

Aromaticity rules

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Standfirst: In 1931, Erich Hückel published a landmark paper and the seed of the now-famous $4n+2$ rule for aromaticity in annulenes that bears his name. Electron counting has since been extended to other classes of compounds, resulting in a multitude of rules aiming to capture the concept of aromaticity — and its impact in chemistry.

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Aromaticity plays an important role in chemistry, despite the fact that it is a concept with a somewhat imprecise definition^{1,2,3}. It is commonly accepted that aromatic compounds are particularly stable and unreactive, whereas anti-aromatic compounds are known to be unstable and reactive. The presence of (anti)aromatic reactants, intermediates, transition states or products therefore has a great influence on reaction mechanisms⁴.

In his initial investigations into the particular stability of conjugated molecules, Hückel explained it through his molecular orbital (MO) theory. He showed that a specific number of π -electrons endowed benzene and related compounds with a closed-shell electronic structure that increased their stability⁵. This work led Doering and Detert, in 1951, to establish the first rule of aromaticity — the now-famous $4n+2$ π -electron rule, widely known as ‘Hückel’s rule’, which states that annulenes with $4n+2$ π -electrons are aromatic — based on their application of Hückel’s MO theory to monocyclic π -conjugated molecules and, in particular, to the cycloheptatrienylium ion⁶.

Since then, a variety of rules have been proposed to determine if a molecule is aromatic. These allow chemists to better understand molecules and their behaviour, as well as identify the formation or elimination of (anti)aromatic species in a reaction, which helps understand and predict possible outcomes. This article will first briefly discuss the most widespread rules associated with different types of aromaticity, then draw attention to their limitations, and finally propose future directions for the development of this fascinating topic.

1.- Most common forms of aromaticity

The Hückel rule

Most of the typical aromatic compounds have high symmetry and degenerate MOs with either a closed-shell structure or a last shell half-filled with same-spin electrons. Either of these two electronic distributions provide an extra stability that is the basis of aromaticity. In the case of monocyclic molecules with the maximum number of conjugated bonds (annulenes, C_nH_n) with D_{Nh} symmetry, the most stable MO has all $2p_z$ -atomic orbitals with in-phase overlap (Figure 1a,i; $2p_z$ -atomic orbitals are shown for benzene). The rest of the MOs are doubly degenerated, except for the highest-energy one for annulenes with even n values (see the MO diagram for benzene in Figure 1a,i). With this MO distribution, closed-shell electronic structures are obtained with 2, 6, 10, 14... π -electrons — that is, with $4n+2$ π -electrons ($n = 1, 2, 3 \dots$), as per the Hückel rule⁵. The synthesis of the cycloheptatrienyl cation ($C_7H_7^+$) in 1954 by Doering and Knox⁷ — which indeed showed a large “amount of resonance stabilization” — represented one of the first successful experimental confirmations of this rule. Cyclic D_{Nh} annulenes with $4n$ π -electrons are antiaromatic⁸.

Open-shell aromaticity

Notably, these $4n+2$ or $4n$ π -electron counting rules for aromatic or antiaromatic annulenes, respectively, were found to depend on the spin-state of the molecules as well as their molecular topology. For example, 50 years ago, Colin Baird showed^{9, 10} that when cyclic D_{Nh} annulenes are in their lowest-lying triplet excited state (T_1), it is those with $4n$ π -electrons (leading to a last shell half-filled with same spin electrons) that have an aromatic character, whereas those with $4n+2$ π -electrons possess an antiaromatic character (as an example, see Figure 1b for the π -orbital occupation in cyclooctatetraene

in its lowest triplet excited state, showing Baird aromaticity). The validity of the ‘Baird rule’ was confirmed by analysis of the planar triplet ground states of some cyclopentadienyl cations¹¹. Recent spectroscopic observation of the triplet diradical state of cyclobutadiene¹² and isolation of a triplet benzene dianion¹³ have also provided additional support for this rule.

In 2008, Soncini and Fowler¹⁴ further extended both rules to high spin states by stating that annulenes of $4n+2$ π -electrons at the lowest-lying electronic states with even spin (singlet, quintet, ...) and those of $4n$ π -electrons at the lowest-lying states with odd spin (triplet, septet, ...) are aromatic. Interestingly, by considering the α ($S = 1/2$) and β ($S = -1/2$) electrons separately, Mandado et al.¹⁵ showed that the Hückel and Baird rules as well as the Soncini-Fowler extension can be fused into a single rule asserting that annulenes with an odd number ($2n+1$) of α and of β electrons are aromatic, while those with an even number ($2n$) of α and of β electrons are antiaromatic. For instance, Figure 1b shows the electronic configuration of π -electrons in the aromatic triplet state of cyclooctatetraene. As can be seen the number of α electrons (five arrows in red) and the number of β electrons (three arrows in blue) are odd numbers. In the case of an annulene with an even number of α electrons and an odd number of β electrons (or the other way round), electron counting does not offer any clue about its global aromatic character.

