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Variation of aromaticity by twisting or expanding the ring content*

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Abstract: Generalization of the Hückel rule predicts that the (anti)aromaticity of a neutral ring is qualitatively reverted upon a single twist of the π-orbital array (Möbius interconversion), and is preserved upon expansion of all the bonds by single C_2 units (ring *carbo*-merization). These opposite effects are addressed from quantitative theoretical and experimental standpoints, respectively. (i) According to most resonance energy (RE) schemes, the RE value of a Möbius ring is *not* the opposite of that of the Hückel version. This also applies to the Aihara's and Trinajstic's topological resonance energy (TRE), where a non-aromatic reference in the topological limit is defined as being "as identical as possible" to the parent ring but just "acyclic". In spite of its conceptual merits, the computing complexity and fictitious character of the TRE acyclic reference resulted in a disuse of TRE as a current energetic aromaticity index. Both the calculation and interpretation of TRE have been revisited in light of a cross-reference between the Hückel and Möbius rings within the Hückel molecular orbital (HMO) framework. Whereas the topological influence of triple bonds is currently neglected in the first-level HMO treatment of π-conjugated systems, a graph-theoretical analysis allows one to differentiate the TRE value of a [3*n*]annulene from those of the corresponding *carbo*-[*n*]annulene. The C_{18} ring of *carbo*-benzene is thus predicted to be slightly more topologically aromatic than that of [18]annulene. (ii) Recent experimental and density functional theory (DFT) theoretical studies of quadrupolar *carbo*-benzene derivatives are presented. The results show that the "flexible aromaticity" of the *p*-$C_{18}Ph_4$ bridge between donor anisyl substituents plays a crucial role in determining the intriguing chemical/spectroscopical/optical properties of these *carbo*-chromophores.

Keywords: aromaticity; *carbo*-benzene; Möbius ring; topological resonance energy; triple bond.

INTRODUCTION

The lively concept of aromaticity of π-conjugated molecules [1] was historically propounded within the framework of the Hückel theory [2], and remains educationally grounded on the so-called "4*n*/4*n* + 2" Hückel rule [3] which predicts that a cyclically nontwisted π-conjugated molecule exhibits aromatic (resp. antiaromatic) physico-chemical properties if the corresponding number of π-electrons has the form 4*n* + 2 (resp. 4*n*) for some integer $n \geq 0$. As these aromatic properties (energetic, structural, mag-

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netic,…) are not uniquely determined [4], the rule remains qualitative in nature. Before addressing the problem of its quantitative transcription, it is noted that the rule is reversed by applying elementary molecular transformations altering not only the electronic configuration (one-electron spin inversion or two-electron ionization), but also the atomic configuration: one-bond 180°-twisting or one-bond C_2-expansion, corresponding to Möbius conversion [5] and local *carbo*-merization, respectively [6]. The quantitative variation of aromaticity upon both latter types of transformations is hereafter addressed from both the theoretical and experimental standpoints.

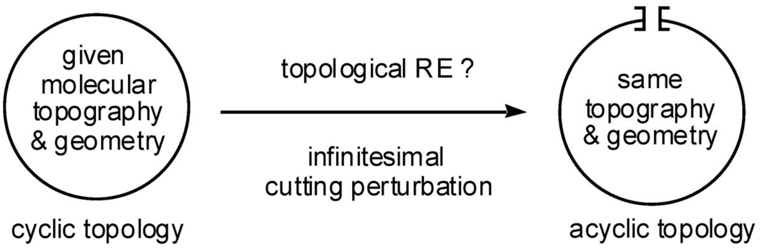
TWISTING THE RING CONTENT: THE MÖBIUS KEY TO AROMATICITY

After a critical survey of various energetic measures of aromaticity proposed in the literature [7], the relative aromaticity of Hückel and Möbius rings will be scrutinized. Their complementary roles for the quantification of topological aromaticity is then investigated not only for cyclenes, but also for conjugated alkynes and cyclynes, and in particular for ring *carbo*-mers.

Critical survey of HMO energetic aromaticity measures

The IUPAC-recommended definition of aromaticity is due to Minkin: “the concept of spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization which provide for their enhanced *thermodynamic stability* (*relative to acyclic structural analogues*) and tendency to retain the structural type in the course of chemical transformations” [4]. The italicized expressions indicate that aromaticity is an *energetic-topological* concept, where the reference *acyclic structural analog* is bound to be as identical as possible to the cyclic system, but just acyclic. Aromaticity can therefore be measured by the corresponding resonance energy (RE), i.e., the energy difference between the considered cyclic structure and its acyclic reference. This reference can be either a virtual valence bond (VB) structure, as in the Pauling–Wheland adiabatic resonance energy (ARE) and its recent developments at the ab initio level [8], or a chemical species. The two types of acyclic reference can also be combined as in Schleyer’s definition of extracyclic resonance energy (ECRE) [8]. Chemical acyclic references and their molecular orbital (MO) models are hereafter investigated. By virtue of its topological nature, particular attention is given to the Hückel MO (HMO) level of theory.

In the topological limit, however, the acyclic reference cannot be described by simple Lewis structures because the bonding topology is not chemically independent from the geometry (Scheme 1).



Scheme 1 Pictorial view of the energetic-topological aromaticity of a given cyclic molecular structure. TRE is the relevant RE at the topological limit [9,10].

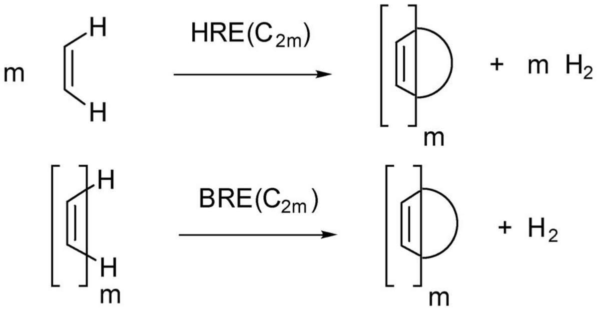
Although the topological limit is attained only formally in the definition of topological resonance energy (TRE, see below) [9,10], it can be chemically approached by molecular RE schemes. Relevant chemical REs must, however, thus be

i. considered as approximates of the absolute energy in the topological limit (not as simple scales);
ii. defined by unambiguous general processes for any molecular structure (for comparative purpose);
iii. evaluated for their specificity of reflecting pure cyclic effects (in particular, vanish for infinite ring sizes).

Many multicomponent acyclic references have been proposed [7]. When treated at the ab initio level, the corresponding REs are termed as aromatic stabilization energies (ASEs). In this case, the chemical species playing the role of the acyclic reference (in the topological sense) may, however, consist in cyclic molecules in order to maintain the same strain as in the cyclic molecule (e.g., in the equation: 3 cyclohexene → benzene + 2 cyclohexane) [11]. In the σ/π separation approximation however, only the σ-system of the reference is cyclically conjugated while the π-system is not. Focusing on π-aromaticity at the HMO level, the fundamental relevance of selected REs is hereafter inspected vs. the above requirements i–iii. These REs are based on various ring-cut processes which were devised from either empirical, perturbational, or topological considerations. They are classified accordingly. In the following, all energetic data are given in units of resonance integral of the "constant β" HMO model ($\beta < 0$), unless otherwise noted.

Empirical REs

Hückel resonance energy (HRE). The first intuitive idea for estimating the energetic aromaticity of a 2*m*-membered ring refers to its formation from *m* of its edges [1a,12]. The ring-cut process of HRE (or delocalization energy, DE) is thus an *m*-fold hydrogenolysis of *m* single bonds occuring in some Kekulé structure (Scheme 2). For benzene, $\mathrm{HRE}(C_6H_6) = 2$, which is very far from the exact topological limit $\mathrm{TRE}(C_6H_6) = 0.273$ (see Fig. 1 and below) [9,10].



Scheme 2 REs of [2*m*]annulenes based on C–C hydrogenolysis processes: HRE (*top*) and BRE (*bottom*).

Calculations also show that HRE of large [2*m*]annulenes tends to infinity as $2(4/\pi - 1)m$ (see Supplementary Information), and HRE is thus definitely not representative of the pure cyclic effects of requirement iii. Moreover, the HRE equation is not unique for dissymmetrically *exo*-conjugated rings where several nonequivalent Kekulé structures can be drawn, and thus does not satisfy requirement ii as well.

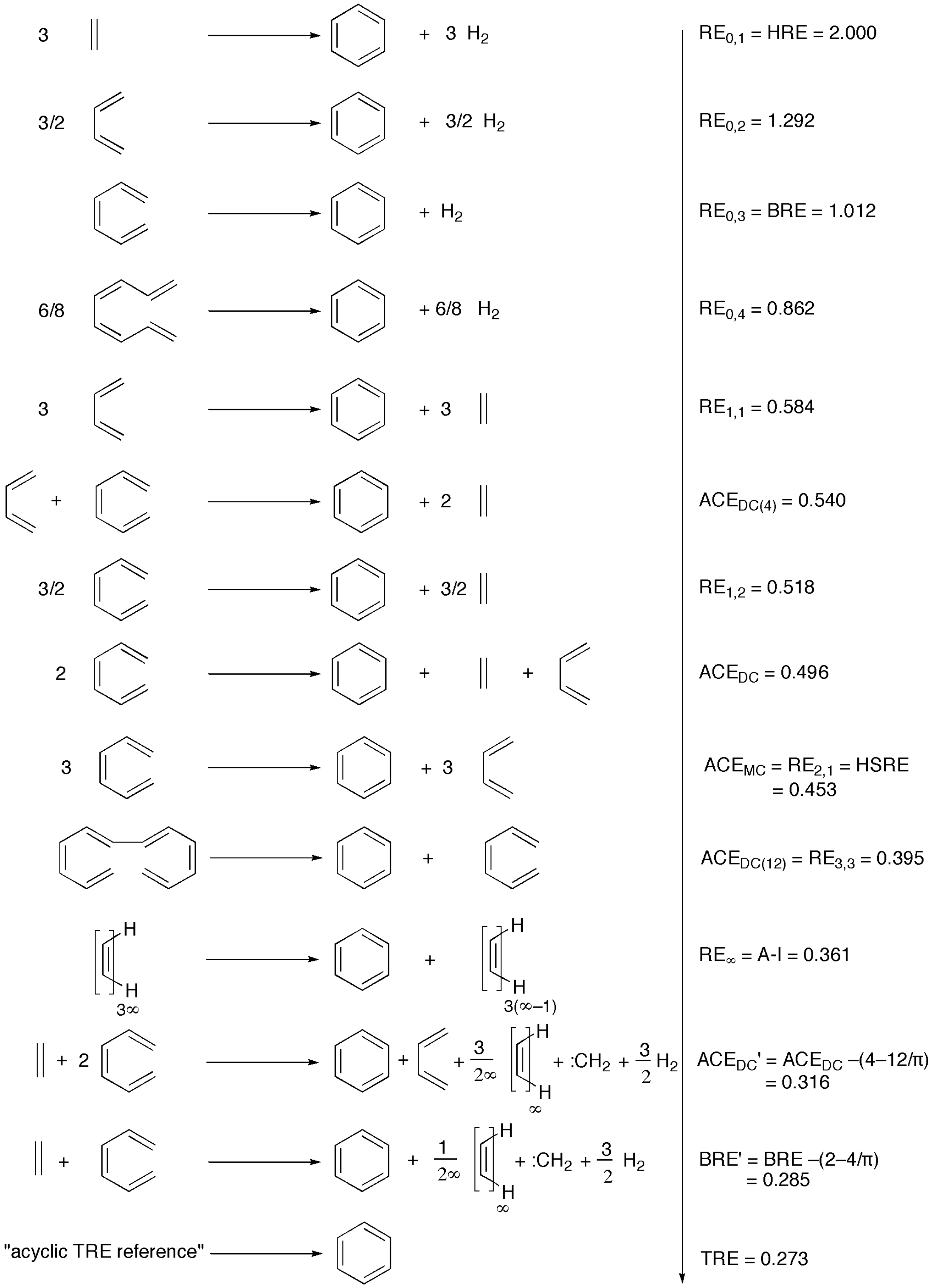


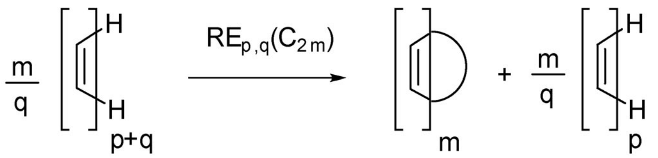
Fig. 1 Variation of the benzene REs as defined by empirical [$\mathrm{RE}_{p,q}(\mathrm{C}_6)$], perturbational (ACEs) or topological (TRE) considerations. The TRE value appears as the lower limit [9,10].

