Connecting and combining rules of aromaticity. Towards a unified theory of aromaticity

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Most of the archetypal aromatic compounds present high symmetry and have degenerate highest-occupied molecular orbitals. These orbitals can be fully occupied resulting in a closed-shell structure or can be same-spin half-filled. This closed-shell or same-spin half-filled electronic structure provides an extra stabilization and it is the origin of several rules of aromaticity such as the Hückel 4N + 2 rule, the lowest-lying triplet excited state 4N Baird rule, the 4N rule in Möbius-type conformation, the 4N + 2 Wade–Mingos rule in closo boranes or the 2(N + 1)² Hirsch rule in spherical aromatic species. Combinations of some of these rules of aromaticity can be found in some particular species. Examples of these combinations will be discussed and the validity of some of these rules will be assessed. Moreover, it is possible to establish connections with some of these rules of (anti) aromaticity and, therefore, they can be partially generalized, which represents a step forward to a future unified theory of aromaticity.

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1 INTRODUCTION

The concept of aromaticity is controversial.¹–⁵ The reason is the nonexistence of a quantum mechanical operator that can be used to extract aromaticity from the wave function and, consequently, this property cannot be experimentally directly measured. This situation in chemistry is relatively common and, in fact, properties such as chemical bonding, molecular similarity, atomic charge, bond order, local spin, oxidation state, conjugation, hyperconjugation, among other important concepts and phenomena in chemistry lack a strict definition.⁶ The term aromatic was initially associated with the particular odor (aroma) of compounds like benzene or toluene.⁷ Today, aromatic compounds are not characterized by its odor anymore, but still are recognized through a series of physicochemical properties. Thus, aromatic molecules are particularly stable and have low reactivity and unusual chemical and physical properties that include the tendency toward bond length equalization and distinctive spectroscopic and magnetic properties, such as diamagnetic ring currents.⁸ Aromatic molecules are cyclic molecules that have some electrons highly delocalized. These molecules cannot be represented by a single Lewis structure, and therefore, two or more resonance structures of the same or similar weight have to be used to correctly represent their electronic and molecular structure. The combination of resonance structures is already an indication of multicenter bonding and, consequently, electronic delocalization in closed two- or three-dimensional (2D or 3D) circuits. Some of the properties of aromatic compounds (energetic stabilization, electron delocalization) are essential for aromaticity and have to be considered primary properties.
Others like the presence of diamagnetic ring currents are the consequence of the former (secondary properties) and may or may not signal aromaticity (Box 1).9

Benzene, benzenoid compounds, and their heteroderivatives are classic organic aromatic compounds. Over time and especially in the last half century, chemists have found other systems with similar properties to those present in classic aromatic compounds. These new compounds share many properties with classical aromatic systems but they also display some differences. Because of that, their particular aromatics have received different names. The list of different types of aromaticity is long.10 Among them we can cite Hückel aromaticity,11–14 Möbius aromaticity,15,16 homoaromaticity,17 heteroaromaticity,18 claromaticity,19 σ-aromaticity,20 δ-aromaticity,21 multiple aromaticity,22 conflicting aromaticity,23 metalloaromaticity,24–27 excited state aromaticity,28–30 Hückel–Baird hybrid aromaticity,31 3D aromaticity,32,33 spherical aromaticity,34,35 cylindrical aromaticity,36–38 disk aromaticity,39 cubic aromaticity,40 octahedral aromaticity,41 chelatoaromaticity,42 quasi-aromaticity,43 push-pull and captodative aromaticity,44 transition state aromaticity,45 or hyperaromaticity.46 The adjective added to aromaticity in each case is used to describe a particular situation. To have so many types of aromatics is useful for classification of molecules but, at the same time, it is desirable to develop principles, laws, or rules that help chemists to identify potential aromatic compounds and to bring order to this controversial property. Since the initial 4N + 2 Hückel rule,11–14 a bunch of rules of aromaticity have been proposed (see Table 1).62 The most relevant for the present review are briefly discussed in the following paragraphs.

The most stable molecular orbital in Dnπ annulenes is formed by the in-phase interactions of all pπ-atomic orbitals. The rest of the orbitals, except the last one for even n values, come by pairs. This particular molecular orbital distribution shown in Figure 1a is the origin of the Hückel rule. In this distribution, closed-shell electronic structures are obtained for the following number of π-electrons: 2, 6, 10, 14, ..., that is, with 4N + 2 π-electrons. Therefore, annulenes with 4N + 2 π-electrons are aromatic and with 4N − 2 π-electrons are antiaromatic.