Molecular topology

Another fascinating phenomenon is Möbius aromaticity, which is found in cyclic conjugated species that have a molecular topology resembling that of a Möbius strip. Möbius aromaticity was first described theoretically by Craig and Paddock¹⁶ for

organometallic systems in 1958 and six years later was further elaborated by Heilbronner for annulenes¹⁷. MOs in Möbius aromatic species have an odd number of out-of-phase overlaps (see Figure 1a,ii). In monocyclic Möbius aromatic species, the closed-shell aromatic electronic configuration is reached with $4n$ π -electrons.

Experimentally, this type of aromaticity was first reported in 2003 by Ajami, Herges et al.¹⁸ with the synthesis of the first stable Möbius aromatic molecule. Four years later, Stępień et al.¹⁹ synthesized the first dynamic Hückel–Möbius system (Figure 1c). The Möbius conformer has a figure-eight structure with a single twist. In metalla-aromatic annulenes, one can have Möbius aromaticity without the need to incorporate a twist in the molecular structure (the so-called Craig–Möbius aromaticity²⁰, Figure 1a,iii).

Ottosson et al.²¹ proposed the ‘aromaticity cube’ shown in Figure 1d to condense the several combinations of (anti)aromaticity in annulenes depending on the number of π -electrons ($4n$ vs. $4n+2$), topology (Hückel vs. Möbius), and electronic-state (S_0 vs. T_1/S_1). Finally, a generalization of the Hückel and Möbius rules can be achieved through the linking number (L_k) that represents the number of times that an annulene winds (taking into account both writhes and twists)²². As an example, two strips $L_k = 1$ and two with $L_k = 3$ (which feature distinct strip winds) are illustrated in Figure 1e. Cyclic conjugated annulenes that have an even L_k follow Hückel’s rule of aromaticity, whereas those having an odd L_k obey Möbius’ rule.

Metalla-aromaticity

The $4n+2/4n$ rules of aromaticity, originally applied to organic compounds, have been extended in the past decades to organometallic, all-metal, and semimetal species. In

these systems, aromaticity is much more complex than in organic molecules because they possess not only π -electron delocalization, but also σ -, δ - or even ϕ -electron delocalization. In addition, they can combine different types of aromaticity at the same time, thus giving rise to double or triple aromaticity, which is referred to as ‘multifold aromaticity’²³. For instance, the Al_4^{4-} ring in the triplet state of $Li_3Al_4^-$ cluster is π -Baird aromatic with 4π -electrons as well as σ_r radial and σ_t tangential Hückel aromatic with two electrons in each of its σ_r and σ_t orbitals²⁴ (see Figure 1f for the molecular structure and electronic configuration of Al_4^{4-}). Similarly B_{19}^- , with its 12 π -electrons, is aromatic in two independent π -systems of 2 and 10 π -electrons²⁵.

Polycyclic aromatic hydrocarbons

The Hückel rule holds strictly only for monocyclic π -conjugated systems in their ground states such as benzene and cyclooctatetraene. It was noticed early on that their polycyclic counterparts (polycyclic aromatic hydrocarbons, PAHs) do not obey this rule. Pyrene, for example, is aromatic despite its 16 π -electrons (Figure 2a). A first attempt to extend the Hückel rule from monocyclic annulenes to PAHs was Platt’s ring perimeter model²⁶, which divided PAHs into two parts: a perimeter and an inner core. The aromatic character of the PAH was considered to be that of the annulene of the perimeter (14 π -electrons in pyrene). This simple adaptation of Hückel’s rule, however, fails to account for the aromaticity of many non-benzenoid polycyclic conjugated hydrocarbons (PCHs), for instance that of bicyclodeca[6.2.0]pentaene (Figure 2b).

The π -sextet rule, proposed in 1972 by Clar^{27, 28} to describe aromaticity in benzenoids (PAHs containing only six-membered rings), proved to be a more versatile model. In this model, aromaticity is regarded as a local property of six-membered rings. An

aromatic π -sextet is defined as a single benzene-like ring, with six localised π -electrons separated from adjacent rings by formal C–C single bonds. For instance, the resonance structure (i) of phenanthrene (in red) in Figure 2c has one more π -sextet than (ii) (in blue), which according to the Clar model means that it represents a more realistic description of the molecular structure and aromaticity of phenanthrene.

An alternative to the Clar rule is the Fries rule²⁹ that is mostly used to determine the dominant Kekulé structure, which is the one possessing the maximum number of Fries sextets (rings that contain formally six π -electrons). The main difference between the Clar and Fries sextets is that the π -electron pair from a C=C double bond shared by two adjacent rings can be assigned to both rings.