Breslow resonance energy (BRE) [13]. The ring-cut process of BRE is a simple hydrogenolysis of one endocyclic C–C bond (Scheme 2). For benzene BRE(C_6H_6) = 1.012 (Fig. 1), and calculations show that for large [2*m*]annulenes, BRE(C_{2m}) tends to a non-zero finite limit BRE_∞ (see Supplementary Information):

$$\mathrm{BRE}\left(C_{2m}\right)\xrightarrow[m\to\infty]{}\mathrm{BRE}_\infty=\left(2-\frac{4}{\pi}\right)\approx 0.727 \qquad (1)$$

Thus, the BRE definition does not satisfy requirement iii. The BRE_∞ limit can, however, be interpreted as the difference in bond energy between ethylene (2) and the infinite annulene (4/π), and the corrected quantity BRE'(C_{2m}) = BRE(C_{2m}) – BRE_∞ (tending to zero as $m \to \infty$) could be considered as a more relevant estimate of the energetic aromaticity, at least for large annulenes. Rather surprisingly, the BRE' definition provides also an excellent approximation of the topological aromaticity of small annulenes: in the case of benzene, for example, BRE'(C_6H_6) = 0.285 (Fig. 1), which happens to be very close (and slightly higher) than the exact topological limit TRE(C_6H_6) = 0.273 (see below) [9,10]. Nevertheless, the BRE and BRE' equations are not unique for dissymmetrically *exo*-conjugated rings, where the 2*m* bonds to be possibly cut are no longer equivalent, and thus do not satisfy requirement ii. To remedy this problem, the definition should be arbitrarily generalized to some average (e.g., an arithmetic mean, weighted or not) of the 2*m* particular equations. In spite of their simplicity, BRE and BRE' remain equivocal approximations of topological aromaticity in the general case.

Homodesmotic REs. In the isogyric HRE and BRE equations, the resemblance between the cyclic molecule and the acyclic reference is limited by the fact that they do not contain the same number of C–C bonds. This number can, however, be preserved by changing the H_2 reactant by H-donor alkenes. Many multicomponent schemes have thus been proposed on the examples of benzene or small annulenes [1a,7,12]. Their generic form for [2*m*]annulenes is shown in Scheme 3, where H-donor [*p*]alkenes couple to [*p* + *q*]polyenes, and where $p \geq 0$ and $q \geq 1$ are constant or vary as *m* (*p*, *q* = *am* + *b*, *a*, *b* constants).



Scheme 3 Generic form of chemical equations defining empirical resonance energies.

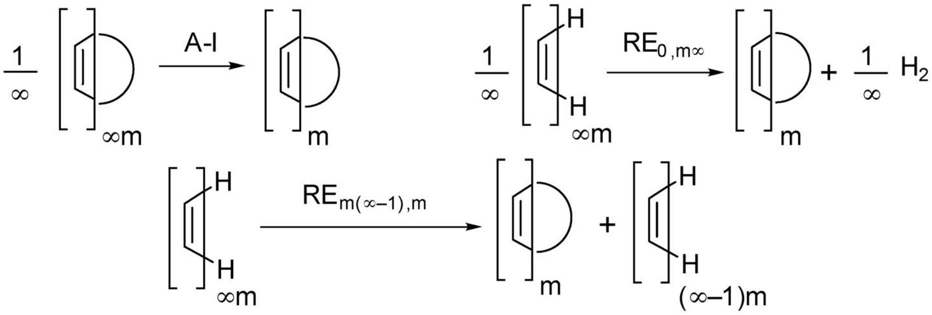
For *p* = 0, the equations are simply isogyric [14] and correspond to HRE and BRE for *q* = 1 and *q* = *m*, respectively. For $p \geq 1$, the equations are homodesmotic [15], and for $p \geq 2$ hyper-homodesmotic [16]. Although many of these reactions have been studied at the experimental and ab initio theoretical level [15b], their respective topological components can be compared through their RE at the HMO level. For [2*m*]annulenes, calculations show that the asymptotic behavior of $\mathrm{RE}_{p,q}(C_{2m})$ at large *m* depends on *p* and *q* (see Supplementary Information):

- *If p and q are finite constants* (as for HRE: *p* = 0, *q* = 1), then: $\mathrm{RE}_{p,q}(C_{2m}) \to \infty$.
- *If p or q varies as m*, then

$$\mathrm{RE}_{p,q}\left(C_{2m}\right)\sim\frac{m}{q}\left[\frac{2}{\sin\left(\dfrac{\pi}{4p+2}\right)}-\frac{8p+4}{\pi}\right] \quad \text{for large } m \qquad (2)$$

- If p is a finite constant (and $q = am + b$, $a \geq 1$) however, $\mathrm{RE}_{p,q}(C_{2m})$ tends to a non-zero finite limit. For example, if $p = 0$ (the H-donor is H_2, as in BRE for $q = m$) the limit is $\mathrm{BRE}_\infty/a \approx 0.727/a$ (see eq. 1), and if $p = 1$ (the H-donor is ethylene) the limit is lower, ca. 0.180/a.
- If p increases with m (as $p = am + b$), then $\mathrm{RE}_{am+b,q}(C_{2m}) \rightarrow 0$, and the essential condition of requirement iii is satisfied.

  For example, if $p = m - 1$ and $q = 1$ (giving integer stoichiometric coefficients in Scheme 3), $\mathrm{RE}_{m-1,1}(C_{2m}) = \mathrm{HSRE}(C_{2m})$, the generalized Hess–Schaad RE (HSRE) [16] corresponding to a m-isoconjodesmic equation [17]. For benzene, $\mathrm{HSRE}(C_6H_6) = 0.453$ remains however quite far from the topological limit [$\mathrm{TRE}(C_6H_6) = 0.273$, Fig. 1]. Moreover, the definition is not uniquely generalized to dissymmetrically *exo*-conjugated rings, and does not fulfill the requirement ii.
- *If p or q is infinite*, then $\mathrm{RE}_{\infty,q}(C_{2m}) = \mathrm{RE}_{p,\infty}(C_{2m}) = \mathrm{RE}_\infty(C_{2m}) \rightarrow 0$, and the essential condition of the requirement iii is satisfied. The chemical equations of RE_∞ are equivalent to the limit schemes of Aihara's A-I [9] or ∞-isoconjodesmic RE [17] (Scheme 4).



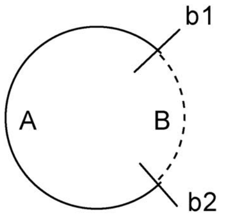
Scheme 4 Equivalent ∞-isoconjodesmic chemical schemes defining RE_∞ for [2*m*]annulenes.

The value for benzene $\mathrm{RE}_\infty(C_6H_6) = 0.361$ is closer to the topological limit (0.273) than all the preceding $\mathrm{RE}_{p,q}$ values (Fig. 1). Moreover, generalization of the RE_∞ definition to dissymmetrically *exo*-conjugated rings is unique because the substitution sequence of the ring is just the period of the infinite acyclic reference. Requirement ii is thus also satisfied. RE_∞ is therefore a very relevant chemical approximation of topological aromaticity.

Perturbational REs

In the search of chemical approximations of the topological limit (Scheme 1), remaining acyclic contributions are not exclusive *a priori*, but must be at least clearly identified. This is achieved by deriving RE expressions from a perturbative analysis of the ring-cut process.

Double-cut aromatic cyclic energy (ACE_{DC}) [18]. Considering a ring made of two fragments A and B, the junction between A and B through bonds b_1 and b_2 is analyzed as a perturbation of the Hamiltonians of the isolated fragments (Fig. 2). It can be shown that the second-order term is actually the sum of two terms, one containing the contributions of the A–B interactions through twice the same bond ($2 \times b_1$ or $2 \times b_2$), the other containing the contributions of the A–B interactions through the two bonds ($b_1 + b_2$).



$$H\Psi = E\Psi \Longrightarrow \begin{cases} H = H_A + H_B + V_{AB}, \quad V_{AB} = V_{b1} + V_{b2} \\ E = E_A + E_B + \varepsilon^{(2)}{}_{AB} + \ldots \end{cases}$$

$$\varepsilon^{(2)}{}_{AB} \; \| $$

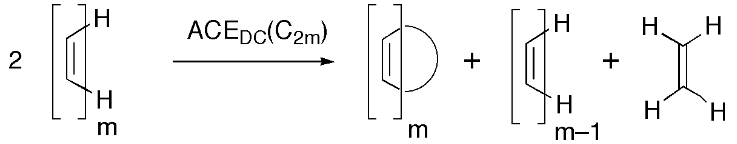
Additive separation acyclic *vs* cyclic effects: $\varepsilon^{(2)}{}_{acyc} + \varepsilon^{(2)}{}_{cyc}$

$$\varepsilon^{(2)}{}_{acyc} = \varepsilon^{(2)}{}_{Ab1B} + \varepsilon^{(2)}{}_{Ab2B} \approx E_{Ab1B} + E_{Ab2B} - 2\,E_A - 2\,E_B$$

$$ACE_{DC} = \varepsilon^{(2)}{}_{cyc} = E + E_A + E_B - E_{Ab1B} - E_{Ab2B}$$

Fig. 2 Schematic derivation of an aromatic cyclic energy (ACE) from a second-order analysis of the total energy of a ring under a double-cut perturbation (ACE_{DC}). ***H*** and *E* denote the Hamiltonian and the ground-state energy of the cyclic system. $\boldsymbol{H}_A$ (resp. $\boldsymbol{H}_B$) and E_A (resp. E_B) denote the Hamiltonian and the ground-state energy of the isolated fragment A (resp. B), respectively. $\varepsilon^{(2)}A_B$ denotes the second-order energy of the double-cut perturbation (of Hamiltonian V_{AB}) through bonds b_1 and b_2. E_{Ab1B} (resp. E_{Ab2B}) denotes the energy after cleavage of the bond b_2 (resp. b_1).

The optimal double-cut of a Kekulé structure is given by selection rules aiming at optimizing the accuracy of the perturbative approach [18,19]. The first rule indicates that the most dissymmetrical cut should be preferred, e.g., $CH_2{=}CH_2$ + H-(CH=CH)$_{m-1}$-H for a [2*m*]annulene. The generic chemical interpretation of ACE_{DC} is given in Scheme 5.



Scheme 5 Generic equation of ACE_{DC} for [2*m*]annulenes [18].

The asymptotic HMO expression of the $ACE_{DC}(C_{2m})$ series is (see Scheme 5 and Supplementary Information)

$$ACE_{DC}\left(C_{2m}\right) \xrightarrow[m\to\infty]{} ACE_{DC\infty} = 4 - \frac{12}{\pi} \approx 0.1802 \tag{3}$$

$ACE_{DC}(C_{2m})$ thus tends to the same non-zero finite limit as does $RE_{1,m+b}(C_{2m})$, whose chemical equation also involves an ethylene molecule on the right-hand side of the equation (see eq. 2). Individual ACE_{DC} values are, however, more satisfactory, e.g., $ACE_{DC}(C_6H_6) = 0.496 < RE_{1,1}(C_6H_6) = 0.584$ and $RE_{1,2}(C_6H_6) = 0.518$ (Fig. 1). Following the same principle as for BRE, the corrected double-cut aromatic cyclic energy $ACE_{DC}' = ACE_{DC} - ACE_{DC\infty}$ formally satisfies the vanishing condition of requirement iii. The value for benzene, $ACE_{DC}'(C_6H_6) = 0.316$, is, however, less satisfactory than $BRE'(C_6H_6) = 0.285$.

The result of the double-cut perturbative approach of ACE_{DC} can be more intuitively appraised by resuming the default of the single-cut approach of BRE. Energetic aromaticity is indeed overestimated by BRE because the additional π-overlap present in the ring (e.g., there are six C–C bonds in benzene, but only five in its hexatriene acyclic reference) is anyway stabilizing even if it would not operate a ring closure: the intrinsic acyclic stabilization ΔE* due to this bond must thus be substracted, thus defining generalized double-cut aromatic cyclic energies as ACE_{DC}* = BRE – ΔE*.

