Article Title: **Connecting and combining rules of aromaticity. Towards a unified theory of aromaticity**

Article Type:

○ OPINION   ○ PRIMER   ○ OVERVIEW

⊙ ADVANCED REVIEW   ○ FOCUS ARTICLE   ○ SOFTWARE FOCUS

Authors:

First author
Miquel Solà*
0000-0002-1917-7450
Universitat de Girona
miquel.sola@udg.edu
No potential conflict of interest

Abstract

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 stabilisation 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 generalised, which represents a step forward to a future unified theory of aromaticity.

Graphical/Visual Abstract and Caption

Caption: Rules of aromaticity are important to rationalize a large number of experimental observations. In some cases, these rules are connected by different formulas and procedures. In other cases, some of these rules have to be combined to explain the aromatic behaviour of certain molecules.

Graphical/Visual Abstract:
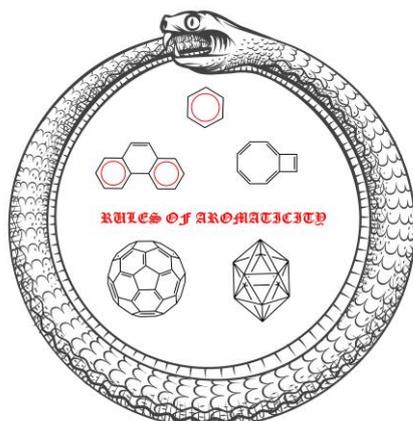
"Rules are rules but no laws"
Gernot Frenking in the ESPA 2018 Conference

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 odour (aroma) of compounds like benzene or toluene.[7] Today, aromatic compounds are not characterized by its odour 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 equalisation 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 multicentre bonding and, consequently, electronic delocalisation 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.[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 aromaticities 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] hyperaromaticity[46]… The adjective added to aromaticity in each case is used to describe a particular situation. To have so many types of aromaticities 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).[47] The most relevant for the present review are briefly discussed in the following paragraphs.

The most stable molecular orbital in D_{nh} annulenes is formed by the in-phase interactions of all p_z-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…, i.e., with 4N+2 π-electrons. Therefore, annulenes with 4N+2 π-electrons are aromatic and with 4N π-electrons are antiaromatic.

On the other hand, in D_{nh} 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 stabilisation 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.[48] 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 4N π-electrons is also aromatic.[49-51]

In 2008, Soncini and Fowler generalised the Hückel and Baird rules. According to Soncini and Fowler's rule[52] the monocyclic structures of 4N+2 π-electrons at the lowest-lying electronic states with even spin (singlet, quintet, ...) and the monocycles of 4N π-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 π-molecular orbital (see Figure 1c) and, as a result, they come by pairs. Consequently, they reach the closed-shell electronic structures for the following number of π-electrons: 4, 8, 12… The electron counting is opposed to that of the Hückel rule and, therefore, Möbius-type annulenes with 4N π-electrons are aromatic and with 4N+2 π-electrons are antiaromatic.

3

The linking number (L_k) rule of Rappaport and Rzepa[53] allows a generalisation 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 4N+2 π-electron rule of aromaticity for the closed-shell ground state, whereas those having an odd L_k obey the Möbius' 4N π-electron rule.

Hückel's rule is strictly valid only for monocyclic conjugated systems. Clar's π-sextet rule formulated in 1972[54] was an attempt to extend the Hückel rule to benzenoid species. Aromatic π-sextets are defined as six π-electrons localised 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 π-sextets, i.e., benzene-like moieties, is the most important for characterisation 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.[55, 56] Indeed, this result is confirmed by many different measures of local aromaticity.[57-59]

In 1984, Glidewell and Lloyd[60] 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[60] 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 non-benzenoid PCHs discussed by Glidewell and Lloyd[60] 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,[61] 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 $[B_nH_n]^{2-}$, *closo* borohydride 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.[62, 63] Both rules are equivalent, since Wade's rule refers to the skeletal electrons (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.

Finally, Hirsch's $2(N+1)^2$ rule of spherical aromaticity[64] 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 characterised by the angular momentum quantum number l (l = 0, 1, 2…). 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-Mingos 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-Mingos rule refers to the *inner* aromaticity of skeletal electrons of the cage, whereas the Hirsch rule describes the *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 generalised, 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.

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-Mingos rules. Such links show that some of these rules can be generalised, paving the way for a future unified law or theory of aromaticity.

Hückel and Baird rules connected

In 2008, Mandado and coworkers[65] 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 α and β terms are analysed separately. This new rule fusing Hückel and Baird's rules states that aromatic annulenes are those having 2N+1 α and β π-electrons, whereas those having 2N α and β π-electrons are antiaromatic. Radical systems having 2N+1 α π-electrons and 2N β π-electrons are found to have conflicting aromaticity being α aromatic and β antiaromatic. Table 2 provides some examples calculated by Mandado et al.[65] To prove the new joined rule it was necessary to use indicators of aromaticity that can be split into α and β components. In particular the authors used scaled n-centre electron delocalisation indices[66] and the π contribution to the out-of-plane zz component of the magnetic shielding tensor, NICS(0)$_{\pi zz}$.[67] As can be seen in Table 2, when the number of α or β π-electrons is odd, the system behaves as an aromatic compound in the corresponding component with positive and large n-centre delocalisation indices and negative NICS(0)$_{\pi zz}$ values. On the other hand, if the number of α or β π-electrons is even, n-centre delocalisation indices are negative and NICS(0)$_{\pi zz}$ values are positive as usual in antiaromatic compounds.

It is worth noting that a connection between Hückel, Baird, and Möbius rules was also obtained[68] 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 4π and not of 2π as in the case of annulenes with Hückel topology.

Hückel, Baird, Möbius, Soncini-Fowler, and Linking number rules connected

The Hückel rule states that annulenes with 4N+2 π-electrons are aromatic and with 4N π-electrons are antiaromatic. In the lowest-lying triplet state, however, the rule is reversed and annulenes with 4N π-electrons are aromatic and with 4N+2 π-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 et al.[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 π-electrons, the topology of the ring, and the considered electronic state one has an aromatic or an antiaromatic annulene.

Hückel and Hirsch rules connected

In 1985, fifteen years before the formulation of the Hirsch rule,[64] Rubin and Ordóñez[69] reported the eigenvalues and degeneracies for the states of n-dimensional spherical harmonics. The solution for the degeneracies are:

$$D_l(n) = \frac{(l+n-2)!}{l!\,(n-1)!}(2l+n-1) \qquad l = 0, 1, 2, \ldots \tag{1}$$

If one sets n = 2 in Eq. 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.[70] 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 n = 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[71] considering the electrons as objects in an arbitrary n-dimensional space of states. From the number of irreducible states in an n-dimensional 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.