On the other hand, in Dnπ annulenes, an electronic structure with open-shell half-filled with same spin electrons is obtained for the following number of π-electrons: 4, 8, 12, ... (see Figure 1b). This open-shell half-filled electronic structure provides aromatic stabilization as well and gives rise to the so-called Baird aromaticity. According to the 4N π-electrons Baird rule,
monocyclic conjugated hydrocarbons of $D_{nh}$ symmetry that are antiaromatic in their singlet ground state are aromatic in their lowest-lying triplet state, and vice versa for those that are aromatic in the ground state. Recent spectroscopic observation of the triplet diradical state of cyclobutadiene gave further support to this rule. It is worth mentioning that, as an extension to this Baird rule, it has been proved that the singlet excited state with the same electronic configuration of the lowest-lying triplet state of annulenes with $4\pi$-electrons is also aromatic.

In 2008, Soncini and Fowler generalized the Hückel and Baird rules. According to Soncini and Fowler’s rule the monocyclic structures of $4\pi+2\pi$-electrons at the lowest-lying electronic states with even spin (singlet, quintet, ...) and the monocycles of $4\pi$-electrons at the lowest-lying states with odd spin (triplet, septet, ...) are aromatic.

Annulenes in a Möbius-type conformation present a phase inversion in the most stable $\pi$-molecular orbital and, as a result, they come by pairs (see Figure 1c). Consequently, they reach the closed-shell electronic structures for the following number of $\pi$-electrons: 4, 8, 12, .... The electron counting is opposed to that of the Hückel rule and, therefore, Möbius-type annulenes with $4\pi$-electrons are aromatic and with $4\pi+2\pi$-electrons are antiaromatic.

The linking number ($L_k$) rule of Rappaport and Rzepa allows a generalization of the Hückel and Möbius rules for annulenes with complicated topologies. The linking number represents the number of times that each curve winds (writhe and twist) around the other in an annulene. The rule states that cyclic conjugated annulenes that have an even $L_k$ follow Hückel’s $4\pi+2\pi$-electron rule of aromaticity for the closed-shell ground state, whereas those having an odd $L_k$ obey the Möbius’ $4\pi$-electron rule.

Hückel’s rule is strictly valid only for monocyclic conjugated systems. Clar’s $\pi$-sextet rule formulated in 1972 was an attempt to extend the Hückel rule to benzenoid species. Aromatic $\pi$-sextets are defined as six $\pi$-electrons localized in a single benzene-like ring separated from adjacent rings by formal C–C single bonds. Clar’s rule states that the Kekulé resonance structure with the largest number of disjoint aromatic $\pi$-sextets, that is, benzene-like moieties, is the most important for characterization of properties of polycyclic aromatic hydrocarbons. Application of this rule to phenanthrene indicates that the resonance structure 2 in Figure 2a is more important than 1. Therefore, according to this rule, outer rings in phenanthrene have a
larger local aromaticity than the central ring.\textsuperscript{67,68} Indeed, this result is confirmed by many different measures of local aromaticity.\textsuperscript{69–71}

In 1984, Glidewell and Lloyd\textsuperscript{55} reported an extension of this rule to polycyclic conjugated hydrocarbons (PCHs) having rings with any even number of carbon atoms in their structure. Glidewell and Lloyd’s rule\textsuperscript{55} states that the total population of π-electrons in PCHs tends to form the smallest \(4N+2\) groups and to avoid the formation of the smallest \(4N\) groups. Figure 2b shows two nonbenzenoid PCHs discussed by Glidewell and Lloyd\textsuperscript{55} in which application of their rule leads to the conclusion that one of the resonance structures (in green in Figure 2b) is more relevant than the other to explain the electronic and molecular properties of these species. Recently, from the analysis of a number of PCHs,\textsuperscript{72} our group modified this rule concluding that PCHs avoid the formation of the smallest \(4N\) group except in the case that avoiding formation of the smallest \(4N\) groups results in the formation of a greater number of large \(4N\) groups.

With a general formula of \([B_nH_n]^{2−}\), \textit{closo} borohydride (BH) clusters have a structure of polyhedron with triangular faces. These clusters possess 3D aromaticity. They obey the Wade \(2N + 2\) electron rule, where \(N\) is the number of vertexes of the polyhedron or Mingos’ rule, that is, \(4N + 2\).\textsuperscript{51,52} Both rules are equivalent, since Wade’s rule refers to the skeletal electrons (SEs; all valence electrons except for those of the B–H bonds), whereas Mingos’ rule also incorporates the exo electrons of the B–H bonds, thus the \(4N + 2\) in Mingos’ rule designates the total number of valence electrons (TNVEs).