A transferable ΔE* value might be the energy ΔE_4 of formation of butadiene from two molecules of ethylene (2 ethylene → butadiene + H_2, $\Delta E_4 = 0.472$), thus giving the expression: $\text{ACE}_{\text{DC}(4)}$ = BRE – ΔE_4 (for benzene: $\text{ACE}_{\text{DC}(4)} = 0.540$: see Fig. 1).

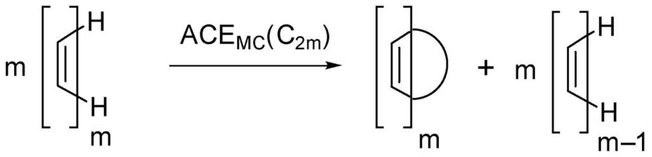
In the ACE_{DC} definition, a more accurate ΔE* value depending on the C–C bond environment is the energy ΔE_{2m} of formation of the longest open fragment (with 2m carbon atoms) from ethylene and the last-but-one longest fragment (for benzene: ethylene + butadiene → hexatriene + H_2: $\Delta E_6 = 0.516 \rightarrow \text{ACE}_{\text{DC}} = \text{ACE}_{\text{DC}(6)} = \text{BRE} - \Delta E_6 = 0.496$: see Fig. 1).

An even better ΔE* value would be the energy ΔE_{4m} of formation of a C–C bond between two open fragments having the size of the whole ring (with 2m carbon atoms), thus giving the expression

$$\text{ACE}_{\text{DC}(4m)} = \text{BRE} - \Delta E_{4m} = \text{RE}_{m,m}\left(C_{2m}\right) \tag{4}$$

For benzene: 2 hexatriene → H-$(\text{CH})_{12}$-H + H_2: $\Delta E_{12} = 0.617 \rightarrow \text{ACE}_{\text{DC}(12)} = 0.395$. Due to symmetry, the double-cut inspiration of the $\text{ACE}_{\text{DC}(4m)}$ definition is not apparent in the chemical equation (Fig. 1), and $\text{ACE}_{\text{DC}(4m)}(C_{2m})$ is equivalent to the generic resonance energy $\text{RE}_{m,m}(C_{2m})$ ($p = q = m$, in Scheme 3). The $\text{ACE}_{\text{DC}(4m)}(C_{2m})$ series vanishes for infinite annulenes and thus satisfies an essential condition of requirement iii.

Multiple-cut aromatic cyclic energy (ACE_{MC}) [20]. The selection rules of the ACE_{DC} definition are required by the second-order limitation of the perturbative expansion [18,19]. In order to avoid this arbitrariness, the double-cut approach was generalized to a multiple-cut version. Given a reference Kekulé structure, the single bonds are simply denoted as "bonds", while the double bonds are capitalized as "Bonds". The zero-order wave function ϕ_0 is taken as the product of the isolated C=C Bond functions φ_i, while their connection through σ-C–C bonds is analyzed as a perturbation. The expansion of the total energy E over charge transfers $\varphi_i \rightarrow \varphi_j^*$ between Bonds through bonds allows for the isolation of properly cyclic contributions from k^{th}-order energy corrections $E(k)$ to $E(0)$, $k = 2, 3, 4\ldots$ depending on the topology. These contributions can be globally interpreted in terms of a multiple-cut aromatic cyclic energy, ACE_{MC}: given a cyclic molecule with N double bonds, ACE_{MC} is equal to the energy of the whole system, minus the energies of the N open systems in which one bond has been cut, plus those of the N subsystems in which one Bond has been removed. Saturating the valence of the disconnected C atoms by H atoms, the chemical equation of ACE_{MC} for [2m]annulenes (Scheme 6) is the hyperhomodesmotic m-isoconjodesmic equation of $\text{RE}_{m-1,1}(C_{2m})$ ($p = m - 1$ and $q = 1$ in Scheme 3), which is also equivalent to the generalized HSRE [16]. Therefore, $\text{ACE}_{\text{MC}}(C_6H_6) = 0.453$ (Fig. 1) and $\text{ACE}_{\text{MC}}(C_{2m}) \rightarrow 0$ as $m \rightarrow \infty$ (see above).



Scheme 6 Generic equation of ACE_{MC} for [2m]annulenes.

Although both ACE_{MC} and HSRE thus satisfy the essential condition of requirement iii for [2m]annulenes, the merit of the ACE definition is its generality for any *exo*-conjugated rings, in agreement with requirement ii. The ACE values however remain dependent on the selected zeroth-order Kekulé structure (the $\text{RE}_{p,q}$ not only depend on the Kekulé structure, but also on the selected particular single bond to be cut). Although the equations can be averaged over all the possible or relevant Kekulé structures, some arbitrariness will remain regarding the resonance weighting method to be used. The fundamental problem of the zeroth-order reference structure is revisited below within the framework of graph theory.

TRE

Although energetic aromaticity measures have been hitherto examined at the HMO level, the chemical equations underlying the RE definitions discussed above can also be considered as ASEs and calculated at higher level of theory (DFT, e.g.) [7]. This is not the case of TRE, which intrinsically refers to graph-theoretical pictures of real molecules, and thus to the HMO level.

TRE of molecular graphs. The topological limit of aromaticity is abstractly but exactly quantified by the TRE defined by Aihara [9] and the Trinajstic's Zagreb group [10] using the graph-theoretical translation of HMO theory. The TRE definition is based on the Sachs theorem [21], allowing for extracting the "energy" of an abstract "acyclic reference" from the characteristic polynomial $P^0(x)$ of the molecular graph G^0, whose roots $\lambda^0{}_i$ $(1 \le i \le n)$ are the HMO energy levels of G^0. The coefficients $a^0{}_k$ of $P^0(x)$ $(0 \le k \le n)$ can indeed be deduced from a decomposition of the molecular graph in terms of so-called Sachs subgraphs, which are constituted by two types of non-incident primary components: edges and rings. Contrary to what is assumed in the definition of the above empirical and perturbational REs (where single bonds are distinguished from double bonds), all the edges are here locally equivalent: this is the key for obeying the requirement ii.

$$P^0\left(x\right)=\sum_{k=0}^{n} a_k^0 x^{n-k} \tag{5a}$$

$$a_0^0=1, \text{and } a_k^0=\sum_{s\in s^0\left(k\right)} \left(-1\right)^{c\left(s\right)} 2^{r\left(s\right)} \quad \text{for } 1\le k\le n \tag{5b}$$

where $S^0(k)$ is the set of Sachs graphs covering k vertices of G^0, and $\mathrm{c}(s)$ is the total number of components and $\mathrm{r}(s)$ is the number of rings in the Sachs graph s.

Discarding the terms involving ring components allows to generate truncated acyclic coefficients $a^{\mathrm{ac}}{}_k$ defining the "acyclic" or "matching" polynomial $P^{\mathrm{ac}}(x)$ from subsets $S^{\mathrm{ac}}(k)$ of Sachs graphs without a ring component $[\mathrm{r}(s) = 0]$ and of order k:

$$S^{\mathrm{ac}}(k) = \{\mathrm{s} \in S^0(k); \mathrm{r}(s) = 0\} \tag{6a}$$

$$P^{\mathrm{ac}}\left(x\right)=\sum_{k=0}^{n} a_k^{\mathrm{ac}} x^{n-k} \tag{6b}$$

$$a_0^{\mathrm{ac}}=1, \text{and } a_k^{\mathrm{ac}}=\sum_{s\in S^{\mathrm{ac}}\left(k\right)} \left(-1\right)^{\mathrm{c}\left(s\right)} \quad \text{for } 1\le k\le n \tag{6c}$$

Though not properly characteristic in nature (it is not the secular determinant of a molecular graph in the general case), $P^{\mathrm{ac}}(x)$ turns out to have real roots only: the latter are thus interpreted as the eigenvalues $x_i = \lambda^{\mathrm{ac}}{}_i$ $(1 \le i \le n)$ of some putative acyclic reference. Ranking the roots of $P^0(x)$ and $P^{\mathrm{ac}}(x)$ in non-increasing order ($\lambda^0{}_1 \ge \lambda^0{}_2 \ge \ldots \ge \lambda^0{}_n$ and $\lambda^{\mathrm{ac}}{}_1 \ge \lambda^{\mathrm{ac}}{}_2 \ge \ldots \ge \lambda^{\mathrm{ac}}{}_n$), the electronic state and the "energy" E^{ac} of the acyclic reference are defined from the same set of occupation numbers of the ith levels, g_i $(i = 0, 1, 2)$, as that corresponding to the considered electronic state and energy E^0 of the cyclic molecule. The TRE value of the latter is finally defined as

$$\mathrm{TRE}=E^0-E^{\mathrm{ac}}=\sum_{i=1}^{n} g_i\left(\lambda_i^0-\lambda_i^{\mathrm{ac}}\right) \tag{7}$$

A concise analytical expression of TRE can be derived for [2*m*]annulenes in the ground state [22]. It is readily checked to converge to zero at infinite size:

$$\mathrm{TRE}\left(C_{2m}\right)=E\left(C_{2m}\right)-\frac{2}{\sin\left(\dfrac{\pi}{4m}\right)}\xrightarrow[m\to\infty]{}0 \tag{8}$$

The TRE value for benzene [$\mathrm{TRE}(C_6H_6) = 0.2726$] is the smallest among all the RE values considered hitherto. It corresponds to the strict effect of the cyclic character of the π-conjugation in the molecules. Since RE ≥ TRE, all other RE values contain non-purely cyclic effects of the π-conjugation, which are globally stabilizing (Fig. 1).

For [4*n* + 2]annulenes, a comparison of the variation of TRE with those of other REs tending to zero at infinite m is shown in Fig. 3. It is remarkable that the best approximation of TRE is here the corrected version BRE' of the early BRE (see eq. 1 and Fig. 1) [13].

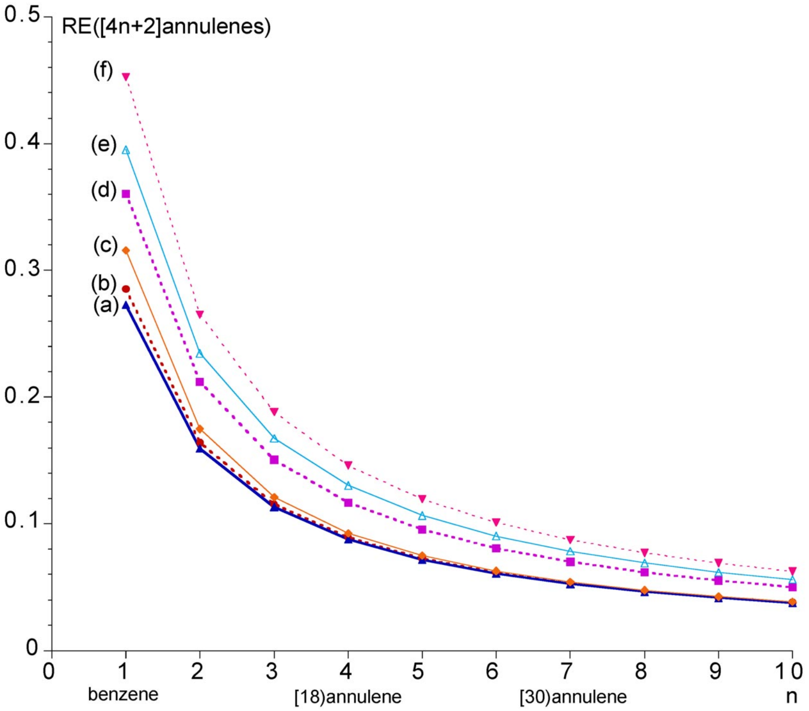


Fig. 3 Variations of (possibly corrected) $\mathrm{RE}(C_{2m})$ values for [4*n* + 2] annulenes ($m = 2n + 1$): (a) TRE: (eq. 8); (b) $\mathrm{BRE}' = \mathrm{BRE} - (2\text{–}4/\pi)$: (eq. 1); (c) $\mathrm{ACE}_{DC'} = \mathrm{ACE}_{DC} - (4 - 12/\pi)$: (eq. 3); (d) $\mathrm{RE}_\infty = A\text{–}I$: (eq. 2) for $q = \infty$; (e) $\mathrm{ACE}_{DC(4m)}$: (eq. 4) ; (f) $\mathrm{ACE}_{MC} = \mathrm{HSRE} = \mathrm{RE}_{m-1,1}(C_{2m})$: (eq. 2) for $p = m - 1$, $q = 1$.