In 1984, Glidewell and Lloyd³⁰ extended the Clar rule to PCHs by stating that the total population of π -electrons in conjugated polycyclic systems tends to form the smallest $4n+2$ groups and avoid the formation of the smallest $4n$ groups. Application of the Glidewell-Lloyd rule to bicyclodeca[6.2.0]pentaene (Figure 2b) for example leads to the conclusion that the resonance structure (i) in red (one small “ $4n+2$ ” 2π -electron ring and one large “ $4n$ ” 8π -electron ring) is more relevant than that in (ii) blue (one small “ $4n$ ” 4π -electron ring and one large “ $4n+2$ ” 6π -electron ring) to explain the electronic and molecular structure of this species — something that could not be predicted using Clar’s rule. Interestingly, Baird’s and Clar’s rules can be combined to explain the triplet state energies of PCHs with fused $4n\pi$ - and $(4n+2)\pi$ -electron rings³¹. For instance, the singlet–triplet energy gap is reduced by 1.7 eV when going from the linear dibenzo[b,h]biphenylene to the kinked dibenzo[a,i]biphenylene (Figure 2d). This reduction can be explained by the presence of an additional triplet biradical Baird-

aromatic π -quartet (at the central 4-membered ring) in the kinked isomer compared to the linear isomer (in addition to the two Hückel-aromatic π -sextets, shown in red), stabilizing the kinked isomer.

Aromaticity in three-dimensions

The determination in 1959 of the structure of $B_{10}H_{10}^{2-}$ ion by Lipscomb³² and the synthesis in 1962 of the first derivatives of *closo*-dodecaborate (see Figure 2e, left) and *closo*-decaborate by Muetterties's group³³ introduced the concept of aromaticity in three dimensions (3D). *Closo* boranes, $[B_nH_n]^{2-}$, are 3D aromatic clusters that have a structure of polyhedron with triangular faces (Figure 2e, left, depicts $[B_{12}H_{12}]^{2-}$). Electron-counting rules to rationalize the molecular structure and electronic configuration of such borane and carborane clusters were established, notably the Wade $2N+2$ and Mingos $4N+2$ electron rules^{34, 35}, where N is the number of vertices of the polyhedron. Since Wade's rule refers to the skeletal electrons (all valence electrons except for those of the B–H bonds), whereas Mingos' also incorporates the *exo* electrons of the B–H bonds, the two rules are actually equivalent. For instance $[B_6H_6]^{2-}$, with its 26 valence electrons, obeys the Mingos rule ($N = 6$) but with 14 skeletal electrons (26 valence electrons – 12 involved in the 6 B–H bonds) it also follows the Wade rule ($N = 6$).

The Wade–Mingos rule is not applicable to condensed polyhedral boranes, i.e., borane clusters made by the fusion of more than a single borane cluster (see Figure 2e, right, for an example of $[B_{12}H_{10}]^{2-}$, a borane made from the fusion of two $[B_7H_7]^{2-}$ clusters). To determine the aromaticity of fused boranes (or condensed polyhedral boranes), Jemmis et al.³⁶ proposed an extension in the form of the *mno* rule. It states that the number of skeletal electron pairs required for a condensed polyhedral borane to be

aromatic is given by $m+n+o$ (here m = number of sub-clusters, n = number of vertices, o = number of single-vertex shared condensations in the polyhedral borane). Interestingly, although the Wade-Mingos rule is followed by Zintl ions such as $[\text{Sn}_{12}]^{2-}$ ^{37, 38}, it does not apply to 3D spherical aromatic compounds such as some charged fullerenes. For these systems, the Hirsch $2(N+1)^2$ rule of aromaticity³⁹ has been developed. It is based on the fact that the π -electron system of a roughly spherical species can be, in a first approximation, considered as an uniform electron gas surrounding the surface of a sphere. This leads to an MO distribution such as that shown in Figure 2f. For these systems, closed-shell configurations are thus reached for 2, 8, 18, 32, 50, 72... electrons. According to the Hirsch rule, icosahedral C_{20}^{2+} , C_{60}^{10+} or C_{70}^{2-} are aromatic fullerenes³⁹. 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 doubly filled should be aromatic. This open-shell spherical aromaticity⁴⁰ is reached when the spherical compounds have $2N^2+2N+1$ electrons and with a spin $S = N+1/2$, as is the case for C_{60}^{-1} with $S = 11/2$.

In a similar fashion, the observed experimental abundances found in experimental mass spectra of alkali, alkaline earth metals, and gold clusters of 2, 8, 18, 20, 34, 40... atoms were successfully explained with the spherical jellium model⁴¹. In this quantum mechanical model, the positive charges of the nuclei and the electron density are assumed to be uniformly distributed in a sphere. The energy levels of valence electrons for such a model are $1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2 1\text{F}^{14} 2\text{P}^6 1\text{G}^{18} 2\text{D}^{10} \dots$ and, therefore, with 2, 8, 18, 20, 34, 40... electrons one gets a closed-shell electronic structure (see Figure 2g), and, consequently, can be considered jellium aromatic. This led to the formulation of

an open-shell jellium aromaticity rule⁴². It is worth noting that both the Wade-Mingos and the jellium rules refer to the *inner* aromaticity of skeletal valence electrons of the cage, whereas the Hirsch rule describes the *outer* aromaticity of the π -electrons delocalized on the surface of the spherical species.