Hückel and Wade-Mingos rules connected

Closo borohydride (BH) clusters[32, 72] are dianions with the general formula $[B_nH_n]^{2-}$ (n = 5 to 12) that are prepared by controlled pyrolysis of diborane.[73] 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 ºC,[74, 75] they are considered 3D aromatic species. *Closo* BHs obey the 2N+2 Wade electron counting rule[62, 76] or the 4N+2 Mingos' rule,[77, 78] in which N are the vertexes of the polyhedron. As said before, these two rules are equivalent, Wade's rule refers to the skeletal electrons (SE), whereas Mingos' rule incorporates also the exo electron pairs corresponding to the B–H bonds, thus referring to the total number of valence electrons (TNVEs).

In previous works,[79, 80] 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 boron hydrides applying the so-called electronic confined space analogy (ECSA) method.[81] The steps followed in the ECSA method are the following: 1) we state the model organic hydrocarbon compound; 2) we transmute each C atom into a B atom and one electron (**eT**); 3) these extra

electrons are replaced by sacrificial atoms (**sA**); 4) 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 B–B bond into a 3c-2e multicentre bond and, consequently, for each B–B 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.[82, 83] 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 $C_4H_4^{2-}$, $C_5H_5^-$, 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.[79] As an example, Figure 5 displays the link between benzene and $[B_7H_7]^{2-}$. Starting from benzene, the electronic transmutation with B^- generates $[B_6H_6]^{6-}$ with chair-like structure. Interestingly, $Li_6B_6H_6$ is planar.[84] 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 $[B_7H_7]^{2-}$.[85] The NICS(0) of -22.8 ppm indicates that $[B_7H_7]^{2-}$ is at least as aromatic as benzene.[79] The relatively low bond length alternation value of 0.17 Å for the B–B bonds gives further support the aromatic character of $[B_7H_7]^{2-}$. Moreover, resonance energies per face calculated by Aihara[86] indicated that $[B_7H_7]^{2-}$ is the most aromatic closo borane $[B_nH_n]^{2-}$ (n = 5–12) after $[B_6H_6]^{2-}$. Interestingly, a BH fragment has 2 valence electrons in the B–H bond and 2 additional valence electrons. Therefore, adding a BH fragment to the closed-shell $[B_6H_6]^{2-}$ species to form $[B_7H_7]^{2-}$ changes the SE by 2 (2N+2 Wade's rule) and the TNVE by 4 (4N+2 Mingo's 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 *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)π Hückel's rule N can be any nonnegative integer and has no relationship with the structure of the annulene.

In a last work,[80] 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 $[B_{15}H_{15}]^{2-}$ to $[B_{19}H_{19}]^{2-}$). We found that application of ECSA to medium and large boron clusters allows us to classify *closo* boranes in three categories according to the N value of the Hückel (4N+2)π 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 *closo* BHs of category 1 (with N = 1) have one pentagonal layer, those of category 2 (with N = 2) have two, and those of category 3 (with N = 3) have three. As can be seen in Figure 6, all annulenes connected with *closo* BHs of category 1 (from $C_4H_4^{2-}$ to $C_8H_8^{2+}$) have six π-electrons, i.e., N = 1 in the 4N+2 rule.

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.

Hückel and Baird rules combined

In 2015, Tovar, Casado, et al.[87, 88] synthesized a quinoidal 1,6-methano[10]annulene compound (**TMTQ**, Figure 7) with a singlet-triplet energy gap (ΔE_{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 8π-electron 1,6-methano[10]annulenyl dication moiety with Baird aromaticity have 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 10π-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 analysed 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.[25, 89] An interesting example corresponds to quintet $^5Ta_3^-$, which is the ground state for 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.[90] From a molecular orbital analysis (see Figure 8), the authors concluded that $^5Ta_3^-$ possesses multiple aromaticity with partial σ-, partial π-, and δ-aromatic character. Our results using multicentre bonding supported this assignment,[91] with MCI values of 0.403, 0.178, and 0.296 e^- for the σ-, π-, and δ-electrons. As can be seen in Figure 8, the system has a closed structure for the δ-valence electrons and, consequently, the δ-system follows the Hückel rule. On the other hand, the σ- and π-systems have open-shell electronic structures and follow the Baird rule. Therefore, $^5Ta_3^-$ has multiple aromaticity that combines Hückel (δ-system) and Baird (σ- and π-systems) aromaticities.

Clar and Baird rules combined

In a recent work,[92] we have shown that Baird and Clar's rules have to be combined to rationalize the T_1 state energies of polycyclic conjugated hydrocarbons (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 T_1 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 meaning 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.[92] 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. $NICS_{XY}$ 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…. 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.

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.[61] 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.[60] 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 (multicentre index[93] 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.

Baird and Hirsch rules combined

Hirsch's rule is based on the fact that the π-electron system of an icosahedral fullerene can be approximated by an 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,…), with each energy level 2*l*+1 times degenerated, and thus all π-shells are completely filled when we have $2(N+1)^2$ electrons (see Figure 11). For such reason, spherical species with $2(N+1)^2$ π-electrons are aromatic, like icosahedral C_{20}^{2+}, C_{60}^{10+}, C_{60}^{12-} or 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).[94]

Table 3 includes a series of C_{60} species with different charges.[94] The magnetic $NICS(1)_{zz}$, the electronic multicentre index (MCI), and the bond length alternation (BLA) indicators of aromaticity are used to discuss the aromaticity of these fullerenes. For C_{60}, which obeys neither the Hirsch nor the $2N^2+2N+1$ rules, all measures point out that it has a non-aromatic or only slightly aromatic character. On the other hand, C_{60}^{10+} appears to be more aromatic than C_{60} with more negative NICS and smaller BLA, in line with Hirsch's rule for a 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 favour 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.

Figures and Tables

TABLE 1. A historical overview of aromaticity rules.

year	main contributor(s)	contribution
1931	Hückel[11-14]	Hückel's (4N+2) π-electron rule of monocyclic annulenes
1954	Platt[95]	Platt's ring perimeter model
1964	Heilbronner,[96] Herges[97]	4N π-electron rule for Möbius-type conformation of annulenes
1965	Breslow[98]	Antiaromaticity of 4Nπ monocyclic annulenes
1971	Wade[62]	2N+2 cage electron rule for closo boranes
1972	Mingos[63]	4N+2 valence electron rule for closo boranes
1972	Baird[28]	4N π-electron rule for the lowest-lying triplet state of annulenes
1972	Clar[54]	Π-sextet rule for benzenoid species
1978	Ovchinnikov[99]	Multiplicity of the ground state of large alternant organic molecules with conjugated bonds
1984	Glidewell, Lloyd[60]	Extension of Clar's rule to polycyclic conjugated hydrocarbons with even number of C atoms
2000	Hirsch[64]	$2(N+1)^2$ rule for spherical aromatic species
2002	Jemmis[100]	Extension of Wade-Mingo's rule to fused boranes, the mno rule
2004	Ruiz-Morales[101]	Y-rule, an improvement of Clar's rule
2008	Soncini, Fowler[52]	A generalisation of Hückel's (4N+2)π rule and Baird's 4Nπ rule to higher excited states
2008	Rzepa[53]	Linking number rule as a generalisation of Hückel's (4N+2)π rule and Möbius' 4Nπ rule
2011	Poater, Solà[94]	$2N^2+2N+1$ (S = N + ½) rule of open-shell spherical aromaticity
2013	Havenith, Nguyen, Ceulemans[39]	Rule for disk aromaticity
2014	Nguyen[36, 37]	Rule for cylindrical aromaticity
2015	Zhao, Li[40]	6N+2 rule of cubic aromaticity