TRE of real molecules. The design of an ab initio version of TRE for measuring the aromaticity of real molecules in their real geometry remains a challenge to be explored. Nevertheless, projection of a real molecule to a relevant HMO picture is a directly applicable alternative through the semi-empirical variable β Hückel method [23,24]. The comparison between different geometries of cyclobutadiene in the singlet spin state is here exemplified (see details in Supplementary Information). For generic rectangular geometries with bond lengths d_1 and d_2 (Scheme 7), the corresponding resonance integrals β_1 and β_2 can thus be calculated from empirical formulae in reference HMO β units [24].

Scheme 7 Equilibrium (B3PW91/6-31G**) and transition state (CASSCF/cc-pVTZ) geometries of cyclobutadiene in the singlet state [25,26]. The variable resonance integrals values given in reference β units are obtained from empirical formulae of ref. [24].

Assuming $\beta_1 \leq \beta_2$ and setting $u = \beta_1/\beta_2$, calculation and factorization of the characteristic and matching polynomials afford the following TRE expression for the ground state of any geometry (Fig. 4):

$$\frac{\mathrm{TRE}}{\beta_2} = 4 - 2\left[1+u^2+\sqrt{2}\,u\right]^{1/2} - 2\left[1+u^2-\sqrt{2}\,u\right]^{1/2} \tag{9}$$

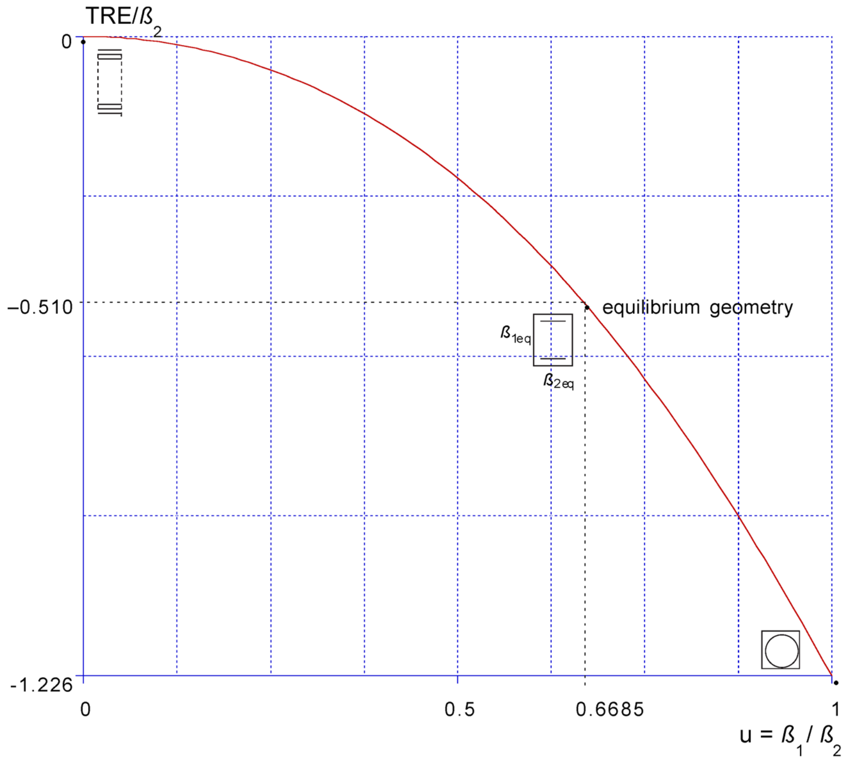


Fig. 4 Variation of the TRE/β_2 value ((eq. 9) where β_2 is given in β units) of singlet cyclobutadiene in geometries ranging from square (u = 1) to infinitely rectangular (u = 0, in the dissociated state C_4H_4 = 2 H–C≡C–H).

In the rectangular equilibrium geometry, calculations at the B3PW91/6-31G** level give d_1 = 1.572 Å and d_2 = 1.334 Å [25], and thus $\mathrm{TRE}_{eq} = -0.606$ for $u = u_{eq} = 0.669$ and $\beta_2 = \beta_{2eq} = 1.1878$. The ground-state singlet cyclobutadiene in its real equilibrium geometry is therefore antiaromatic, but ca. twice less than in the constant β HMO reference (–1.226 for $\beta_1 = \beta_2 = 1$).

In the particular interconversion transition-state square geometry, calculations at the complete active space self-consistent field (CASSCF) level give $d_1 = d_2 = 1.447$ Å [26], and thus $\mathrm{TRE}_{\mathrm{TS}} = -1.057$ for $u = u_{\mathrm{sq}} = 1$ and $\beta_2 = \beta_{\mathrm{TS}} = 0.8622$. The squared cyclobutadiene is thus slightly less antiaromatic in the real transition state geometry than in the constant β reference (–1.226 for $\beta_1 = \beta_2 = 1$) [9,10,22].

Relative aromaticity of Hückel and Möbius rings

Given a cyclic nuclear topology of sp^2-hybridized atoms, two types of orbital topology may be assigned to the strip embedding the axes of the remaining p-orbitals: strips with zero or an even number of twists are said of Hückel type, those with an odd number of twists are said of Möbius type. At the HMO level, all the Hückel-type molecules are equivalent to the prototype with no twist, and all Möbius-type molecules are equivalent to the prototype with a single twist. Therefore, only the basic prototypes with zero or one twist are henceforth implicitly considered. According to the Heilbronner rule (the generalized Hückel rule for Möbius rings) [5a], the Möbius version of an aromatic (resp. antiaromatic) Hückel ring is qualitatively antiaromatic (resp. aromatic). However, whereas all first aromatic and antiaromatic Hückel-type [2*m*]annulenes are known (for $m > 1$), none of the antiaromatic or aromatic Möbius-type [2*m*]annulenes have been hitherto evidenced [5b]. Although the difference in stability is primarily due to the steric constraint enforced by the Möbius topology, the relative topological aromaticity of stereoisomeric Hückel and Möbius cyclic molecules deserves to be scrutinized. Given a σ-skeleton G of some neutral Lewis structure, the Hückel and Möbius forms are denoted as G^0 and G^1. Since the two forms have the same acyclic reference (corresponding to the open planar strip of p-orbitals "with the same conjugation"), whatever is the RE scheme:

$$\mathrm{RE}\left(G^0\right) - \mathrm{RE}\left(G^1\right) = E\left(G^0\right) - E\left(G^1\right) \tag{10}$$

Due to its topological nature, TRE is particularly relevant for the analysis of the orbital topology effects. Thus, plotting TRE(G^0) values vs. TRE(G^1) values over a set of 88 neutral unicyclic molecules reveals three subsets of points with specific regular variations (Fig. 5).

Each subset actually corresponds to a well-defined structural type depending on the parity of the ring size and on the topology of the susbtituents. An acyclic substituent R is thus said of even type, if at least one path joining the anchoring atom of the ring to one of the terminal atoms consists in an even number of bonds. Otherwise, R is said of odd type. For example, $-\mathrm{CH{=}CH_2}$, $-\mathrm{C({=}CH_2){-}CH{=}CH_2}$, $-\mathrm{C^\bullet({-}CH_2^\bullet)_2}$ are of even type, while $-\mathrm{CH_2^\bullet}$, $-\mathrm{CH{=}CH{-}CH_2^\bullet}$, $-\mathrm{C^\bullet(CH{=}CH_2)_2}$ are of odd type.

i. For odd-membered ring, TRE(G^0) = TRE(G^1). This is a consequence of the Pairing theorem.
ii. For even-membered rings, two situations depend on the nature of the substituents.
    ii-a If all the substituents are of even type, TRE(G^1) is roughly proportional to TRE(G^0) with inverse factors f and $1/f$ for aromatic and antiaromatic Hückel forms, respectively:

$$\mathrm{TRE}(\text{antiaromatic } G^1 \text{ or } G^0) \approx -f\,\mathrm{TRE}(\text{aromatic } G^0 \text{ or } G^1),\ f = 2.7 \pm 0.3 \tag{11}$$

Monocationic and monoanionic species with an odd-membered ring (such as $\mathrm{C_3H_3^+}$, $\mathrm{C_5H_5^-}$,…) also satisfy eq. 13. This is empirically interpreted by the existence of an approximate expression of the acyclic reference energy E^{ac} in terms of a weighted mean of the energies E^0 and E^1 of the Hückel and Möbius forms, respectively:

- If G^0 is aromatic and G^1 antiaromatic: $E^{\mathrm{ac}} \approx \dfrac{E^1 + f_0 E^0}{1 + f_0}$ with $f_0 = 2.8242$

$$E^{\mathrm{ac}} \approx 0.7385\,E^0 + 0.2615\,E^1 \tag{12a}$$

- If G^1 is aromatic and G^0 antiaromatic: $E^{ac} \approx \dfrac{E^0 + f_1 E^1}{1 + f_1}$ with $f_1 = 2.6056$

$$E^{ac} \approx 0.7227\, E^1 + 0.2774\, E^0 \tag{12b}$$

The quality of these approximations for TRE calculation is very good (ΔTRE < 0.03 for $-1.2 \leq \text{TRE} \leq +0.4$, see Supplementary Information), and remains acceptable if the same value $f = (f_1 + f_2)/2 \approx 2.70$ is adopted for both types of graph.

ii-b If at least one of the substituents is of odd type, TRE(G^1) varies smoothly with TRE(G^0). This nonlinear correlation must be related to the existence of an empirical equation (eq. 13b) allowing for a highly accurate calculation of E^{ac} from E^0 and E^1 only. It should be noted that truncation of (eq. 13b) to the first term gives (eq. 13a), which holds very crudely for all kinds of molecular graph but is not sufficient for relevant estimation of TRE values (eq. 13a would be equivalent to eq. 12a and 12b for $f_0 = f_1 = 1$):

$$E^{ac} \approx (E^0 + E^1)/2 \tag{13a}$$

$$E^{ac} = (E^0 + E^1)/2 + 0.1305\,(E^0 - E^1)^2 + 0.0956\,(E^0 - E^1)^3 + 0.1046\,(E^0 - E^1)^4 \tag{13b}$$

The quality of the approximation (eq. 13b) for TRE calculation is excellent (ΔTRE < 0.003 for $-0.6 \leq \text{TRE} \leq +0.4$, see Supplementary Information).

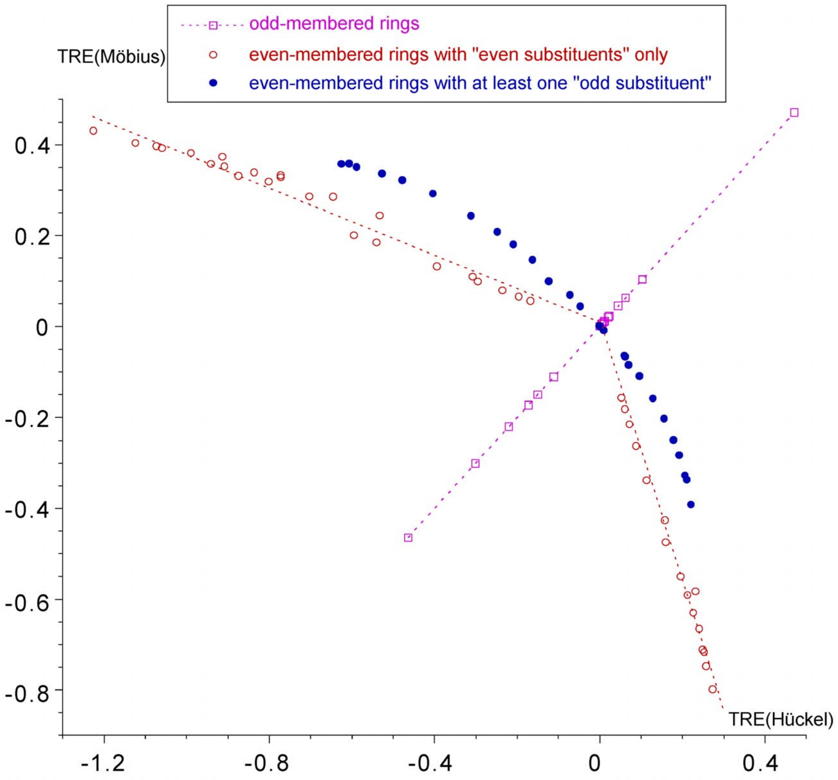


Fig. 5 Correlations between the TREs of the Möbius and Hückel forms of 88 neutral unicyclic totally conjugated hydrocarbons (see Supplementary Information).