In some large cylindrical molecules such as nanotubes, cycloparaphenylenes, or certain boron and boron nitride clusters, among others, the aromaticity can be described by the hollow cylinder model (HCM)⁴³. Solution of the Schrödinger equation for a particle in this HCM gives MOs that can be separated into radial (located in the different layers of the cylinder and perpendicular to the cylinder axis) and tangential (located in the outer part of the cylinder and parallel to the cylinder axis, see Figure 3). This distribution gives rise to the $4n+2m$ rule of radial and tangential aromaticity, n and m being the number of degenerated and non-degenerated MOs, respectively. Finally, certain orbital occupations have been associated with disk⁴⁴, cubic⁴⁵ or tetrahedral⁴⁶ aromaticities.

2.- Limitations of the rules

To quote Prof. Frenking at the 11th Congress on Electronic Structure: Principles and Applications held in Toledo, referring to the 18-electron rule: “Rules are rules but no laws. They can be broken”. Indeed, although aromaticity rules are in many cases used as a ‘back-of-an-envelope’ tool for the rationalization of the physicochemical properties of many compounds, their scope is limited. A discussion of a few specific limitations of these rules can serve to highlight this.

1. The electron counting rules are useful to identify (anti)aromatic compounds but they cannot provide a quantitative measure of (anti)aromaticity.
2. Aromatic rings exist that cannot be classified as either Hückel or Baird because they are a combination of both. This is the case of TMTQ (see Figure 4a), a molecule featuring a 1,6-dimethylenemethano[10]annulene (M10A) ring exo-substituted with two 5-dicyanomethyl-thiophene moieties at the peripheries. In its singlet ground state (S_0), TMTQ has a quinoidal structure (see Figure 4a, left) and exhibits a small singlet-triplet energy gap (ΔE_{ST}) of only 4.9 kcal/mol. The high stability of the T_1 state of TMTQ can be explained either through the Baird-aromaticity of the central ring, with its 8π -electron 1,6-methano[10]annulenyl dication moiety ($M10A^{2+}$, see Figure 4a, right, ionic structure) or through the Hückel-aromaticity of a closed-shell 10π -electron Hückel-aromatic ring and two terminal dicyanomethyl radicals (see Figure 4a, center, diradical structure). Calculations suggest that the M10A ring in the T_1 (and S_1) state of TMTQ is about 85% Hückel and 15% Baird⁴⁷.

3. A similar situation is found in some metallacycles that cannot be classified exclusively as Hückel or Craig-Möbius (see Figure 4b, which represents any metallabenzene, for example $\text{Ir}^{\text{I}}(\text{C}_5\text{H}_5)(\text{PPh}_3)_2$) because they have a hybrid Hückel-Möbius character⁴⁸, with different contributions of both Hückel and Craig-Möbius aromaticities.

4. Moreover, especially in metallacycles, electron counting is often not straightforward. For example, the six-membered ring of metallabenzenes (for instance that of $(\text{PPh}_3)_2\text{Os}(\text{C}_5\text{H}_5)(\text{CO})_2^+$) has been considered Hückel aromatic with 6π - or 10π -electrons or Möbius aromatic with 8π -electrons⁴⁹. The different electron counting is due to disputable participation of the metal *d* orbitals in π -bonding.

5. The (anti)aromatic character of annulenes has also been shown to fade away quite rapidly as their ring size increases⁵⁰. Annulenes with large rings have negligible aromatic stabilization energies irrespective if they follow the Hückel rule or not^{51, 52, 53}.

6. $\text{C}_{80}\text{H}_{30}$ is a nonplanar nanographene that contains five- and seven-membered rings. For this species, the presence of a π -aromatic circuit (a circuit with a high electron delocalization) that has formally 75 π -electrons has been reported⁵⁴, which does not follow any of the known rules of aromaticity. It is likely that this situation is not unique and can be present in other nanographene flakes.

3.- Future directions

Since Hückel's rule was first proposed, new rules of aromaticity and new connections between these rules have continuously been established in an attempt to capture the concept of aromaticity and explain and quantify its impact on the reactivity of chemical

compounds. The identification of nanographene flakes or non-alternant PAHs with new molecular motifs possessing useful properties — such as tuned ΔE_{ST} for organic optoelectronics applications (for example as materials for singlet fission, thermally activated delayed fluorescence or for triplet–triplet annihilation) — or strong non-covalent complexation in supramolecular chemistry is a growing area of molecular design.