Finally, Hirsch’s \(2(N + 1)^2\) rule of spherical aromaticity\textsuperscript{96} is based on the fact that the π-electron system of a fullerene can be, in a first approximation, considered as a spherical electron gas on the surface of a sphere. The wave functions of this electron gas are characterized by the angular momentum quantum number \(l\) (\(l = 1, 2, \ldots\)). Each energy level is \(2l + 1\) times degenerated, and, therefore, all π-shells are completely filled with \(2(N + 1)^2\) electrons. The \(4N + 2\) Wade–Mings rule and the Hirsch rule are two different rules of 3D aromaticity. The origin of the difference is that the two rules refer to two different types of 3D aromaticity. The Wade–Mings rule refers to the \textit{inner} aromaticity of SEs of the cage, whereas the Hirsch rule describes the \textit{outer} aromaticity of the electrons delocalized on the surface of the spherical species.

As discussed in this review, the aromatic character of some molecules can only be explained by combination of some of the aforementioned rules of aromaticity. Moreover, some rules of (anti)aromaticity have been shown to be connected by different formulas and procedures and, therefore, they can be partially generalized, which represents a step forward to a future unified law or theory of aromaticity. This review highlights some examples in which rules of aromaticity have to be combined to explain aromaticity or in which their connection is possible.

## 2 | CONNECTING RULES

In this section, we discuss connections that have been reported between the Hückel rule and other rules like the Baird, Möbius, Soncini–Fowler, linking number, Hirsch, and Wade–Mings rules. Such links show that some of these rules can be generalized, paving the way for a future unified law or theory of aromaticity.

### 2.1 | Hückel and Baird rules connected

In 2008, Mandado et al.\textsuperscript{73} published an interesting paper showing that the Hückel \(4N + 2\) π- and Baird \(4N\) π-electron rules for lowest-lying singlet and triplet annulenes, respectively, reduce to a general aromaticity rule when the \(\alpha\) and \(\beta\) terms are analyzed separately. This new rule fusing Hückel and Baird’s rules states that aromatic annulenes are those having \(2N + 1\) \(\alpha\) and \(\beta\) π-electrons, whereas those having \(2N\) \(\alpha\) and \(\beta\) π-electrons are antiaromatic. Radical systems having \(2N + 1\) \(\alpha\) π-electrons and \(2N\) \(\beta\) π-electrons are found to have conflicting aromaticity being \(\alpha\) aromatic and \(\beta\) antiaromatic. Table 2 provides some examples calculated by Mandado et al.\textsuperscript{73} To prove the new joined rule it was necessary to use indicators of aromaticity that

| Molecule | \(N^{\alpha}\) | \(N^{\beta}\) | \(s^{\alpha\alpha}\) | \(s^{\alpha\beta}\) | NICS(0)_{ex}_{zz} | NICS(0)_{ex}_{anz} |
|----------|----------------|---------------|-----------------|----------------|----------------|------------------|
| \(C_2H_4\) | 2 | 2 | –0.299 | –0.299 | 117.52 | 117.52 |
| \(C_2H_6\) | 3 | 1 | 0.302 | 0.383 | –15.07 | –6.66 |
| \(C_2H_6^+\) | 3 | 3 | 0.361 | 0.361 | –17.88 | –17.88 |
| \(C_2H_4^-\) | 3 | 2 | 0.364 | –0.266 | –17.67 | 74.86 |
| \(C_2H_4^+\) | 5 | 3 | 0.325 | 0.361 | –24.67 | –16.28 |
| \(C_2H_6^-\) | 4 | 3 | –0.242 | 0.364 | 100.55 | –16.27 |
| \(C_2H_6^+\) | 5 | 4 | 0.322 | –0.233 | –24.46 | 114.74 |