These correlations between TRE values of Möbius and Hückel unicycles suggest a strong relationship between the "abstract" acyclic reference and the "real" Hückel and Möbius unicycles. These empirical relationships, however, do not systematically apply to ionic species: an easy way to calculate the acyclic eigenvalues is still desired. The fundamental complementary roles of the Hückel and Möbius forms in the definition of the acyclic reference is addressed in the next section.

Chemical interpretation of TRE: The Möbius key

In spite of its fundamental relevance, TRE is sparingly invoked by organic chemists for assessing the aromaticity of molecules in order to predict related properties (energetic but also geometric or magnetic). Beside the effects of few paradoxical predictions [27], this disuse is due to the conceptual and mathematical complexity of the TRE calculation as compared to more empirical approaches [1a,12]. Application of the Sachs theorem is indeed a tedious task that is not easily implementable. The matching polynomial can, however, be more rapidly generated from various graph analyses based on either ring fragmentation, ring masking, or ring twisting processes [28a]. The latter can be summarized by stating that the matching polynomial is actually the arithmetic mean of the characteristic polynomials of the corresponding Hückel and Möbius chemical graphs. For a unicyclic molecule, the twisting analysis reads:

$$P^{\mathrm{ac}}(x)=\frac{1}{2}\left[P^{0}(x)+P^{1}(x)\right] \tag{14a}$$

where $P^0(x)$ and $P^1(x)$ denote the characteristic polynomials of its Hückel and Möbius versions, respectively. This equation is the exact polynomial version of the approximate energetic version (eq. 13a). This equation has been generalized to polycyclic molecule as:

$$P^{\mathrm{ac}}(x)=\frac{1}{2^{N}}\sum_{j=0}^{2^{N}-1}P^{j}(x) \tag{14b}$$

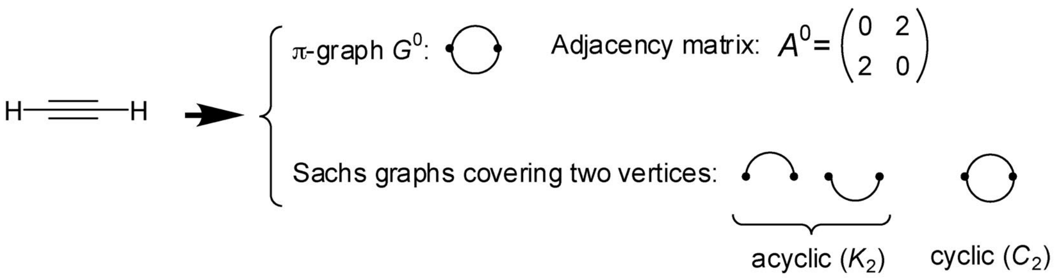
where $P^j(x)$, $j \geq 1$, denote the characteristic polynomials of the $2^N - 1$ generalized graph G^j of the Hückel graph G^0 [28a]. The generalized graphs are derived by twisting one or more bonds belonging to different rings of G^0, and are thus of Möbius type. It is, however, noteworthy that no generalized graphs contains Möbius circuits only: at least one of the circuits remains of Hückel type.

Beyond a molecular property, aromaticity is a ring property [4] which may take as many values as rings in a polycyclic molecule. Partial aromaticity inside a polycycle is thus currently estimated by the values of NICS at the centers of irreducible rings (also called fundamental circuits) [1c–e,h,i], e.g., 2 in biphenyl and naphthalene, 3 in anthracene and phenanthrene, 32 in buckminsterfullerene, some of them being equivalent by symmetry. The definition of a partial TRE for quantifying the local aromaticity of a given circuit c_i inside a polycycle is thus a challenge that has been tackled in different ways [29]. The definition of a partial acyclic polynomial $P_{\mathrm{ci}}{}^{\mathrm{ac}}(x)$ from the Sachs theorem (by removing from $P^0(x)$ only the Sachs graphs involving the cyclic component of the considered circuit) is the natural way [29b]. The problem is that $P_{\mathrm{ci}}{}^{\mathrm{ac}}(x)$ may have non-real roots that cannot be interpreted as "energies". Retaining the real parts of the complex roots (directly or by approximation methods) is a possibility that remains, however, somewhat arbitrary [29e]. A method proposed by Aihara appeared to be a rigorous alternative, but relies on a mathematical conjecture that has not been proved nor disproved hitherto [29c].

TRE of conjugated cyclynes

Most of the RE schemes aiming at quantifying π-aromaticity were developed for molecules containing a single π-conjugated system. Within the framework of the HMO theory, their topographical representation is thus based on simple graphs of degree three. The graphs can be approximated to be nonweighted for cyclenes with small bond-length alternation, but require to be weighted for heterocycles and strongly antiaromatic cyclenes (e.g., for cyclobutadiene: see above). Pseudo-degenerate π-systems involving (triply) bonded sp-hybridized atoms are currently treated by considering orthogonal components independently: out-of-plane HMOs of a conjugated cyclenyne are thus approximated to be identical to the HMOs of the corresponding conjugated cyclene (e.g., in benzyne vs. benzene). The purely topological approximation is justified for most systems made of sp^2-conjugated carbons only ($d_{sp^2-sp^2} \approx 1.40 \pm 0.05$ Å), but becomes less acceptable for systems involving sp-conjugated carbons ($d_{sp-sp} \approx 1.25$ Å $\pm$ 0.05 Å << 1.40 Å) [30]. The distinction between sp^2–sp^2 bonds and sp–sp bonds can actually be made purely topological in nature without resorting to a β-variable Hückel treatment (i.e., to graph weighting): the topological influence of the presence of triple bonds in a conjugated hydrocarbon is here adressed by considering non-simple but nonweighted graphs.

TRE of acetylene. Acetylene possesses degenerate π-MOs due to the $D_{\infty h}$ molecular symmetry. The graph-theoretical picture of the acetylene π-MOs is a digon, and the off-diagonal coefficients of the associated adjacency matrix $A^0 = (a^0_{ij})$ are equal to 2 (a^0_{ij} = number of edges between vertices i and j) [31]. The π-bonds of acetylene are thus represented by a "looped edge", suggesting that the molecule can be regarded as a "two-membered ring" (Scheme 8).



Scheme 8 Graph representation of the π-MO system of acetylene as a "two-membered ring".

Beyond the formalism, the digon analysis making acetylene a [2]annulene is actually suggested by the observation of quasi-circular local diatropic π currents above the two carbon atoms induced by a magnetic field perpendicular to the C–C axis (Fig. 6) [32]. It must be noticed that both orthogonal π_z and π_{xy} systems contribute to the diatropic ring current in a given plane (Fig. 6), showing that they do not independently operate on their own "local aromaticity".

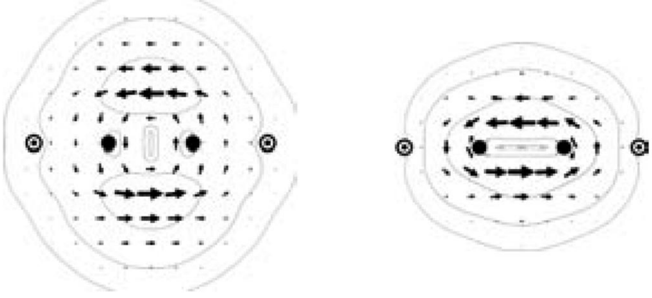


Fig. 6 Current density maps of acetylene (black dots feature carbon atoms). The planes of the maps are distant by 1a$_0$ from the nuclear axis and perpendicular to the external magnetic field. The two maps depict the diatropic contributions of the out-of-plane π_z MOs (*left*) and in-plane π_{xy} MOs (*right*) (ipsocentric CTOCD-*DZ*/6-31G**//B3PW91/6-31G** level) [32a].

According to Scheme 8, the secular determinant of acetylene thus reads

$$P^0(x) = x^2 - 4$$

This characteristic polynomial can also be obtained by application of the Sachs theorem and (eq. 5):

$$a_0^0 = 1, a_1^0 = 0,$$

$$a_2^0 = \det(A) = \sum_{s \in S^0(2)} (-1)^{c(s)} 2^{r(s)} = (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^1 = -4$$

The coefficients $a^{ac}{}_k$ ($k = 0, 1, 2$) of the matching polynomial $P^{ac}(x)$ of acetylene can be obtained by excluding from the Sachs graphs performing a k-matching, all those containing the C_2 cyclic component through (eq. 6):

$$a_0^{ac} = 1, a_1^{ac} = 0,$$

$$a_2^{ac} = \sum_{s \in S^{ac}(2)} (-1)^{c(s)} = (-1)^1 2^0 + (-1)^1 2^0 = -2$$

and thus

$$P^{ac}(x) = x^2 - 2$$

By generalization of the principles of chemical graph theory, the formal ground-state energy of the graph G^0 (the energy of one of the two π-electron pairs) is identified to the sum of the absolute eigenvalues:

$$E^0(G^0) = 4$$

The graph energy is thus equal to the sum of the HMO energies of the orthogonal π-systems considered as independent: $E^0(G^0) = E_\pi(\text{acetylene}) = 2E_\pi(\text{ethylene}) = 4$.

Following the same principle, the energy of the neutral acyclic reference is given by

$$E^{ac}(G^0) = 2\sqrt{2}$$

According to (eq. 7), the TRE of acetylene is thus

$$\mathrm{TRE}(C_2H_2) = E^0(G^0) - E^{ac}(G^0) = 4 - 2\sqrt{2} \approx 1.172$$

Acetylene can thus be claimed to be twice more "topologically aromatic" than the iso-π-electronic cyclopropenium cation (TRE = 0.536), and ca. three times more topologically aromatic than other $4n + 2$-electrons unicyclic systems: cyclobutadiene dication and dianion (TRE = 0.305), cyclopentadienide (TRE = 0.317), and benzene (TRE = 0.273).

Going further in the analogy, one may wonder about the definition of a Möbius version G^1 of the two-membered ring G^0. Let $P^1(x)$ denote the corresponding putative characteristic polynomial. Application of the Sachs formula (eq. 6) yields

$$a_0^1 = 1, a_1^1 = 0,$$

$$a_2^1 = \sum_{s \in S^1(2)} (-1)^{c(s)+r(s)} 2^{r(s)} = (-1)^1 2^0 + (-1)^1 2^0 - (-1)^1 2^1 = 0$$

and $P^1(x) = x^2$. The polynomial can also be obtained as $\det(A^1 - xI)$, where A^1 is deduced from the adjacency matrix A^0 (Scheme 8) by replacing the off-diagonal coefficients equal to 2 = 1 + 1 by 1 – 1= 0 (in the Möbius C_2 component, one edge is bonding, the other is anti-bonding).

The arithmetic mean of $P^0(x)$ and $P^1(x)$ reads

$$\frac{1}{2}\left[P^0(x)+P^1(x)\right]=\frac{1}{2}\left[x^2-4+x^2\right]=x^2-2=P^{\mathrm{ac}}(x)$$

The general formula (eq. 14a) expressing $P^{\mathrm{ac}}(x)$ from the characteristic polynomials of the Hückel and Möbius graphs thus formally applies to two-membered rings as well.

The two-electron "Möbius acetylene" has a zero graph energy, and can thus be regarded as the acetylene molecule in the second excited state (or the biscarbene form in the VB language):

$E^1(G^1) = 2 \times 0 = 0$

The energy of the two-electron acyclic reference remains the same: $E^{\mathrm{ac}}(G^0) = 2\sqrt{2}$

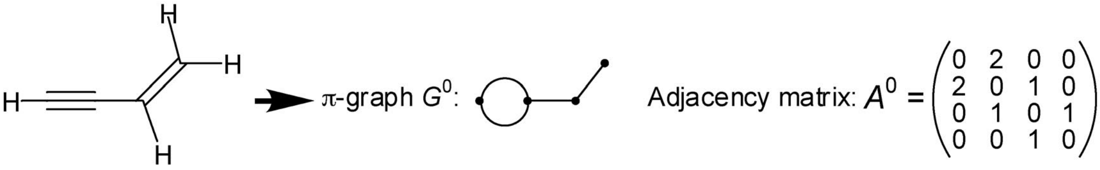
The "TRE value of Möbius acetylene" can therefore be formally defined as

TRE (Möbius acetylene) = $E^1(G^1) - E^{\mathrm{ac}}(G^0) = 0 - 2\sqrt{2} = -2.828$

The "Möbius acetylene" is therefore formally twice more antiaromatic than the cyclopropenide anion (TRE = –1.464) and even more than cyclobutadiene (TRE = –1.226).