As previously stated, applying Hückel's rule to PAHs was initially not straightforward and necessitated the development of the Clar π -sextet model. Similarly, applying Clar's rule to nanographenes with rings of different sizes is challenging and will require further research. The rules that govern the local and global aromaticity in nanographene flakes or non-alternant PAHs are not completely understood and this will be for sure a highly active area of experimental (with AFM and STM images) and theoretical of research in the future. These developments are necessary because some of these nanographene flakes are of low stability and as such are difficult to synthesize and not useful in practical applications. Nanographenes with increased stabilities could be prepared if we knew how to increase their aromaticity.

In a similar manner, the Hückel and Baird rules of (anti)aromaticity did not hold in large annulenes. Preliminary results seem to point out that the Soncini and Fowler generalization of the Hückel-Baird rules to high spin states may also not be followed when the states considered have spins larger than 2 or 3⁵⁵. The generalization of the Hückel and Möbius rules with L_k is likely to fail for large L_k because annulenes after several writhes and twists may lose electron delocalization capability due to the reduction of efficient $2p_z$ overlap. Similarly, Hirsch's rule seems applicable only to species with 50

π -electrons or fewer⁵⁶. These results highlight again the limits of the electron-counting rules and the need to clearly establish them.

Perhaps more important than drawing up different rules for different situations or classes of compounds is the idea to generalize the existing rules and connect them to each other, through different formulas and procedures⁵⁷. This has long been a concern in aromaticity research. Examples of this are Mandado's rule, which unifies the Hückel, Baird, and Soncini-Fowler rules, or the Ottosson cube that connects the Hückel, Baird, and Möbius rules and their extensions (Soncini-Fowler and linking number rules). Similarly, the Hückel and Hirsch rules can be connected by the solution of the Schrödinger equation for a particle in an n -dimensional sphere (for $n = 2$ and 3 , respectively)⁵⁸, and the $(4n+2)$ Hückel and Wade-Mingos rules by the so-called electronic confined space analogy⁵⁹. In this analogy, any classical 2-dimensional annulene such as cyclopentadienyl anion (Figure 4c) can be transformed into a *closo* borane cluster by electron transmutation (eT , change of C by isoelectronic B⁻), adding a BH⁴⁺ sacrificial agent (sA), and allowing structural relaxation (sR). In the whole process, the total number of valence electrons remains constant (TNVE = 26)⁵⁹, which highlights the equivalence between the π and 3D aromaticities of these systems.

All these connections represent steps forward on the road to a unified theory of aromaticity, which in turn would help better capture this key concept in chemistry and its implication on molecules' reactivity.

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FIGURE CAPTIONS

Figure 1. Aromaticity rules for annulenes. a) Orbital distribution in Hückel and Möbius topologies. (i) $2p_z$ -atomic orbitals of benzene with in-phase overlap; bottom: MO diagram. (ii,iii) MOs in Möbius aromatic species, either an organic system featuring a twist (ii) or a metalla-aromatic annulene, which can have a metal ion as phase inversion centre (iii). Bottom: MO diagram. b) Molecular orbital π -electron distribution in cyclooctatetraene. c) Molecular structure of di-*p*-benzihexaphyrin, bold lines indicate the 28 π -electron conjugation pathway. Hückel (left) and Möbius (right) conformations; d) Ottosson's cube to determine aromaticity depending on the characteristics of a system: $4n$ vs. $4n+2$ electrons, S_0 vs T_1/S_1 electronic states and Hückel vs. Möbius topology. e) Examples of strips with linking numbers L_k equal to 1 (1 twist (i) or 1 writhe (ii)) or 3 (3 twists (iii) or 2 twists, 1 writhe (iv)). f) Molecular structure and electronic configuration of Li_3Al_4^- in its triplet state.

Figure 2. Extension of aromaticity rules to polycyclic aromatic hydrocarbons and 3D systems. a) Platt's perimeter rule, illustrated here for pyrene, the perimeter of which is highlighted in red. b) Structure of bicyclodeca[6.2.0]pentaene, and illustration of the Glidewell-Lloyd rule. The resonance structure (i) in red (with a small " $4n+2$ " 2π -electron ring and a large " $4n$ " 8π -electron ring) is more relevant than the (ii) one in blue (with a small " $4n$ " 4π -electron ring and a large " $4n+2$ " 6π -electron ring) to understand this molecule; c) Illustration of Clar's π -sextet rule for phenanthrene. Here the resonance structure (i), shown in red, has 2 π -sextets whereas the structure (ii), shown in blue, has only 1, making (i) a more realistic description of the molecular structure and aromaticity of the system. d) The combination of Clar's and Baird's rules rationalizes the fact that the kinked structure of linear dibenzo-biphenylene is more stable than its linear counterpart by the presence of an additional triplet biradical Baird-aromatic π -quartet in the kinked system. e) The molecular structure of $[\text{B}_{12}\text{H}_{12}]^{2-}$ (left) and $[\text{B}_{12}\text{H}_{10}]^{2-}$ (right) f) MO diagram of C_{60}^{+10} . With its 50 π -electrons, it follows the Hirsch rule of spherical aromaticity; g) MO diagram of Na_{20} . With its 20 valence electrons, it is aromatic according to the jellium model.