Table 2: Number of \(\alpha\) and \(\beta\) π-electrons (\(N^{\alpha}, N^{\beta}\)), scaled \(n\)-center electron delocalization indices (\(s^{\alpha\alpha}, s^{\alpha\beta}\)) and \(\pi\) contribution to the out-of-plane \(zz\) tensor component of the nucleus independent chemical shifts (NICS(0)_{ex}_{zz}, NICS(0)_{ex}_{anz}) for some selected species. (Reprinted with permission from Reference 73. Copyright 2008 AIP Publishing)
can be split into $\alpha$ and $\beta$ components. In particular, the authors used scaled $n$-center electron delocalization indices\textsuperscript{74} and the $\pi$ contribution to the out-of-plane $zz$ component of the magnetic shielding tensor, nucleus-independent chemical shift (NICS(0)$_{zzz}$).\textsuperscript{75} As can be seen in Table 2, when the number of $\alpha$ or $\beta$ $\pi$-electrons is odd, the system behaves as an aromatic compound in the corresponding component with positive and large $n$-center delocalization indices and negative NICS(0)$_{zzz}$ values. On the other hand, if the number of $\alpha$ or $\beta$ $\pi$-electrons is even, $n$-center delocalization indices are negative and NICS(0)$_{zzz}$ values are positive as usual in antiaromatic compounds.

It is worth noting that a connection between Hückel, Baird, and Möbius rules was also obtained\textsuperscript{76} by considering the symmetry of the space in which electrons get delocalized (cylindrical for annulenes) and taking into account that in the case of a Möbius strip the boundary condition involves a rotation of $4\pi$ and not of $2\pi$ as in the case of annulenes with Hückel topology.

2.2 | Hückel, Baird, Möbius, Soncini–Fowler, and linking number rules connected

The Hückel rule states that annulenes with $4N + 2$ $\pi$-electrons are aromatic and with $4N$ $\pi$-electrons are antiaromatic. In the lowest-lying triplet state, however, the rule is reversed and annulenes with $4N$ $\pi$-electrons are aromatic and with $4N + 2$ $\pi$-electrons are antiaromatic. The same situation is found for annulenes that have Möbius topology ($L_k = 1$). Interestingly, if one considers the lowest-lying triplet state of a Möbius annulene with an odd linking number, the rule is the same as the Hückel rule. But the lowest-lying quintet state of a Möbius annulene follows the Baird rule. Ottosson and coworkers\textsuperscript{29} used a cube similar to the Rubik cube to connect the Hückel, Baird, and Möbius rules. Figure 3 depicts an extended version of this cube that, in addition, incorporates the Soncini–Fowler and linking number rules. Depending on the number of $\pi$-electrons, the topology of the ring, and the considered electronic state one has an aromatic or an antiaromatic annulene.

2.3 | Hückel and Hirsch rules connected

In 1985, 15 years before the formulation of the Hirsch rule,\textsuperscript{56} Rubin and Ordóñez\textsuperscript{77} reported the eigenvalues and degeneracies for the states of $n$-dimensional spherical harmonics. The solution for the degeneracies is:

$$D_l(n) = \frac{(l+n-2)!}{l!(n-1)!} (2l+n-1), \quad l = 0, 1, 2, \ldots$$ \hspace{1cm} (1)

If one sets $n = 2$ in Equation (1), one gets $2l + 1$, which is the degeneracy of a second-order spherical harmonics (circle of radius $r$). Given that to reach a closed-shell structure, these orbitals have to be double occupied, then one obtains the Hückel $4N + 2$ rule. If one now considers $n = 3$, one gets $(l + 1)^2$, which is the degeneracy of a 3D spherical harmonics (sphere of radius $r$). Again if you double fill the orbitals with electrons, you reach the Hirsch $2(N + 1)^2$ rule (R. Berger, personal communication, 2017). Then, both Hückel and Hirsch rules derive from the same common equation corresponding to the $n$-dimensional spherical harmonics for different $n$ values ($n = 2$ for Hückel's rule and 3 for Hirsch's rule). Mathematically, these two rules are connected by the same common principle. One may ask which will be the principle for higher dimensional spheres. For a hypothetical 4D sphere of radius $r$, one gets $(l + 1)(l + 2)(2l + 3)/6$, so the electron counting for 4D spherical aromaticity is 2, 10, 28, 60, … electrons resulting in the $(N + 1)(N + 2)(2N + 3)/3$ rule.

Finally, let us mention that another connection of Hückel and Hirsch rules was established by Shainyan\textsuperscript{78} considering the electrons as objects in an arbitrary $n$-dimensional space of states. From the number of irreducible states in an $n$-dimensional

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Extended Ottosson’s cube summarizing several combinations of rules of (anti)aromaticity for annulenes}
\end{figure}
space of states, which is 2\(n + 1\), one can recover the Hückel rule by placing two electrons in each state. Taking into account that any \(n\)-dimensional spaces includes all the \((n - k)\)-dimensional subspaces and filling with electrons all subspaces, one reaches the Hirsch rule.