Before being applied to *carbo*-annulenic species, the formalism is first applied below to model fragments thereof.

TRE of butenyne. Butenyne can be regarded as a singly *exo*-conjugated C_2 "ring" (Scheme 9). This C_4 fragment is also a model of the vertex environments in the ring *carbo*-mers of annulenes (see below).



Scheme 9 Representation of the π-MO system of butenyne as a singly *exo*-conjugated C_2 ring.

The coefficients of the characteristic polynomial can be obtained by either application of the Sachs theorem, or calculating $\det(A^0 - xI)$. The coefficients of the matching polynomial can be obtained similarly by either application of the Sachs (eq. 6), or of (eq. 14a) from the characteristic polynomial of the "Möbius enyne" [$P^1(x) = \det(A^1 - xI)$], where A^1 is deduced from A^0 by replacing the off-diagonal coefficients equal to 2 by 0):

$P^0(x) = x^4 - 6x^2 + 4$

$P^1(x) = x^4 - 2x^2$

$P^{\mathrm{ac}}(x) = x^4 - 4x^2 + 2$

The energies of the neutral graph of butenyne and of the neutral acyclic reference, identified to the corresponding sums of the absolute eigenvalues, are therefore

$E^0(G^0) = 6.3246$

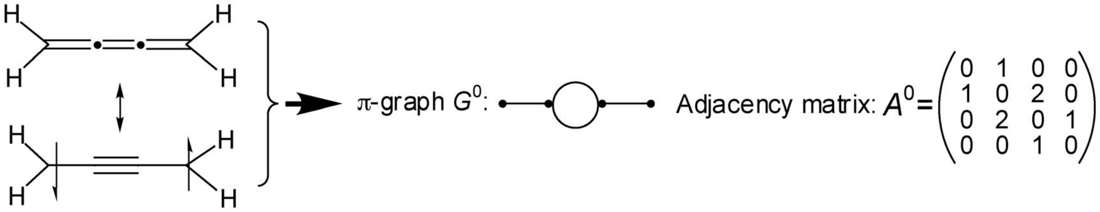
$E^{\mathrm{ac}}(G^0) = 5.2263$

It is noteworthy that the graph energy E^0 (in negative β units) is smaller than the sum of the energies of the orthogonal π-systems considered independently: E_π(butadiene) + E_π(ethylene) = 6.4721. In contrast to the case of acetylene exhibiting two identical π-systems, the coupling between the two different π-systems introduced by the non-simple graph approach of Scheme 9 is therefore destabilizing. The difference (6.4721 – 6.3246 ≈ 0.148) can be regarded as a measure of the non-degeneracy of the orthogonal π-systems (equivalently, of the two C_2 edges) of butenyne. Finally:

TRE(butenyne) = 1.098

Butenyne is therefore less "aromatic" than acetylene (TRE = 1.172), but the effect of the vinyl substituent remains quite weak.

TRE of butatriene. Butatriene can be regarded as a doubly *exo*-conjugated C_2 "ring" (Scheme 10). This illustrates that C_2 component more generally results from the occurence of a sp–sp bond rather than from a pure triple bond. This C_4 fragment is also a model of the edges of the ring *carbo*-mers of annulenes (see below).



Scheme 10 Representation of the π-MO system of butatriene as a doubly *exo*-conjugated C_2 "ring".

The coefficients of the characteristic polynomials of butatriene and Möbius butatriene are obtained by either application of the Sachs theorem through (eq. 5), or by calculating the corresponding secular determinants. The acyclic polynomial is obtained by application of (eq. 14a):

$P^0(x) = x^4 - 6x^2 + 1$

$P^1(x) = x^4 - 2x^2 + 1$

$P^{ac}(x) = x^4 - 4x^2 + 1$

The energies of the neutral graph of butatriene and of the neutral acyclic reference, identified to the corresponding sums of the absolute eigenvalues, are therefore:

$E^0(G^0) = 5.6568$

$E^{ac}(G^0) = 4.8990$

Here again, the orthogonal π-systems are different and the non-simple graph energy E^0 (in negative β units) is lower than the sum of their energies calculated independently: E_π(butadiene) + E_π(ethylene) = 6.4721. The difference (6.4721 – 5.6568 ≈ 0.8163) can be regarded as a measure of the non-degeneracy of the orthogonal π-systems (i.e., of the C_2 edges) of butatriene.

From eq. 7, finally:

TRE(butatriene) = 0.758

Butatriene is therefore much less "aromatic" than butenyne (TRE = 1.098). This could be intuitively predicted from the relative contributions of the triple character of the sp–sp bonds in the Lewis structures of these molecules (Schemes 9 and 10).

TRE of the carbo-cyclopropenylide anion. The graph G^0 of $[C_9H_3]^-$ is considered as a "tetracycle" whose primitive ring components are a C_9 macrocycle and the three C_2 components of the isolated sp–sp bonds. The molecular graph thus contains $2^4 = 16$ generalized circuits, consisting in $2^3 = 8$ equivalent C_9 simple circuits, three equivalent C_2 simple circuits, three equivalent double circuits (made of the union of two C_2 components), one triple circuit (made of the union of the three C_2 components), and the empty circuit. According to the Mizoguchi theorem [28b], 16 generalized graphs are thus defined, 15 of them being of the Möbius type. Due to molecular symmetry, only five nonequivalent types of generalized graphs remain: they are denoted as G^j ($j = 0$–4), depending on the minimum number and location of the twisted edges (Fig. 7).

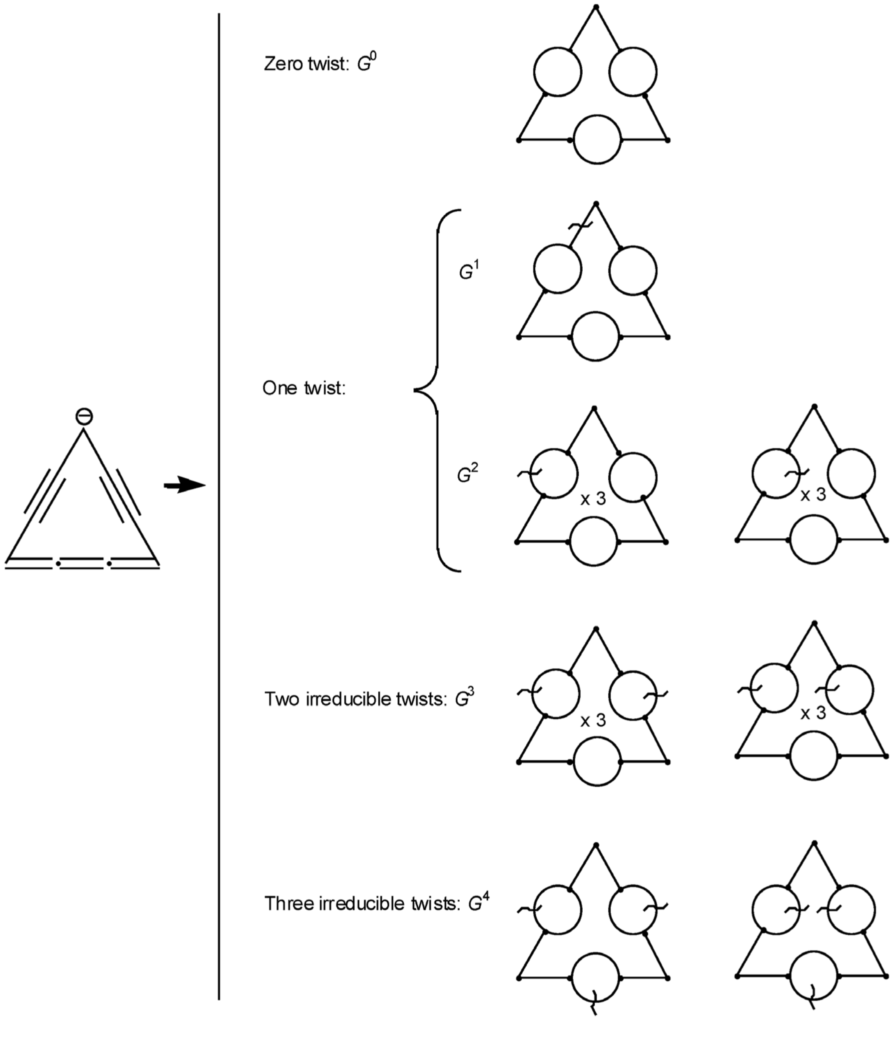


Fig. 7 The five nonequivalent types of the 16 generalized graphs of the *carbo*-cyclopropenylide skeleton (C_9H_3).

The corresponding characteristic polynomials of G^0–G^4 are

$$P^0(x) = x^9 - 18x^7 + 108x^5 - 228x^3 + 72x - 16$$

$$P^1(x) = x^9 - 18x^7 + 108x^5 - 228x^3 + 72x + 16$$

$$P^2(x) = x^9 - 14x^7 + 60x^5 - 80x^3 + 32x$$

$$P^3(x) = x^9 - 10x^7 + 28x^5 - 28x^3 + 8x$$

$$P^4(x) = x^9 - 6x^7 + 12x^5 - 8x^3$$

Using eq. 14b, the total acyclic polynomial is thus equal to

$$P^{ac}(x) = 1/16\ [P^0(x) + P^1(x) + 6\ P^2(x) + 6\ P^3(x) + 2\ P^4(x)] = x^9 - 12x^7 + 48x^5 - 70x^3 + 24x$$

The energies of the anionic graph of $[C_9H_9]^-$ and of the corresponding anionic acyclic reference are deduced by weighting the lowest roots of $P^0(x)$ and $P^{ac}(x)$ by the 10 π_z electrons, respectively.

$$E^0(C_9H_3^-) = 15.8708$$

$$E^{ac}(C_9H_3^-) = 13.0210$$

Application of eq. 7 finally gives

$$\mathrm{TRE}(C_9H_3^-) = 2.8498$$

The global TRE actually accounts for the aromaticity of the 16 generalized circuits of the polycycle. For comparative purpose, the partial TRE value for the eight C_9 macrocycles only is, however, needed. Although the challenge of defining partial TREs of individual true circuits inside polycycles has been tackled by several authors [29], the definition of TRE for a set of circuits had not been explicitly addressed until recently [28a]. Re-interpretation of Aihara's bond RE (here denoted as bRE) [33] indeed showed that the bRE of a p–q bond is the partial TRE for all the circuits revealing a Möbius type when the p–q bond is twisted. It happens that if the p–q bond is any of the sp–sp^2 bonds of the *carbo*-cyclopropenyl skeleton, the twisted circuits in the corresponding generalized graph G^1 are exactly the eight C_9 macrocycles of interest. The corresponding partially acyclic polynomial is, therefore, given by eq. 14a:

$$Q_{pq}(x) = P^{ac'}(x) = 1/2\ [P^0(x) + P^1(x)] = x^9 - 18x^7 + 108x^5 - 228x^3 + 72x$$

The same polynomial can also be generated through Gutman's approach [29b], by removing the contributions of the eight C_9 equivalent rings from eq. 5, giving the $P^0(x)$ coefficients ($0 \le k < 9 \rightarrow a^{ac'}{}_k = a^0{}_k$, and $a^{ac'}{}_9 = a^0{}_9 - 8\ (-1)^1 2^1 = -16 + 16 = 0$).

The ground-state energy of the corresponding anion is calculated by weighting the highest roots of $P^{ac'}(x)$ (i.e., the lowest energy levels) by the 10 π_z electrons:

$$E^{ac'}(C_9H_3^-) = 15.6942$$

Using the total energy of the *carbo*-cyclopropenylide anion [$E^0(C_9H_3^-) = 15.8708$], the partial TRE value is obtained from eq. 7:

$$\mathrm{TRE}'(C_9H_3^-) = \mathrm{TRE}(8xC_9, C_9H_3^-) = E^0(C_9H_3^-) - E^{ac'}(C_9H_3^-) = 0.1766$$

The aromatic parent is the cyclopropenium cation, whose TRE value is given by (eq. 8) [22]:

$$\mathrm{TRE}(C_3H_3^+) = 2[1 - \cos(\pi/6)]/\sin(\pi/6) = 0.5359$$

The *carbo*-cyclopropenylide anion is thus three times less aromatic than the cyclopropenium parent.