TABLE 2. Number of α and β π-electrons ($N^{\pi\alpha}$, $N^{\pi\beta}$), scaled n-centre electron delocalisation indices ($^S\Delta^{\pi\alpha}$, $^S\Delta^{\pi\beta}$) and π contribution to the out-of-plane zz tensor component of the nucleus independent chemical shifts (NICS(0)$_{\pi zz\alpha}$, NICS(0)$_{\pi zz\beta}$) for some selected species.[a]

Molecule	$N^{\pi\alpha}$	$N^{\pi\beta}$	$^S\Delta^{\pi\alpha}$	$^S\Delta^{\pi\beta}$	NICS(0)$_{\pi zz\alpha}$	NICS(0)$_{\pi zz\beta}$
C_4H_4	2	2	-0.299	-0.299	117.52	117.52
C_4H_4	3	1	0.302	0.383	-15.07	-6.66
C_6H_6	3	3	0.361	0.361	-17.88	-17.88
$C_6H_6^+$	3	2	0.364	-0.266	-17.67	74.86
C_8H_8	5	3	0.325	0.361	-24.67	-16.28
$C_8H_8^+$	4	3	-0.242	0.364	100.55	-16.27
$C_8H_8^-$	5	4	0.322	-0.233	-24.46	114.74

[a] Data extracted from ref. 65 with permission. Copyright 2018 AIP Publishing.

TABLE 3. NICS(1)$_{zz}$ (in ppm) and MCI (in electrons) values for neutral and charged C_{60}.

System	Symmetry	Ring	NICS(1)$_{zz}$	MCI[b]	BLA	Spin
C_{60}	I_h	6-MR	0.8	18	0.058	S = 0
		5-MR	21.5	11		
C_{60}^{1-}	I_h	6-MR	-1.4	17	0.002	S = 11/2
		5-MR	-19.9	49		
C_{60}^{19+}	I_h	6-MR	-14.9	19	0.013	S = 9/2
		5-MR	-25.3	41		
C_{60}^{10+}	I_h	6-MR	-18.6	11	0.030	S = 0
		5-MR	-29.5	17		

[a] Data extracted from ref. 94 with permission. Copyright 2011 Royal Society of Chemistry. [b] MCI values multiplied by 1000.

FIGURE 1. Distribution of molecular orbitals and electrons in (a) Hückel aromatic compounds, (b) Baird lowest lying triplet state aromatic compounds, and (c) Möbius aromatic compounds. The orbital in red can be present or not depending on the number of C atoms of the annulene.

(a) 4N+2 π-electrons　　(b) 4N π-electrons　　(c) 4N π-electrons

FIGURE 2. (a) Two out of the five Kekulé resonance structures of phenanthrene and their corresponding Clar aromatic π-sextets indicated with a circle. The structure with the largest number of aromatic π-sextets is the so-called Clar's structure and (b) Application of the Glidewell-Lloyd rule to two polycyclic conjugated hydrocarbons.

1

Clar's structure

(a)