### 2.4 Hückel and Wade–Mingos rules connected

**Closo** BH clusters\(^{32,79}\) are dianions with the general formula \([B_nH_n]^{2−}\) \((n = 5–12)\) that are prepared by controlled pyrolysis of diborane.\(^{80}\) They have the structure of a polyhedron with triangular faces and because of their high stability, for instance, \([B_{12}H_{12}]^{2−}\) decomposes at 600°C.\(^{81,82}\) They are considered 3D aromatic species. **Closo** BHs obey the \(2N + 2\) Wade electron counting rule\(^{51,83}\) or the \(4N + 2\) Mingos’ rule,\(^{52,84}\) in which \(N\) are the vertexes of the polyhedron. As said before, these two rules are equivalent; Wade’s rule refers to the SE, whereas Mingos’ rule incorporates also the exo electron pairs corresponding to the B–H bonds, thus referring to the TNVEs.

In previous works,\(^{85,86}\) together with Poater, Viñas, and Teixidor, we established a connection between the Hückel rule for 2D classical aromaticity and the Wade–Mingos rule for 3D aromaticity in **closo** BHs. To reach this objective, we first established a link between hydrocarbons and boronhydrides applying the so-called electronic confined space analogy (ECSA) method.\(^{87}\) The steps followed in the ECSA method are the following: (a) we state the model organic hydrocarbon compound; (b) we transmute each C atom into a B atom and one electron \(eT\); (c) these extra electrons are replaced by sacrificial atoms \(sA\); (d) and finally (if necessary) we generate the new boronhydride compound by structural relaxation \(sR\). As sacrificial atoms we use any cation without valence electrons such as \(H^+, B^{3+}\), or \([BH_4]^+\) among others and, therefore, in the ECSA procedure the number of valence electrons remains unaltered. These cations have empty valence orbitals perfectly suited to form multicenter bonds. For each sacrificial atom, we transform a 2c-2e \(BB\) bond into a 3c-2e multicenter bond and, consequently, for each \(BB\) bond, we can add a sacrificial atom. As an example of the procedure, in Figure 4a we apply the ECSA method in the case of acetylene. Species analogous to \(III\) and \(V\) in Figure 4a have been previously reported.\(^{88,89}\) On the other hand, compounds \(II\), \(IV\), and \(VI\) remain unknown yet. Therefore, ECSA applied to hydrocarbons leads to known boronhydrides but, more importantly, it allows the design of new interesting molecules.

When we applied the ECSA method to \(C_2H_4^{2−}\), \(C_3H_5^{−}\), \(C_6H_6\), and \(C_7H_7^{+}\), we found that these species were connected with **closo** BH \([B_5H_5]^{2−}\), \([B_6H_6]^{2−}\), \([B_7H_7]^{2−}\), and \([B_8H_8]^{2−}\), respectively.\(^{85}\) As an example, Figure 5 displays the link between benzene and \([B_6H_6]^{2−}\). Starting from benzene, the electronic transmutation with \(B^−\) generates \([B_5H_5]^{6−}\) with chair-like structure. Interestingly, \(Li_6B_6H_6\) is planar.\(^{90}\) The sacrificial group we add to \([B_6H_6]^{6−}\) is \([BH_4]^+\) leading to hexagonal pyramid \([B_7H_7]^{2−}\) that is not a minimum, but relaxes to a pentagonal bipyramid \([B_7H_7]^{2−}\).\(^{91}\) The NICS(0) of \(-22.8\) ppm indicates that \([B_7H_7]^{2−}\)
can be considered at least as aromatic as benzene. The relatively low bond length alternation (BLA) value of 0.17 Å for the B–B bond gives further support to the aromatic character of \([B_7H_7]^2−\). Moreover, resonance energies per face calculated by Aihara indicated that \([B_nH_{2n}]^{2−}\) is the most aromatic \textit{closo} borane \([B_6H_{12}]^{2−}\) \((n = 5–12)\) after \([B_8H_{16}]^{2−}\). Interestingly, a BH fragment has two valence electrons in the B–H bond and two additional valence electrons. Therefore, adding a BH fragment to the closed-shell \([B_4H_6]^{2−}\) species to form \([B_7H_7]^{2−}\) changes the SE by 2 \((2N + 2 \text{ Wade’s rule})\) and the TNVE by 4 \((4N + 2 \text{ Mingos’ rule})\).