For further comparison, the TRE value of the [9]annulenide anion $C_9H_9^-$ is given by eq. 8 [22]:

$$\mathrm{TRE}(C_9H_9^-) = E^0(C_9H_9^-) - E^{ac}(C_9H_9^-) = 2[1 - \cos(\pi/18)]/\sin(\pi/18) = 0.1750$$

The cyclyne structure is, therefore, just very slightly more aromatic than the corresponding cyclene structure.

TRE of carbo-benzene. Following the same principles as those set out for the *carbo*-cyclopropenylide anion (see Supplementary Information), the partial TRE for the 64 C_{18} macrocycles of the *carbo*-benzene graph (Fig. 8) reads

$$\mathrm{TRE}\ (C_{18}H_6) = 0.08906$$

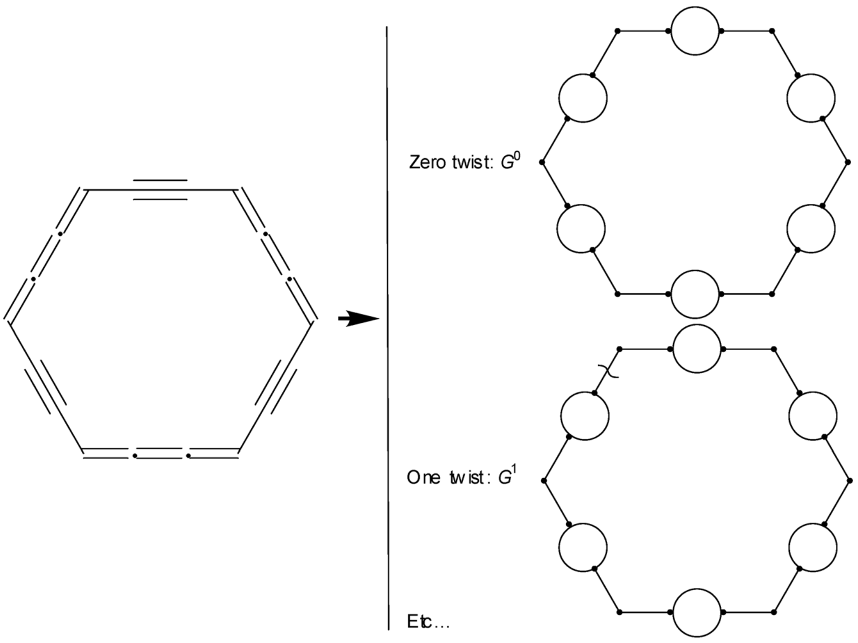


Fig. 8 The first Hückel and Möbius types of the 128 generalized graphs of *carbo*-benzene ($C_{18}H_6$). In the graph G^1 (twisted once on any of the 12 sp–sp^2 bonds), all the 64 C_{18} components are of Möbius-type.

Carbo-benzene is thus found to be very slightly more aromatic than the [18]annulene parent [TRE($C_{18}H_{18}$) = 0.08765], and three times less aromatic than benzene [TRE(C_6H_6) = 0.27259]. These variations are parallel to those observed for the *carbo*-cyclopropenylide anion.

Further prospects of the TRE of cyclynes. The above formalism can be applied to the partial TREs of the 2^n equivalent macrocycles of any *carbo*-[*n*]annulenic species. For *carbo*-cyclobutadiene and the *carbo*-cyclopentadienylium cation, the following values are obtained (see Supplementary Information):

TRE ($C_{12}H_4$) = – 0.4001

TRE ($C_{15}H_5^+$) = 0.1052

According to eq. 8, *carbo*-cyclobutadiene is, therefore, very slightly more antiaromatic than [12]annulene [TRE($C_{12}H_{12}$) = –0.3944], and three times less antiaromatic than cyclobutadiene [TRE(C_4H_4) = –1.2263]. Conversely, the *carbo*-cyclopentadienylium cation is very slightly more aromatic than the [15]annulenium cation [TRE($C_{15}H_{15}^+$) = 0.1048], and three times less aromatic than the cyclopentadienylide anion [TRE($C_5H_5^-$) = 0.3168]. These variations are thus basically identical to those observed for the aromaticity of the *carbo*-cyclopropenylide anion and *carbo*-benzene.

The formalism can also be used for other conjugated alkynes, and in particular for non-*carbo*-meric cyclynes. This challenge will be addressed in a future work.

In conclusion, the non-simple graph approach allows to generalize the concept of aromaticity to sp–sp bonds considered as "cyclic" C_2 components. It not only gives further consistency to the relationships between the energetic and magnetic criteria of aromaticity (local ring currents occur above sp–sp bonds; see Fig. 6), but also allows to distinguish between the aromatic characters of cyclynes and corresponding cyclenes by applying a graph-theoretical coupling between quasi-degenerate orthogonal π-systems.

EXPANDING THE RING CONTENT: FROM BENZENE TO CENTRO-SYMMETRIC CARBO-BENZENES

On the relative aromaticity of benzene and *carbo*-benzene

The prediction of the Hückel rule symmetry by even C_2-expansion of a π-conjugated ring has been systematically confirmed and refined at the theoretical level (using various methods, from HMO to post-HF, through DFT) for the ring *carbo*-mers of annulenes and heterocyclic versions [17,25,34]. This has been achieved by using aromaticity indices (REs and ASEs, MO analysis, GEO and HOMA, ^{1}H chemical shifts and NICS,...) [1], but also fundamentally suitable tools for each of the classical criteria of aromaticity: TRE calculation from a HMO projection of the molecular picture for the energetic criterion, ELF analysis of the electron density for the geometric criterion [34a], mapping of the ring current density for the magnetic criterion [32a] (Fig. 9).

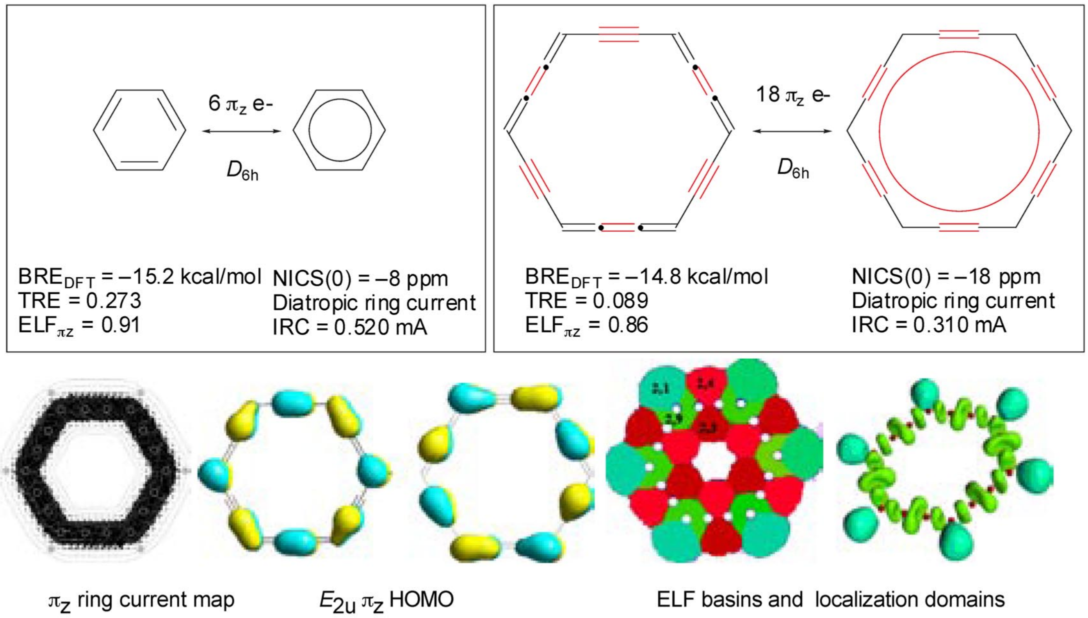


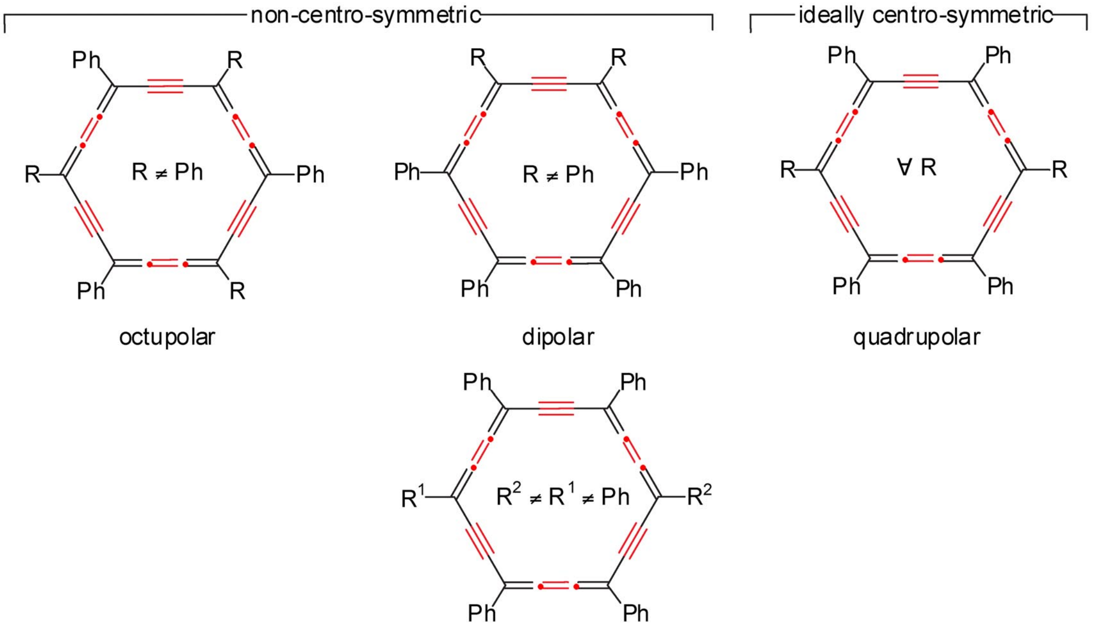
Fig. 9 Illustrative summary of theoretical results aiming at apraising the aromatic character of *carbo*-benzene according to the magnetic, energetic, and structural/electron density criteria.

These results clearly suggest that *carbo*-benzene is energetically and geometrically slightly less aromatic, but magnetically much more aromatic than benzene according to NICS. Although the two kinds of "static" and "dynamic" criteria have been proposed to vary independently [17,35], such a sharp orthogonality may appear somewhat provocative. However, whereas the size-dependence is explicit for magnetic measures, it is only implicit for energetic measures. For illustration, whereas the magnetic susceptibility exaltation is *directly proportional* to the surface area encompassed by the ring, the total energy depends in a concealed way on the total number of electrons occupying the MOs (the basic quantum effects operating differently in the reference structure). Several authors suggested to correct this complex size effect by dividing crude resonance energies (whatever the "de-cyclization" reaction scheme) by the number of electrons occupying the active π-MOs, thus defining resonance energies per electron (REPE), which were assumed to be more directly comparable for molecules of different size [10,12]. Similar normalization can also apply to magnetic measures. There is however no *a priori* requirement that "quantitative aromaticity" should be normalized to ring size, unless it has to be done for both energetic and magnetic measures. For example, the Breslow $REPE_{DFT}$ of benzene and *carbo*-benzene are equal to –15.2/6 = –2.53 and –14.8/18 = – 0.82 kcal/mol/e, respectively, while their respective NICS per electron are equal to –8/6 = –1.3 and –18/18 = –1.0 ppm/e. *Carbo*-benzene then becomes formally less aromatic than benzene for both criteria, but the loss of aromaticity remains higher for the energetic criterion than for the magnetic criterion. This illustrates how literary over-interpretations of quantitative aromaticity measures might be misleading.

The prediction of the Hückel rule was however also qualitatively confirmed at the experimental level for the benzene ring by the synthesis and characterization of a dozen of *carbo*-benzene or *carbo*$_2$-benzene derivatives [6,17]. *Carbo*-benzenes are generally less stable than their benzene parents, but their aromaticity is primarily revealed by the planarity of the C_{18} rings and by the—anyway—appreciable stability of the three formal dialkynyl butatriene edges appearing in their Kekulé structures. Details are published elsewhere [6,41,43,46], but a concise structural typology is proposed below.