YES

NO

YES

NO

(b)
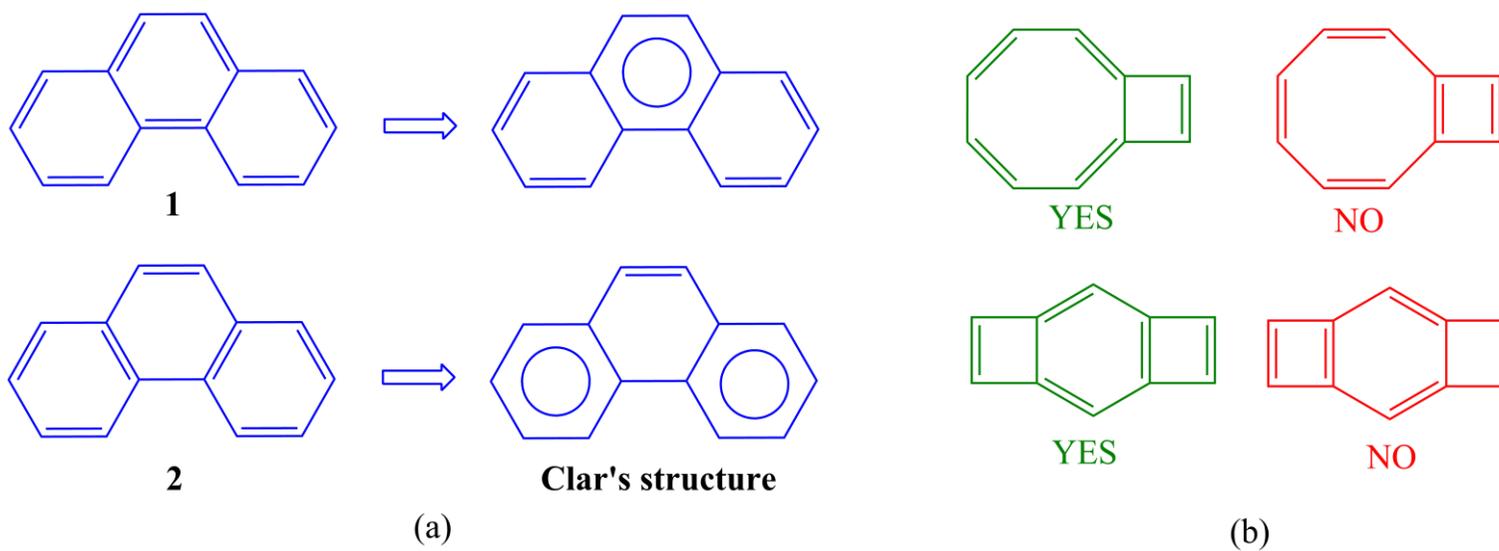
FIGURE 3. Extended Ottosson's cube summarizing several combinations of rules of (anti)aromaticity for annulenes.
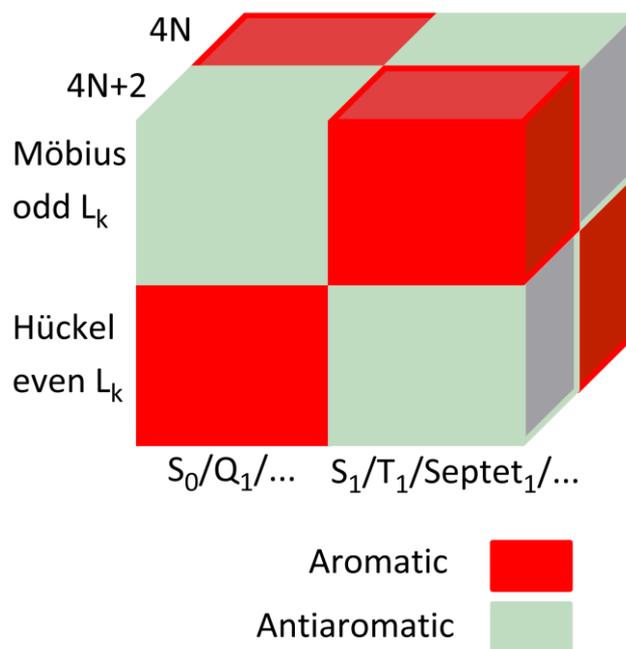
FIGURE 4. A series of compounds derived from the application of ECSA to acetylene. In the first row, we have acetylene (**I**) and two structures obtained from **I** by electronic transmutation (**eT**) and second row correspond to structures generated by the addition of up to three H$^+$ as sacrificial atoms (**sA**, red atoms) to compound **III** with a triple B–B bond.
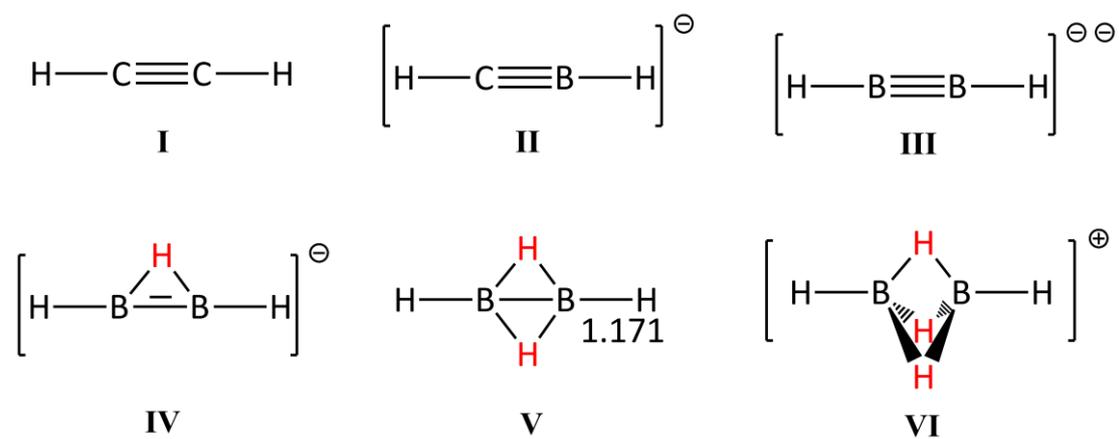
FIGURE 5. ECSA applied to benzene leads to *closo* borane $B_7H_7^{2-}$ by using BH^{+4} as sacrificial atom (**sA**). The total number of 36 valence electrons remains constant throughout the process.
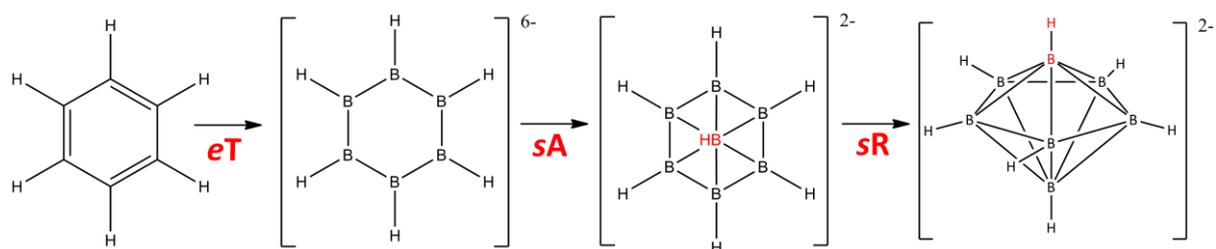
FIGURE 6. Analogy between boron hydrides and hydrocarbons based on Hückel's rule. Below each figure NICS(0) value (in italics, in ppm) is included. Reprinted with permission from Ref. 80. Copyright 2016 Wiley.


-26.1
$[B_5H_5]^{2-}$

-31.0
$[B_6H_6]^{2-}$

-22.8
$[B_7H_7]^{2-}$

-19.1
$[B_8H_8]^{2-}$

-23.5
$[B_9H_9]^{2-}$

-6.3
$[C_4H_4]^{2-}$

-12.7
$[C_5H_5]^{1-}$

-8.1
$[C_6H_6]$

-6.3
$[C_7H_7]^{1+}$

-6.8
$[C_8H_8]^{2+}$

a) n = 1 in 4n+2 Hückel's rule

-29.4
$[B_{10}H_{10}]^{2-}$

-27.0
$[B_{11}H_{11}]^{2-}$

-29.6
$[B_{12}H_{12}]^{2-}$

-23.0
$[B_{13}H_{13}]^{2-}$

-25.4
$[B_{14}H_{14}]^{2-}$

-11.9
$[C_8H_4]^{2-}$

-13.7
$[C_9H_9]^{1-}$

-13.7
$[C_{10}H_{10}]$

-13.2
$[C_{11}H_{11}]^{1+}$

-12.7
$[C_{12}H_{12}]^{2+}$

b) n = 2 in 4n+2 Hückel's rule

-24.7
$[B_{15}H_{15}]^{2-}$

-27.7
$[B_{16}H_{16}]^{2-}$

-30.3
$[B_{17}H_{17}]^{2-}$

-28.4
$[B_{18}H_{18}]^{2-}$

-26.8
$[B_{19}H_{19}]^{2-}$

-16.5
$[C_{12}H_{12}]^{2-}$

-16.5
$[C_{13}H_{13}]^{1-}$

-16.1
$[C_{14}H_{14}]$

-15.5
$[C_{15}H_{15}]^{1+}$

-14.8
$[C_{16}H_{16}]^{2+}$

c) n = 3 in 4n+2 Hückel's rule

FIGURE 7. Covalent, diradical, and polar mesomeric structures relevant to explain the electronic structure of compound **TMTQ**. Extracted from ref. 31 with permission. Copyright 2016 Wiley.


TMTQ-a   TMTQ-b   TMTQ-c
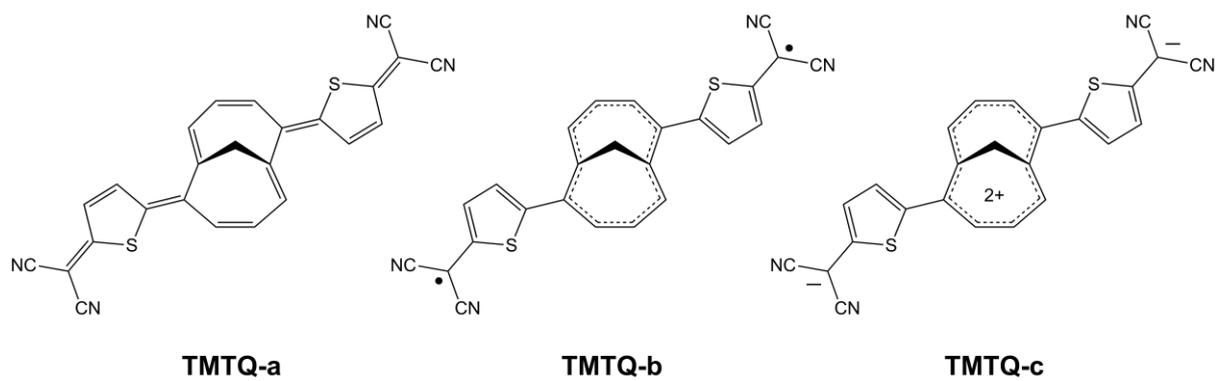
FIGURE 8. The molecular orbitals of the valence electrons of $^5Ta_3^-$.