As a whole, the ECSA method provides a link between the highly stable classical aromatic hydrocarbon reference compounds fulfilling the \(4N + 2\) Hückel rule and the corresponding \textit{closo} BHs clusters that obey the \(4N + 2\) Wade–Mingos rule. Noticeably, the value of \(N\) has not the same meaning in one equation and the other. In \(4N + 2\) Wade–Mingos’ rule \(N\) refers to the number of vertexes occupied by boron atoms, whereas in \((4N + 2)\pi\) Hückel’s rule \(N\) can be any nonnegative integer and has no relationship with the structure of the annulene.

In a last work, we extended the application of ECSA to medium and large BH clusters, specifically to bicapped structures (from \([B_{10}H_{10}]^{2−}\) to \([B_{14}H_{14}]^{2−}\) but also to those presenting three parallel planes (from \([B_{13}H_{15}]^{2−}\) to \([B_{19}H_{19}]^{2−}\) ). We found that application of ECSA to medium and large boron clusters allows us to classify \textit{closo} boranes in three categories according to the \(N\) value of the Hückel \((4N + 2)\pi\) rule. Each category increases in geometrical difficulty but, more importantly, it is possible to associate each category with the number of pentagonal layers in the structure perpendicular to the main axis. Figure 6 shows that all \textit{closo} BHs of Category 1 \((N = 1)\) have one pentagonal layer, those of Category 2 \((N = 2)\) have two, and those of Category 3 \((N = 3)\) have three. As can be seen in Figure 6, all annulenes connected with \textit{closo} BHs of Category 1 \((C_4H_4^{2−}\) to \(C_6H_6^{2+}\)) have six \(\pi\)-electrons, that is, \(N = 1\) in the \(4N + 2\) rule.

### 3 COMBINING RULES

In this section, we introduce several examples in which, to explain the aromatic character of some compounds, the Hückel rule has to be combined with the Baird rule or the Baird rule has to be joined with the Clar, Glidewell–Lloyd, and Hirsch rules.

#### 3.1 Hückel and Baird rules combined

In 2015, Tovar and coworkers synthesized a quinoidal 1,6-methano[10]annulene compound (TMTQ, Figure 7) with a singlet–triplet energy gap \((\Delta E_{ST})\) of only 4.9 kcal/mol, the singlet being the ground state. The small energy gap was attributed to stabilization of the lowest-lying triplet state \((T_1)\) through Baird-aromaticity of the central 1,6-methano[10]annulene ring. If this is true, it would mean that the resonance structure TMTQ-c in Figure 7 with an \(8\pi\)-electron 1,6-methano[10]annulenyl dication moiety with Baird aromaticity has a significant weight in the wave function of the lowest-lying triplet state of TMTQ. In principle, the resonance structure TMTQ-b with a closed-shell \(10\pi\)-electron Hückel-aromatic ring and two terminal dicyanomethyl radicals could also have a substantial contribution to the wave function of TMTQ in its \(T_1\) state. To analyze whether the electronic properties of TMTQ in its first triplet state are better explained by resonant structure TMTQ-b (Hückel aromaticity) or TMTQ-c (Baird aromaticity), together with Ottosson and coworkers,31 we decided to perform a computational study of the electronic structure of TMTQ in its \(T_1\) state. We analyzed the atomic charges, the atomic spin densities, and the aromaticity of the 1,6-methano[10]annulene ring. The conclusion was that the influence of Baird aromaticity in the triplet state of TMTQ was limited to 12% at most. Therefore, the aromaticity of 1,6-methano[10]annulene ring of TMTQ in its \(T_1\) state is mainly of Hückel type, although some influence of Baird aromaticity exists. This means that the 1,6-methano[10]annulene ring mixes the closed-shell Hückel-aromaticity (TMTQ-b) with the open-shell Baird aromaticity (TMTQ-c), and consequently, it can be described as a triplet biradical Hückel-Baird aromatic hybrid species. Interestingly, the electronic structure of these Hückel–Baird aromatic hybrids is described at the same time with the Hückel and the Baird rules.