Figure 3. Cylindrical aromaticity. The shape of some delocalized HOMOs of B_{27}^+ . The MOs comprise radial and tangential components. Reprinted with permission from ref. 43 with license CC BY-NC 3.0.

Figure 4. Combining or connecting rules. a) Combination of Hückel's and Baird's rules in TMTQ; b) Combination of Hückel and Craig-Möbius in metallacycles. The metal center with its ligands is placed in the vertex containing the d_{xz} and d_{yz} orbitals; c) Equivalence of Hückel's and Wade-Mingo's rules through the electronic confined space analogy⁵⁹. Here the cyclopentadienyl anion is converted into a *closo* hexaborane $[\text{B}_6\text{H}_6]^{2-}$ cluster by electron transmutation (eT , where C is replaced by isoelectronic B⁻), followed by the addition of a BH^{4+} sacrificial agent, and final relaxation of the structure into the $[\text{B}_6\text{H}_6]^{2-}$ octahedral cluster.

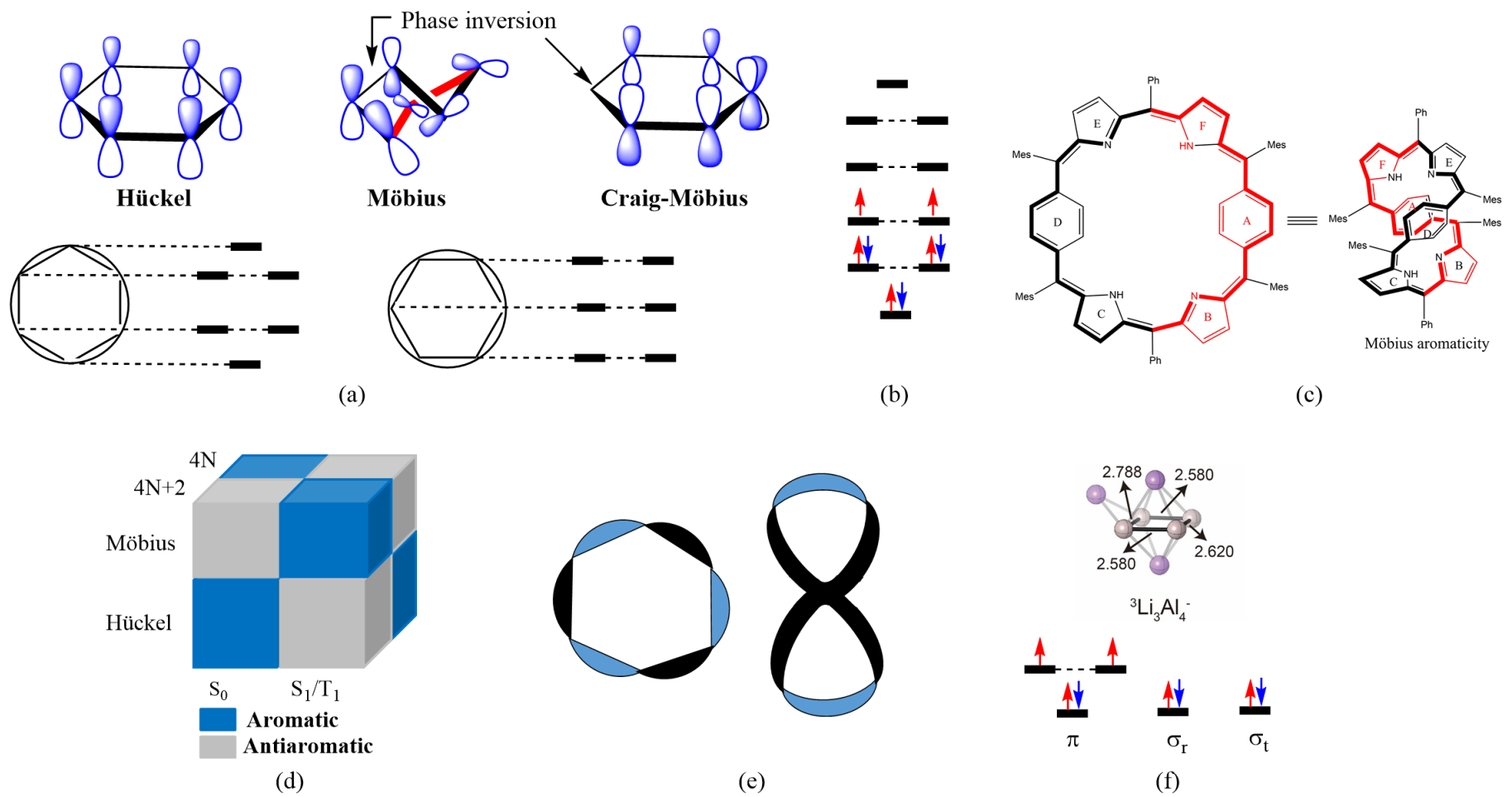


FIGURE 1

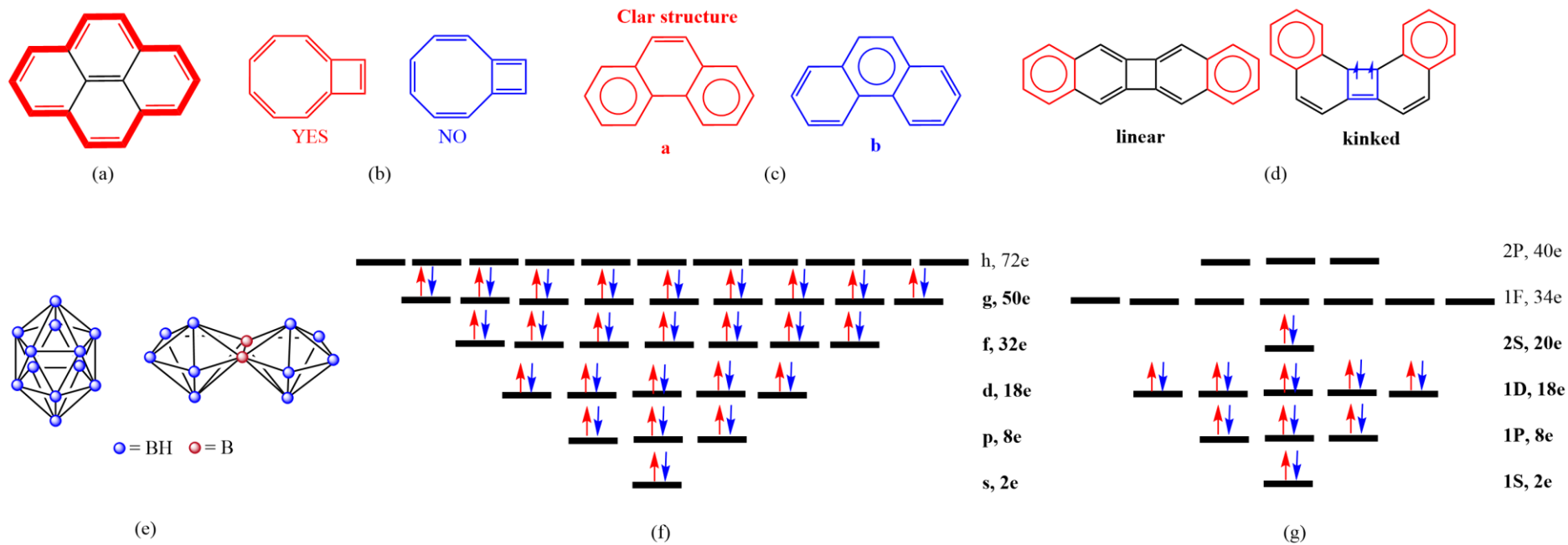


FIGURE 2

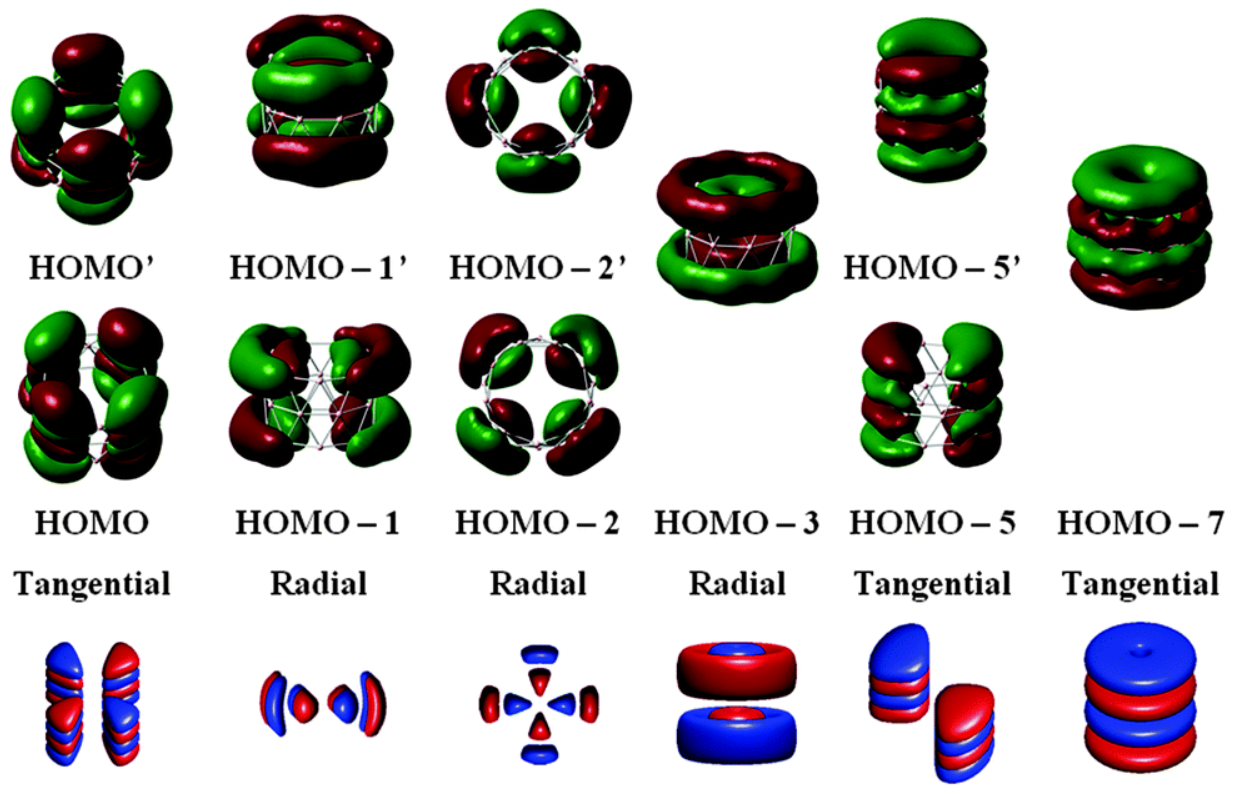


FIGURE 3

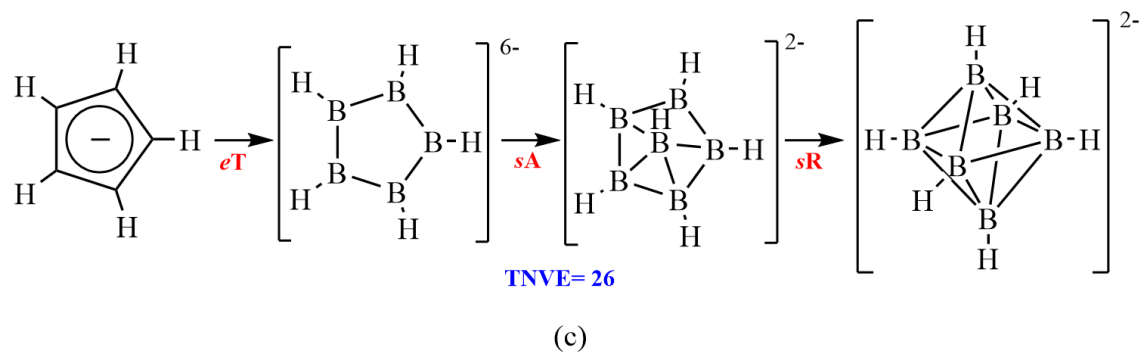
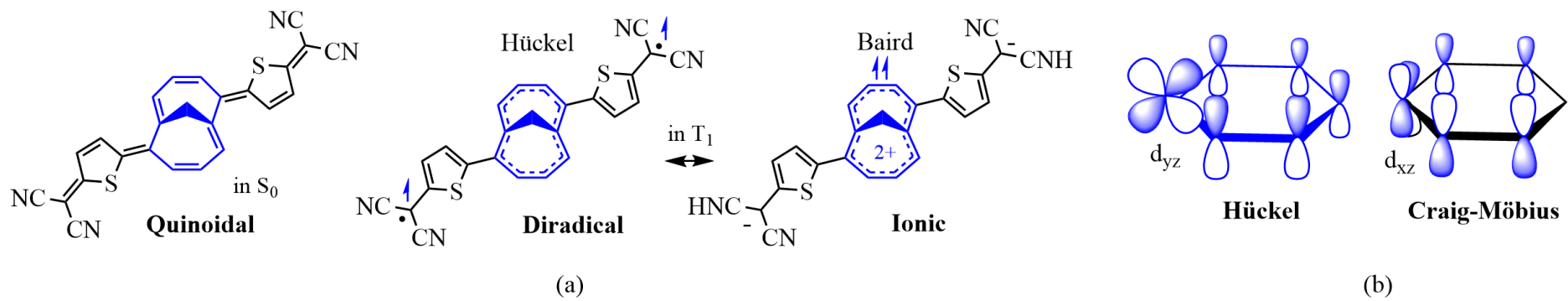


FIGURE 4