$^5Ta_3^-$

$(1a_1')^2$ $(2a_1')^2$ $(1a_2'')^2$ $(1e_1')^4$ $(1e'')^2$ $(3a_1')^2$ $(2e')^2$
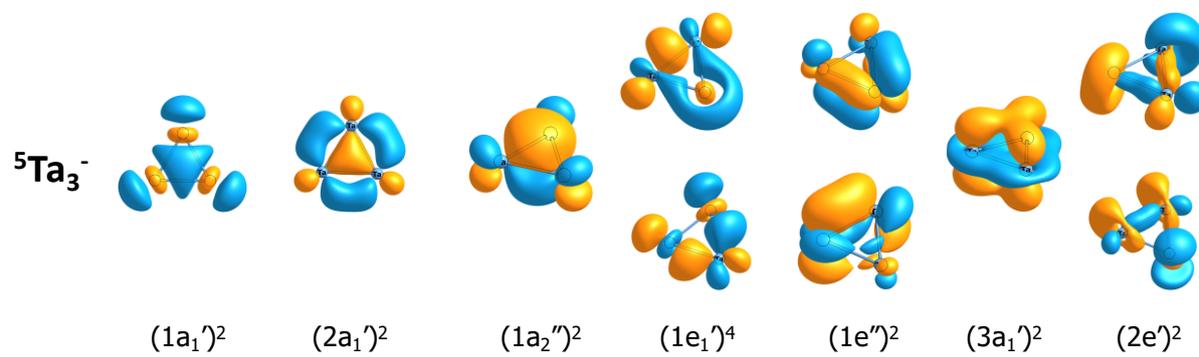
FIGURE 9. Benzannulated cyclobutadiene linear and kinked isomers.
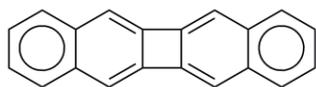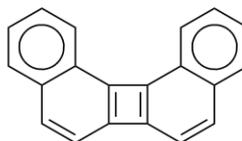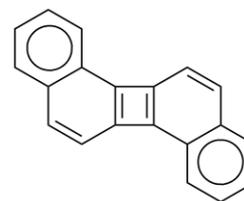
A3LL   *cis*-**A3BB**   *trans*-**A3BB**

FIGURE 10. In blue the most stable structure of molecules **I** and **II** in their closed-shell singlet state. In red, alternative structures of these molecules that do not follow the Glidewell-Lloyd rule.
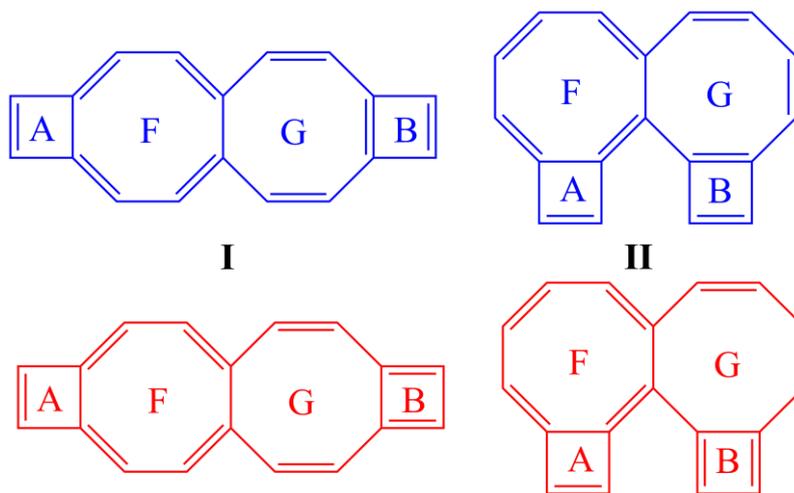
FIGURE 11. Distribution of molecular orbitals in spherical systems. Numbers in red correspond to closed-shell structures (Hirsch's rule) and numbers in blue to the open-shell half-filled with same spin electrons structures ($2N^2+2N+1$ rule).
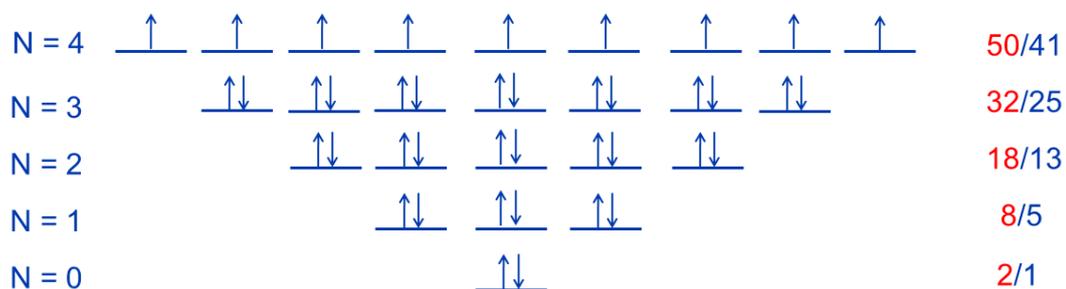
$$2, 8, 18, 32, 50, 72, 98\ldots = 2(N+1)^2$$

$$1, 5, 13, 25, 41, 61, 75\ldots = 2N^2+2N+1 \; (S=N+\tfrac{1}{2})$$

> **Counting rules:**
>
> The electron counting rules are useful to identify aromatic compounds, although they cannot provide a quantitative measure of aromaticity. To reach a quantitative description of aromaticity is challenging because of the lack of a strict definition of the concept of aromaticity, although one can have a first indication by using different descriptors of aromaticity.

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 polycyclic conjugated hydrocarbons containing cyclobutadiene, cyclooctatetraene, or pentalene as central 4N π-electron units fused with 4N+2 π-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+ ½) 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.