The aromaticity in metalloaromatic species is particularly complex. An interesting example corresponds to quintet \(^5\text{Ta}_3^-\), which is the ground state for \(\text{Ta}_3^-\) anion. The electronic structure and chemical bonding of this all-metal cluster was investigated by means of photoelectron spectroscopy and density functional theory calculations in 2008 by Wang et al. From a molecular orbital analysis (see Figure 8), the authors concluded that \(^5\text{Ta}_3^-\) possesses multiple aromaticity with \(\sigma\), \(\pi\), and \(\delta\)-characteristic. Our results using multicenter bonding supported this assignment, with multicenter index (MCI) values of 0.403, 0.178, and 0.296 e\(^−\) for the \(\sigma\), \(\pi\), and \(\delta\)-electrons. As can be seen in Figure 8, the system has a closed structure for the \(\delta\)-valence electrons and, consequently, the \(\delta\)-system follows the Hückel rule. On the other hand, the \(\sigma\) and \(\pi\)-systems have open-shell electronic structures and follow the Baird rule. Therefore, \(^5\text{Ta}_3^-\) has multiple aromaticity that combines Hückel (\(\delta\)-system) and Baird (\(\sigma\)- and \(\pi\)-systems) aromaticities.
3.2 Clar and Baird rules combined

In a recent work, we have shown that Baird and Clar’s rules have to be combined to rationalize the T1 state energies of PCHs that contain cyclobutadiene, cyclooctatetraene, or pentalene as central 4N π-electron units fused with 4N + 2 π-electrons units. When comparing different isomeric PCHs, an influence of T1 state aromaticity of the central 4N π-electron unit is observed and the most stabilized compounds display Baird quartets or octets (disjoint triplet diradical Baird-aromatic 4N π-electron rings). This is the case, for instance, of linear A3LL and kinked cis and trans A3BB benzannelated cyclobutadiene isomers (see Figure 9, L means lineal and B bent). (U)B3LYP/6-311+G(d,p) calculations show that the singlet–triplet energy gap of 2.75 eV in the linear isomer is reduced by about 1.7 eV in the kinked A3BB isomers. The reason for the significant reduction in the singlet–triplet energy gap when going from linear to kinked benzannelated cyclobutadiene isomers can be found in the local aromaticities of the different rings. NICSXY and ACID plots, and FLU values of the triplet states show that in the linear A3LL isomer there are two Clar π-sextets in the external rings (Figure 9), which are the most aromatic. For the kinked cis and trans A3BB isomers, we have the same two Clar π-sextets in the external rings together with a π-Baird quartet in the...
central cyclobutadiene ring. This additional π-Baird quartet is the reason for the higher stability of the triplet in the kinked cis and trans A3BB isomers as compared to the linear A3LL isomer. As can be seen in Figure 9, Clar structures of the linked isomers place 4π-electrons in the cyclobutadiene ring, which in the triplet state provide Baird aromaticity to this ring. On the other hand, the Clar structure of linear A3LL isomer locates 8π-electrons in the inner biphenylene unit. These 8π-electrons cannot generate a π-Baird octet because aromatic π-sextets, π-quartets, π-octets, etc. have to be disjoint. These linear and kinked benzannelated cyclobutadiene isomers represent a nice example in which combination of the Clar and Baird rules provides an explanation for a physical phenomenon.

3.3 Baird and Glidewell–Lloyd rules combined

Let us now discuss the case of molecules I and II in Figure 10 with a cyclobutadiene ring fused to each cyclooctatetraene ring of octalene.72 The most stable structure for these molecules in their closed-shell singlet state is shown in blue in Figure 10. Alternative structures depicted in red in Figure 10 are also minima. They are less stable than those in black by 1.7 and 4.9 kcal/mol at the B3LYP/6-311G(d,p) level of theory, as expected from Glidewell–Lloyd rule.55 However, the closed-shell singlet state is not the ground state for these molecules. The ground state is an open-shell singlet state that is 4.3 and 3.2 kcal/mol more stable for I and II, respectively, than the closed-shell singlet state. In the open-shell singlet state the molecules are better described by the red structures in Figure 10 with the biradical character located in rings B that become aromatic as expected from the Baird rule (MCI97 of 0.030 as compared to that of cyclobutadiene of 0.009). Therefore, a combination of Glidewell–Lloyd and Baird rules are required to explain the open-shell singlet ground state of molecules I and II in Figure 10.
3.4 | Baird and Hirsch rules combined

Hirsch’s rule is based on the fact that the \( \pi \)-electron system of an icosahedral fullerene can be approximated by a spherical electron gas surrounding the surface of a sphere. The corresponding wave functions of this electron gas are characterized by the angular momentum quantum number \( l \) (\( l = 0, 1, 2, \ldots \)), with each energy level \( 2l + 1 \) times degenerated, and thus all \( \pi \)-shells are completely filled when we have \( 2(N + 1)^2 \) electrons (see Figure 11). For such reason, spherical species with \( 2(N + 1)^2 \) \( \pi \)-electrons are aromatic, like icosahedral \( \text{C}_{20}^{2+}, \text{C}_{60}^{10+}, \text{C}_{60}^{12-} \) or \( \text{C}_{80}^{8+} \).

