the five non-equivalent rings of neutral C₈₀ indicate a non-aromatic or slightly aromatic character of this system that has no I_h but S₆ symmetry. NICS(1)_{zz} values for the C₈₀⁸⁺ system assign a slightly more aromatic character to this system compared to C₈₀, even though MCI values are almost the same. And finally, C₈₀⁵⁻ appears as the most aromatic species, even confirmed by the lower BLA value.

Finally, it would be interesting to check that this rule can be applied to inorganic species. Table 5 lists the results obtained

Table 5 NICS(1)_{zz} and MCI values for Ge₁₂ derivatives

| Systems | Symmetry | NICS(1) _{zz} ^a | MCI ^b | r(Ge,Ge) ^c | Spin |
|---------------------------------|----------------|------------------------------------|------------------|-----------------------|---------|
| Ge ₁₂ ²⁻ | I _h | -5.5 | 0.049 | 2.685 | S = 0 |
| Ge ₁₂ ^{1-d} | I _h | -405.9 | 0.113 | 2.685 | S = 5/2 |
| Ge ₁₂ ^{4+d} | I _h | -69.0 | 0.088 | 2.685 | S = 0 |

^a Unit is ppm. ^b Unit is electrons. ^c Unit is Å. ^d Ge₁₂¹⁻ and Ge₁₂⁴⁺ calculations at the Ge₁₂²⁻ optimized geometry.

for spherene Ge₁₂ derivatives.¹⁶ As can be seen, Ge₁₂²⁻ is found to be moderately aromatic and the aromaticity of these species clearly increases for the derivatives following the 2(N + 1)² rule (Ge₁₂⁴⁺) and 2N² + 2N + 1 rule (Ge₁₂¹⁻).

As a whole, we have provided evidence for the existence of open-shell spherical aromaticity in the case of 2N² + 2N + 1 species. It is likely that this 2N² + 2N + 1 (with S = N + 1/2) rule may become a powerful tool for researchers who work in the quest for stable single high-spin molecules for their use as single-molecule based magnets.¹⁷

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Notes and references

‡ Computational methods: geometry optimizations and calculation of MCI and NICS(1)_{zz} indices have been performed with the Gaussian 09¹⁸ and ESI-3D¹⁹ programs at the B3LYP/6-31G* level of theory.²⁰ NICS(1)_{zz} values have been computed through the GIAO method. The magnetic shielding tensor has been calculated for ghost atoms located at 1 Å above the ring centers determined by the non-weighted mean of the heavy atom coordinates. It is worth noting that NICS calculations for open-shell systems are approximate since they contain only the contributions arising from the perturbation of the wavefunction due to the external magnetic field.^{4,21}

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