Acknowledgments

References

1.   Balaban AT. Is Aromaticity Outmoded? *Pure & Appl. Chem.* 1980, 52:1409-1429.
2.   Lloyd D. What is aromaticity? *J. Chem. Inf. Comp. Sci.* 1996, 36:442-447.
3.   Hoffmann R. The many guises of aromaticity. *Am. Sci.* 2015, 103:18-22.
4.   Solà M. Why Aromaticity Is a Suspicious Concept? Why? *Front. Chem.* 2017, 5:22.
5.   Merino G, Solà M. Celebrating the 150th anniversary of the Kekulé benzene structure. *Phys. Chem. Chem. Phys.* 2016, 18:11587-11588.
6.   Frenking G, Krapp A. Unicorns in the world of chemical bonding models. *J. Comput. Chem.* 2007, 28:15-24.
7.   Hofmann AW. On Insolinic Acid. *Proc. Royal Soc. London* 1856, 8:1-3.
8.   Islas R, Heine T, Merino G. The Induced Magnetic Field. *Acc. Chem. Res.* 2012, 45:215-228.
9.   Zhao L, Grande-Aztatzi R, Foroutan-Nejad C, Ugalde JM, Frenking G. Aromaticity, the Hückel 4 n+2 Rule and Magnetic Current. *ChemistrySelect* 2017, 2:863-870.
10.   Solà M. Aromaticity. In: Wang Z, ed. *Encyclopedia of Physical Organic Chemistry*. Vol. 6. Weinheim: John Wiley & Sons; 2017, 511-542.
11.   Hückel E. Quantentheoretische Beiträge zum Benzolproblem I. Die Elektronenkonfiguration des Benzols und verwandter Verbindungen. *Z. Physik* 1931, 70:104-186.
12.   Hückel E. Quanstentheoretische Beiträge zum Benzolproblem II. Quantentheorie der induzierten Polaritäten. *Z. Physik* 1931, 72:310-337.
13.   Hückel E. Quantentheoretische Beiträge zum Problem der aromatischen und ungesättigten Verbindungen. III. *Z. Physik* 1932, 76:628-648.
14.   Hückel E. The theory of unsaturated and aromatic compounds. *Z. Elektrochemie* 1937, 43:752-788, 827-849.
15.   Stępień M, Szyszko B, Latos-Grażyński L. Three-Level Topology Switching in a Molecular Möbius Band. *J. Am. Chem. Soc.* 2010, 132:3140-3152.
16.   Herges R. Topology in Chemistry: Designing Möbius Molecules. *Chem. Rev.* 2006, 106:4820-4842.
17.   Williams RV. Homoaromaticity. *Chem. Rev.* 2001, 101:1185-1204.
18.   Pozharskii AF. Heteroaromaticity *Chem. Heterocycl. Compd.* 1985, 21:717-749.
19.   Balaban AT, Klein DJ. Claromatic Carbon Nanostructures. *J. Phys. Chem. C* 2009, 113:19123-19133.
20.   Alexandrova AN, Boldyrev AI. σ-Aromaticity and σ-Antiaromaticity in Alkali Metal and Alkaline Earth Metal Small Clusters. *J. Phys. Chem. A* 2003, 107:554-560.
21.   Zhai H-J, Averkiev BB, Zubarev DY, Wang L-S, Boldyrev AI. δ Aromaticity in $[Ta_3O_3]^-$. *Angew. Chem. Int. Ed.* 2007, 46:4277-4280.
22.   Feixas F, Matito E, Duran M, Poater J, Solà M. Aromaticity and electronic delocalization in all-metal clusters with single, double, and triple aromatic character. *Theor. Chem. Acc.* 2011, 128:419-431.
23.   Kuznetsov AE, Birch KA, Boldyrev AI, Li X, Zhai H-J, Wang L-S. All-Metal Antiaromatic Molecule: Rectangular Al_4^{4-} in the $Li_3Al_4^-$ Anion. *Science* 2003, 300:622-625.
24.   Feixas F, Matito E, Poater J, Solà M. Metalloaromaticity. *WIREs Comput. Mol. Sci.* 2013, 3:105-122.
25.   Boldyrev AI, Wang L-S. All-metal aromaticity and antiaromaticity. *Chem. Rev.* 2005, 105:3716-3757.
26.   Fernández I, Frenking G, Merino G. Aromaticity of metallabenzenes and related compounds. *Chem. Soc. Rev.* 2015, 44:6452-6463.
27.   Mercero JM, Boldyrev AI, Merino G, Ugalde JM. Recent developments and future prospects of all-metal aromatic compounds. *Chem. Soc. Rev.* 2015, 44:6519-6534.

28. Baird NC. Quantum organic photochemistry. II. Resonance and aromaticity in the lowest $^3\pi\pi^*$ state of cyclic hydrocarbons. *J. Am. Chem. Soc.* 1972, 94:4941-4948.

29. Rosenberg M, Dahlstrand C, Kilså K, Ottosson H. Excited State Aromaticity and Antiaromaticity: Opportunities for Photophysical and Photochemical Rationalizations. *Chem. Rev.* 2014, 114:5379-5425.

30. Ottosson H. Organic photochemistry: Exciting excited-state aromaticity. *Nat. Chem.* 2012, 4:969-971.

31. Jorner K, Feixas F, Ayub R, Lindh R, Solà M, Ottosson H. Analysis of a Compound Class with Triplet States Stabilized by Potentially Baird Aromatic [10]Annulenyl Dicationic Rings. *Chem. Eur. J.* 2016, 22:2793-2800.

32. King RB. Three-Dimensional Aromaticity in Polyhedral Boranes and Related Molecules. *Chem. Rev.* 2001, 101:1119-1152.

33. Garcia-Borràs M, Osuna S, Luis JM, Swart M, Solà M. The role of aromaticity in determining the molecular structure and reactivity of (endohedral metallo)fullerenes. *Chem. Soc. Rev.* 2014, 43:5089-5105.

34. Chen ZF, King R. Spherical aromaticity: Recent work on fullerenes, polyhedral boranes, and related structures. *Chem. Rev.* 2005, 105:3613-3642.

35. Bühl M, Hirsch A. Spherical aromaticity of fullerenes. *Chem. Rev.* 2001, 101:1153-1183.

36. Pham HT, Duong LV, Nguyen MT. Electronic Structure and Chemical Bonding in the Double Ring Tubular Boron Clusters. *J. Phys. Chem. C* 2014, 118:24181-24187.

37. Duong LV, Pham HT, Tam NM, Nguyen MT. A particle on a hollow cylinder: the triple ring tubular cluster B_{27}^+. *Phys. Chem. Chem. Phys.* 2014, 16:19470-19478.

38. An W, Bulusu S, Gao Y, Zeng XC. Relative stability of planar versus double-ring tubular isomers of neutral and anionic boron cluster B_{20} and B_{20}^-. *J. Chem. Phys.* 2006, 124:154310.

39. Tai TB, Havenith RWA, Teunissen JL, Dok AR, Hallaert SD, Nguyen MT, Ceulemans A. Particle on a Boron Disk: Ring Currents and Disk Aromaticity in B_{20}^{2-}. *Inorg. Chem.* 2013, 52:10595-10600.

40. Cui P, Hu H-S, Zhao B, Miller JT, Cheng P, Li J. A multicentre-bonded $[Zn^I]_8$ cluster with cubic aromaticity. *Nature Commun.* 2015, 6:6331.

41. El Bakouri O, Duran M, Poater J, Feixas F, Solà M. Octahedral aromaticity in $^{2S+1}A_{1g}$ X_6^q clusters (X = Li–C and Be–Si, S = 0–3, and q = −2 to +4). *Phys. Chem. Chem. Phys.* 2016, 18:11700-11706.