In the same way that Baird’s \( 4N \) rule represented the extension of Hückel’s \( 4N + 2 \) rule to lowest-lying triplet states, those 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 when the spherical compounds have \( 2N^2 + 2N + 1 \) electrons and with a spin \( S = N + \frac{1}{2} \) (Figure 11).

Table 3 includes a series of \( \text{C}_{60} \) species with different charges. The magnetic NICS(1)\(_{zz}\), the electronic MCI, and the BLA indicators of aromaticity are used to discuss the aromaticity of these fullerenes. For \( \text{C}_{60} \), which obeys neither the Hirsch nor the \( 2N^2 + 2N + 1 \) rules, all measures point out that it has a nonaromatic or only slightly aromatic character. On the other hand, \( \text{C}_{60}^{10+} \) appears to be more aromatic than \( \text{C}_{60} \) with more negative NICS and smaller BLA, in line with Hirsch’s rule for a

### Table 3

| System  | Symmetry | Ring   | NICS(1)\(_{zz}\) | MCI* | BLA  | Spin |
|---------|----------|--------|-----------------|------|------|------|
| \( \text{C}_{60} \) | \( I_6 \) | 6-MR   | 0.8             | 18   | 0.058| \( S = 0 \) |
| \( \text{C}_{60}^{1-} \) | \( I_6 \) | 5-MR   | 21.5            | 11   |
| \( \text{C}_{60}^{10+} \) | \( I_6 \) | 6-MR   | -1.4            | 17   | 0.002| \( S = 11/2 \) |
| \( \text{C}_{60}^{12-} \) | \( I_6 \) | 5-MR   | -19.9           | 49   |
| \( \text{C}_{60}^{19+} \) | \( I_6 \) | 5-MR   | -14.9           | 19   | 0.013| \( S = 9/2 \) |
| \( \text{C}_{60}^{10+} \) | \( I_6 \) | 6-MR   | -25.3           | 41   |
| \( \text{C}_{60}^{18-} \) | \( I_6 \) | 5-MR   | -29.5           | 17   |

* MCI values multiplied by 1,000.
system with 50 electrons. Moreover, C_{60}^{19+} and C_{60}^{1−} with \( S = 9/2 \) and \( 11/2 \), respectively, thus following the \( 2N^2 + 2N + 1 \) (\( S = N + \frac{1}{2} \)) rule, appear to be the most aromatic. These results for charged C_{60} species together with additional evidence for charged C_{20} and C_{80} and Ge_{12} cluster provide strong support in favor of the \( 2N^2 + 2N + 1 \) rule. This new \( 2N^2 + 2N + 1 \) rule for spherical open-shell aromaticity is the result of the combination of Hirsch and Baird rules.

### 4 | CONCLUSION

Since the original formulation of the \( 4N + 2 \) Hückel rule in 1931, several rules of aromaticity have been reported. In these rules, the magic numbers that provide aromaticity are the number of electrons required to reach a closed-shell or open-shell half-filled with same spin electrons electronic configuration. Interestingly, it is possible to find connections between certain rules of aromaticity. These connections, which have been described in the present review, represent a step forward towards a potential unified theory of aromaticity. On the other hand, combination of several rules of aromaticity are in some cases needed to rationalize experimental observations as, for instance, to explain the stability of the lowest-lying triplet state of hybrid Hückel–Baird species or some PCHs containing cyclobutadiene, cyclooctatetraene, or pentalene as central \( 4N \) \( \pi \)-electron units fused with \( 4N + 2 \) \( \pi \)-electrons units. Combination of rules can also be used to formulate new rules of aromaticity as in the case of the \( 2N^2 + 2N + 1 \) (\( S = N + \frac{1}{2} \)) rule. Given the relevance of the aromaticity concept and the need for a better comprehension of this phenomenon, it is likely that connection and combination of existing rules and formulation of new rules will develop further in the coming years.

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### CONFLICT OF INTEREST

The author has declared no conflicts of interest for this article.

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