42. Calvin M, Wilson KW. Stability of Chelate Compounds. *J. Am. Chem. Soc.* 1945, 67:2003-2007.

43. Palusiak M, Simon S, Solà M. Interplay between Intramolecular Resonance-Assisted Hydrogen Bonding and Aromaticity in o-Hydroxyaryl Aldehydes. *J. Org. Chem.* 2006, 71:5241-5248.

44. Shainyan BA, Fettke A, Kleinpeter E. Push–Pull vs Captodative Aromaticity. *J. Phys. Chem. A* 2008, 112:10895-10903.

45. Schleyer PvR, Wu JI, Cossio FP, Fernandez I. Aromaticity in transition structures. *Chem. Soc. Rev.* 2014, 43:4909-4921.

46. Kudavalli JS, Boyd DR, Coyne D, Keeffe JR, Lawlor DA, MacCormac AC, More O'Ferrall RA, Rao SN, Sharma ND. Hyperaromatic Stabilization of Arenium Ions. *Org. Lett.* 2010, 12:5550-5553.

47. Feixas F, Matito E, Poater J, Solà M. Rules of Aromaticity. In: Alikhani E, Chauvin R, Lepetit C, Silvi B, eds. *Applications of Topological Methods in Molecular Chemistry*. Vol. 22. Berlin: Springer; 2016, 321-336.

48. Kostenko A, Tumanskii B, Kobayashi Y, Nakamoto M, Sekiguchi A, Apeloig Y. Spectroscopic Observation of the Triplet Diradical State of a Cyclobutadiene. *Angew. Chem. Int. Ed.* 2017, 56:10183-10187.

49. Karadakov PB. Ground- and Excited-State Aromaticity and Antiaromaticity in Benzene and Cyclobutadiene. *J. Phys. Chem. A* 2008, 112:7303-7309.

50. Karadakov PB. Aromaticity and Antiaromaticity in low-lying electronic states of cyclooctatetraene. *J. Phys. Chem. A* 2008, 112:12707-12713.

51. Feixas F, Vandenbussche J, Bultinck P, Matito E, Solà M. Electron delocalization and aromaticity in low-lying excited states of archetypal organic compounds. *Phys. Chem. Chem. Phys.* 2011, 13:20690-20703.

52. Soncini A, Fowler PW. Ring-current aromaticity in open-shell systems. *Chem. Phys. Lett.* 2008, 450:431-436.

53. Rappaport SM, Rzepa HS. Intrinsically Chiral Aromaticity. Rules Incorporating Linking Number, Twist, and Writhe for Higher-Twist Möbius Annulenes. *J. Am. Chem. Soc.* 2008, 130:7613-7619.

54. Clar E. *The Aromatic Sextet*. New York: Wiley; 1972.

55. Solà M. Forty years of Clar's aromatic π-sextet rule. *Front. Chem.* 2013, 1:22.

56. Randić M, Balaban AT. Local aromaticity and aromatic sextet theory beyond Clar. *Int. J. Quantum Chem.* 2018, 118:e25657.

57. Cyrański MK, Stepién BT, Krygowski TM. Global and local aromaticity of linear and angular polyacenes. *Tetrahedron* 2000, 56:9663-9967.

58. Schulman JM, Disch RL. Aromatic Character of [n]Helicenes and [n]Phenacenes. *J. Phys. Chem. A* 1999, 103:6669-6672.

59. Portella G, Poater J, Bofill JM, Alemany P, Solà M. Local Aromaticity of [n]Acenes, [n]Phenacenes, and [n]Helicenes (n = 1 − 9). *J. Org. Chem.* 2005, 70:2509-2521.

60. Glidewell C, Lloyd D. MNDO study of bond orders in some conjugated bi- and tri-cyclic hydrocarbons. *Tetrahedron* 1984, 40:4455-4472.

61. El Bakouri O, Poater J, Feixas F, Solà M. Exploring the validity of the Glidewell–Lloyd extension of Clar's π-sextet rule: assessment from polycyclic conjugated hydrocarbons. *Theor. Chem. Acc.* 2016, 135:205.

62. Wade K. The Structural Significance of the Number of Skeletal Bonding Electron-Pairs in Carboranes, the Higher Boranes and Borane Anions, and Various Transition-Metal Carbonyl Cluster Compounds. *J. Chem. Soc. D: Chem. Commun.* 1971:792-793.

63. Mingos DMP. A General Theory for Cluster and Ring Compounds of the Main Group and Transition Elements. *Nature Phys. Sci.* 1972, 236:99-102.

64. Hirsch A, Chen Z, Jiao H. Spherical aromaticity in icosahedral fullerenes: The $2(N+1)^2$ rule. *Angew. Chem. Int. Ed.* 2000, 39:3915-3917.

65. Mandado M, Graña AM, Pérez-Juste I. Aromaticity in spin-polarized systems: Can rings be simultaneously alpha aromatic and beta antiaromatic? *J. Chem. Phys.* 2008, 129:164114.

66. Mandado M, González-Moa MJ, Mosquera RA. QTAIM n-center delocalization indices as descriptors of aromaticity in mono and poly heterocycles. *J. Comput. Chem.* 2007, 28:127-136.

67. Fallah-Bagher-Shaidaei H, Wannere CS, Corminboeuf C, Puchta R, Schleyer PvR. Which NICS Aromaticity Index for Planar Rings Is Best? *Org. Lett.* 2006, 8:863-866.

68. Kumar P. Continuous group and electron-count rules in aromaticity. *J. Chem. Sci.* 2018, 130:17.

69. Rubin MA, Ordóñez CR. Eigenvalues and degeneracies for n-dimensional tensor spherical harmonics. *J. Math. Phys.* 1984, 25:2888-2894.

70. Berger R. Personal communication. 2017.

71. Shainyan BA. Electron-counting rules, three-dimensional aromaticity, and the boundaries of the Periodic Table. *J. Phys. Org. Chem.* 2011, 24:619-620.

72. Greenwood NN. Ludwig Mond Lecture. Taking stock: the astonishing development of boron hydride cluster chemistry. *Chem. Soc. Rev.* 1992, 21:49-57.

73. Polak RJ, Obenland C. Pyrolysis of Diborane. Formation of Decaborane in Continuous Flow Reactor. *Ind. Eng. Chem. Prod. Res. Dev.* 1964, 3:234-238.

74. Pitt MP, Paskevicius M, Brown DH, Sheppard DA, Buckley CE. Thermal Stability of $Li_2B_{12}H_{12}$ and its Role in the Decomposition of $LiBH_4$. *J. Am. Chem. Soc.* 2013, 135:6930-6941.

75. Udovic TJ, Matsuo M, Unemoto A, Verdal N, Stavila V, Skripov AV, Rush JJ, Takamura H, Orimo S-i. Sodium superionic conduction in $Na_2B_{12}H_{12}$. *Chem. Commun.* 2014, 50:3750-3752.

76. Wade K. *Electron-deficient Compounds*. London: Nelson and Sons, Ltd.; 1971.

77. Mingos DMP. A General Theory for Cluster and Ring Compounds of the Main Group and Transition Elements. *Nature Phys. Sci.* 1972, 236:99-102.

78. Mingos DMP. Polyhedral skeletal electron pair approach. *Acc. Chem. Res.* 1984, 17:311-319.

79. Poater J, Solà M, Viñas C, Teixidor F. π Aromaticity and Three-Dimensional Aromaticity: Two sides of the Same Coin? *Angew. Chem. Int. Ed.* 2014, 53:12191-12195.

80. Poater J, Solà M, Viñas C, Teixidor F. Hückel's Rule of Aromaticity Categorizes Aromatic closo Boron Hydride Clusters. *Chem. Eur. J.* 2016, 22:7437-7443.

81. Poater J, Solà M, Viñas C, Teixidor F. A Simple Link between Hydrocarbon and Borohydride Chemistries. *Chem. Eur. J.* 2013, 19:4169-4175.

82. Li S-D, Zhai H-J, Wang L-S. $B_2(BO)_2^{2-}$ Diboronyl Diborene: A Linear Molecule with a Triple Boron–Boron Bond. *J. Am. Chem. Soc.* 2008, 130:2573-2579.

83. Shoji Y, Matsuo T, Hashizume D, Fueno H, Tanaka K, Tamao K. A Stable Doubly Hydrogen-Bridged Butterfly-Shaped Diborane(4) Compound. *J. Am. Chem. Soc.* 2010, 132:8258-8260.

84. Alexandrova AN, Birch KA, Boldyrev AI. Flattening the $B_6H_6^{2-}$ Octahedron. Ab Initio Prediction of a New Family of Planar All-Boron Aromatic Molecules. *J. Am. Chem. Soc.* 2003, 125:10786-10787.

85. Klanberg F, Eaton DR, Guggenberger LJ, Muetterties EL. Chemistry of boranes. XXVIII. New polyhedral borane anions, $B_8H_8^{2-}$, $B_8H_8^{.-}$, and $B_7H_7^{2-}$. *Inorg. Chem.* 1967, 6:1271-1281.

86. Aihara J. Three-dimensional Aromaticity of Polyhedral Boranes. *J. Am. Chem. Soc.* 1978, 100:3339-3342.

87. Streifel BC, Zafra JL, Espejo GL, Gómez-García CJ, Casado J, Tovar JD. An Unusually Small Singlet–Triplet Gap in a Quinoidal 1,6-Methano[10]annulene Resulting from Baird's 4n π-Electron Triplet Stabilization. *Angew. Chem. Int. Ed.* 2015, 54:5888-5893.

88. Streifel BC, Zafra JL, Espejo GL, Gómez-García CJ, Casado J, Tovar JD. Corrigendum: An Unusually Small Singlet–Triplet Gap in a Quinoidal 1,6-Methano[10]annulene Resulting from Baird's 4n π-Electron Triplet Stabilization. *Angew. Chem. Int. Ed.* 2016, 55:9122-9122.

89. Feixas F, Matito E, Poater J, Solà M. Metalloaromaticity. *WIREs Comput. Mol. Sci.* 2013, 3:105-122.

90. Wang B, Zhai H-J, Huang X, Wang L-S. On the Electronic Structure and Chemical Bonding in the Tantalum Trimer Cluster. *J. Phys. Chem. A* 2008, 112:10962-10967.

91. Feixas F, Matito E, Duran M, Poater J, Solà M. Aromaticity and electronic delocalization in all-metal clusters with single, double, and triple aromatic character. *Theor. Chem. Acc.* 2011, 128:419-431.

92. Ayub R, Bakouri OE, Jorner K, Solà M, Ottosson H. Can Baird's and Clar's Rules Combined Explain Triplet State Energies of Polycyclic Conjugated Hydrocarbons with Fused 4nπ- and (4n + 2)π-Rings? *J. Org. Chem.* 2017, 82:6327-6340.

93. Feixas F, Matito E, Poater J, Solà M. Quantifying aromaticity with electron delocalisation measures. *Chem. Soc. Rev.* 2015, 44:6434-6451.

94. Poater J, Solà M. Open-shell spherical aromaticity: the $2N^2+2N+1$ (with S = N+1/2) rule. *Chem. Commun.* 2011, 47:11647-11649.

95. Platt JR. The Box Model and Electron Densities in Conjugated Systems. *J. Chem. Phys.* 1954, 22:1448-1455.

96.	Heilbronner E. Hückel Molecular Orbitals of Möbius-Type Conformation of Annulenes. *Tetrahedron Lett.* 1964, 5:1923-1928.

97.	Ajami D, Oeckler O, Simon A, Herges R. Synthesis of a Möbius aromatic hydrocarbon. *Nature* 2003, 426:819-821.

98.	Breslow R. Antiaromaticity. *Chem. Eng. News* 1965, 43:90-100.

99.	Ovchinnikov AA. Multiplicity of the ground state of large alternant organic molecules with conjugated bonds. *Theor. Chim. Acta* 1978, 47:297-304.

100.	Jemmis ED, Balakrishnarajan MM, Pancharatna PD. Electronic Requirements for Macropolyhedral Boranes. *Chem. Rev.* 2002, 102:93-144.

101.	Ruiz-Morales Y. The Agreement between Clar Structures and Nucleus-Independent Chemical Shift Values in Pericondensed Benzenoid Polycyclic Aromatic Hydrocarbons: An Application of the Y-Rule. *J. Phys. Chem. A* 2004, 108:10873-10896.

Further Reading

1.	Aromaticity. *Chem. Rev.* 2001, 101, Issue 5.

2.	Papers presented at the ESF Exploratory Workshop: New Perspectives on Aromaticity, Exeter, UK, 2003. *Phys. Chem. Chem. Phys.* 2004, 6, Issue 2, pp. 217-339.

3.	Delocalization-pi and sigma. *Chem. Rev.* 2005, 105, Issue 10.

4.	Structural Effects of Aromaticity and π-Electron Delocalization. *Struct. Chem.* 2007, 18, Issue 6.

5.	Aromaticity and Molecular Symmetry. *Symmetry* 2010, 2, Issues 1 to 4.

6.	Aromaticity and Metal Clusters, Chattaraj PK, ed. Taylor & Francis/CRC Press, Boca Raton, 2011.

7.	Aromaticity, electron delocalization and related molecular properties. *Phys. Chem. Chem. Phys.* 2011, 13, Issue 46.

8.	R. Gleiter and G. Haberhauer, Aromaticity and Other Conjugation Effects, Wiley-VCH, Weinheim, 2012.

9.	Challenges in Aromaticity: 150 Years after Kekulé's Benzene. *Chem. Soc. Rev.* 2015, 17, Issue 18.

10.	Celebrating the 150th anniversary of the Kekulé benzene structure. *Phys. Chem. Chem. Phys.* 2016, 18, Issue 17.