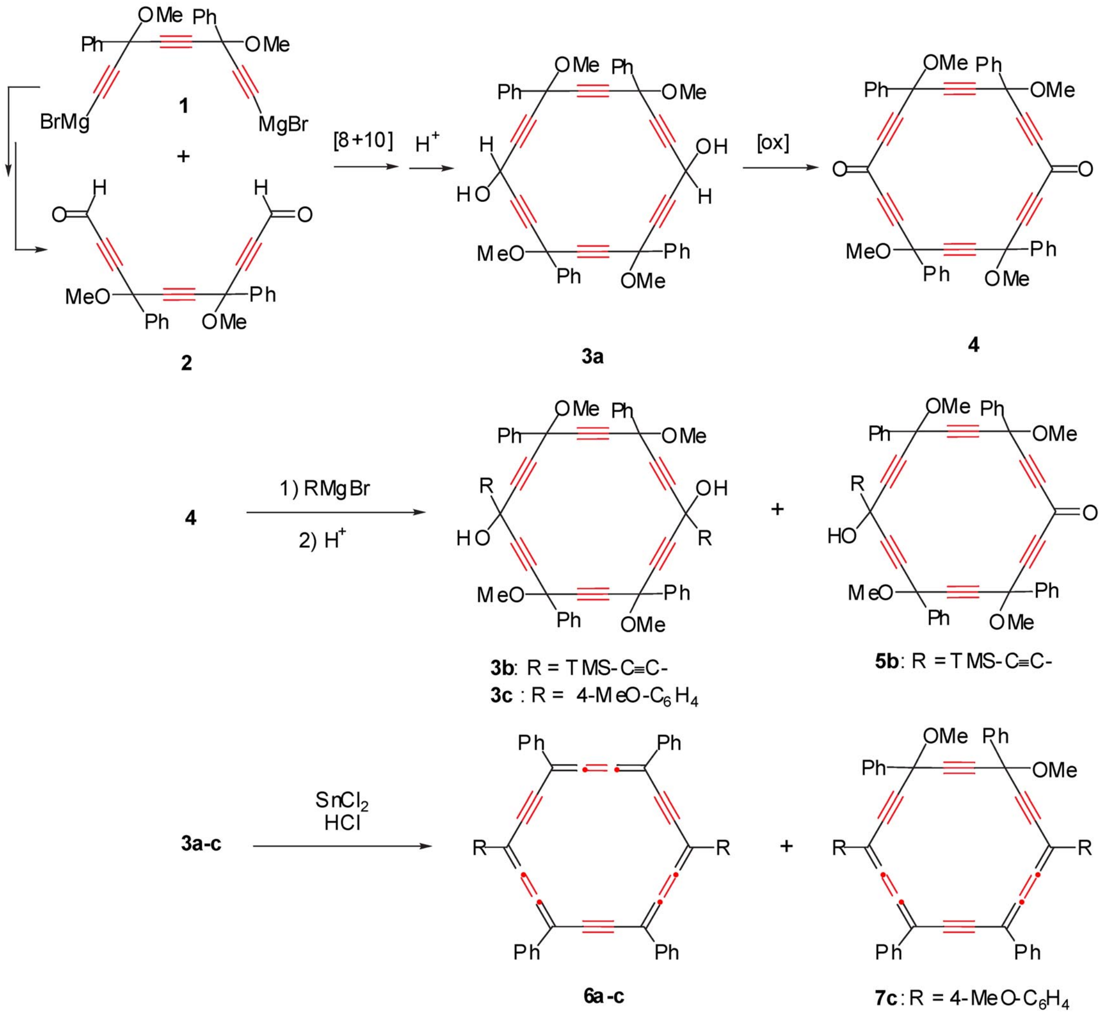
Multipolar typology of *carbo*-benzenes: A rationale for synthesis and properties

Two types of *carbo*-benzenes synthesized to date can indeed be distinguished according to the possible centro-symmetry of their substitution pattern (Scheme 11).



Scheme 11 Symmetry-based typology of the *carbo*-benzene derivatives synthesized to date with up to three different kinds of substituents.

The typology shown in Scheme 11 underlies not only the allowed physico-chemical—in particular, photophysical—properties, but also the allowed most convergent synthetic strategies based on optimal [(18 – n) + n] schemes for the C_{18} ring formation process of the [6]pericyclynic precursor. Non-centro-symmetric representatives may thus possess second-order nonlinear optical properties (sizeable quadratic hyperpolarizability β) [36], but require poorly convergent syntheses based on [11 + 7] and [14 + 4] schemes for octupolar [37] and dipolar representatives [38,39], respectively. In contrast, centro-symmetric representatives may only possess higher-order nonlinear optical properties (e.g., sizeable cubic hyperpolarizability γ) [40], and can be prepared more easily via a versatile [6]pericyclynedione precursor obtained by a [8 + 10] macrocycle formation process [38,41]. Although homoleptic hexaphenyl- and hexaalkynyl-*carbo*-benzenes could be alternatively obtained by [11 + 7] or [14 + 4] routes [37–39,42], the [8 + 10] strategy is particularly valuable for di-heteroleptic quadrupolar targets (Scheme 12). For comparison, whereas the pericyclynediol precursor **3b** of bis(trimethylsilylethynyl)-tetraphenyl-*carbo*-benzene **6b** was initially prepared via a [14 + 4] route in 12 steps [38], the same [6]pericyclynediol **3b** could be later obtained via the [8 + 10] route in 10 steps and the same 3 % overall yield [41]. The [6]pericyclynediol **3b** was produced by double addition of the corresponding Grignard alkynide to the [6]pericyclynedione **4**, itself prepared by optimized dioxidation of the [6]pericyclynediol **3a**. The key-intermediates **3a** and **4** were obtained and used as near-statistical mixtures of 14 and 5 diastereoisomers, respectively, and **4** could be henceforth considered as a potential versatile key-intermediate for a generic series of quadrupolar tetraphenyl-*carbo*-benzenes [41]. Reductive aromatization of **3a** and **3b** allowed to obtain tetraphenyl-*carbo*-benzene **6a** in 80 % purity to obtain, and pure dialkynyl-tetraphenyl-*carbo*-benzene **6b** in 10 % yield [39].



Scheme 12 [8 + 10] synthetic route to quadrupolar *carbo*-benzenes (TMS = $SiMe_3$).

The four phenyl substituents of the quadrupolar *carbo*-benzene derivatives **6** being kept as versatile reference π-conjugated substituents, their π-accepting vs. π-donating response is anticipated to be revealed by the corresponding π-donating vs. π-accepting character of the *para*-substituents R. Referring to the Q_{zz} maximal diagonal element of the quadrupole tensor (Fig. 10), the mesomeric flexibility of the phenyl substituents is illustrated by the quite high Q_{zz} value of hexaphenyl-*carbo*-benzene (Q_{zz} = –317 D.Å at the B3PW91/6-31G** level of calculation). According to the same criterion, the H and ethynyl substituents appear much less flexible ($Q_{zz}[C_{18}H_6]$ = –103 D.Å, $Q_{zz}[C_{18}(C_2H)_6]$ = –168 D.Å). The acidic character of sp^2-C–H and sp-C…C–H units are anticipated to induce π-donation toward the π-flexible phenyl groups by hyper-conjugation (C–H ↔ C:$^-$, H$^+$: the π-electrons being pushed away by the underlying negative σ-charge). And indeed, the quadrupole moment was calculated to be higher in the ideally C_2-symmetric tetraphenyl derivatives than in the corresponding nonphenylated D_{6h} or D_{2h} parent. The lateral donating character is maximized for R = OH or O$^-$ in the tetraphenyl-*carbo*-hydroquinone (Q_{zz} = –258 D.Å) or its dianion (Q_{zz} = –400 D.Å).

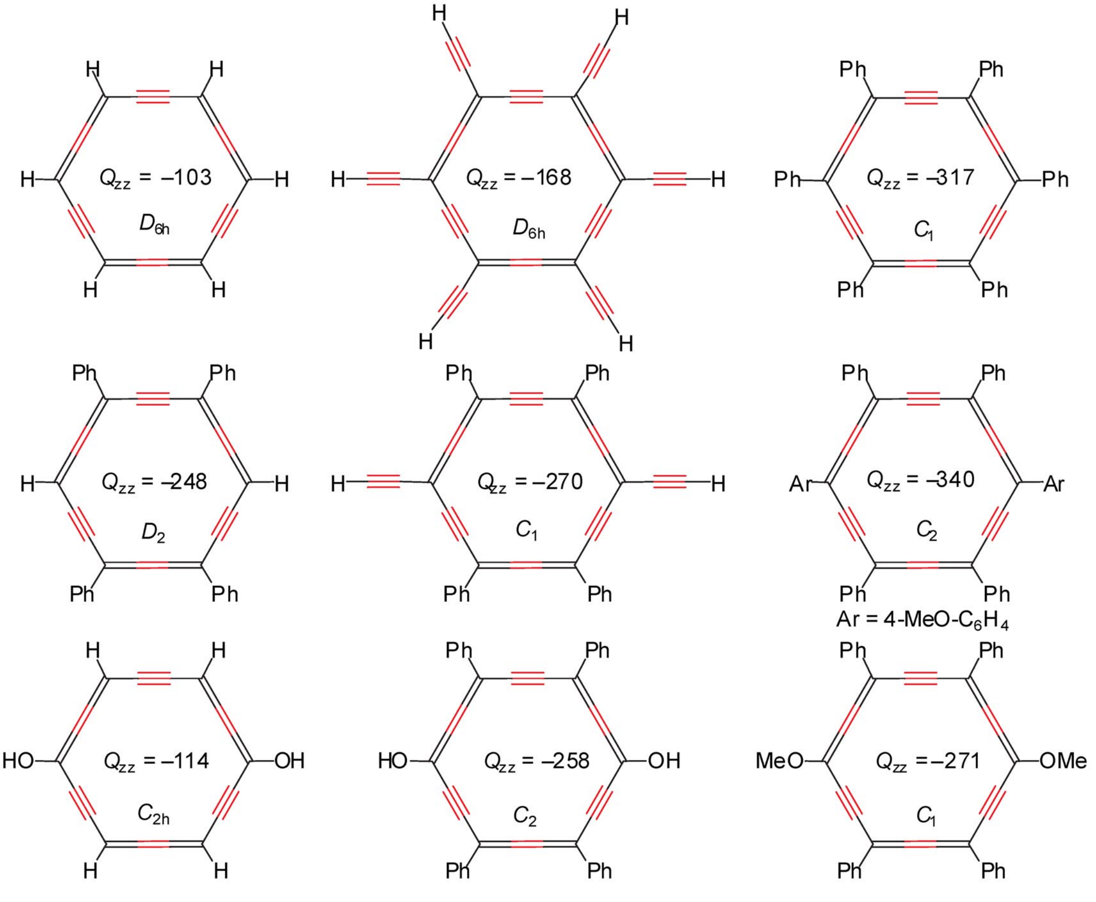
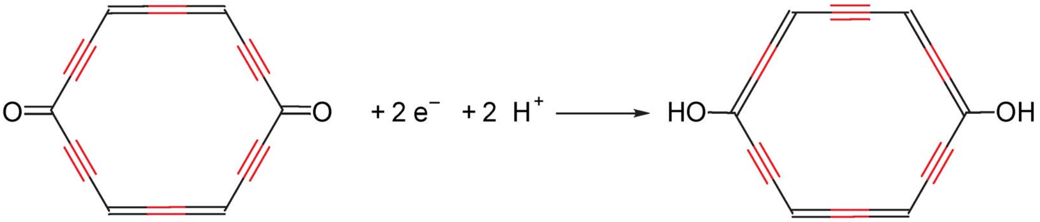


Fig. 10 Representative centro-symmetric *carbo*-benzenes and the corresponding maximum diagonal element Q_{zz} of the electric quadrupole tensor calculated at the B3PW91/6-31G** level (field-independent basis, in D.Å units). Geometry optimization was performed under the indicated symmetry constraints. Ar = *p*-anisyl group.

In all the examples of Fig. 10, the central *carbo*-benzene ring is expected to be intrinsically resistant towards π-donation, and thus plays the role of a passive transmitting bridge between the R and

Ph substituents. The *carbo*-benzene ring was indeed shown to behave as a full 18 π-electron reservoir, even masking the π-donor effect of an amino substituent in dipolar *carbo*-chromophores [25a]. This behavior is a consequence of the aromaticity of the *carbo*-benzene ring, but the situation is reversed for the challenging *carbo*-quinoid motif [43]. The latter indeed formally contains 16 endocyclic paired π-electrons, and, as a consequence of this antiaromatic character, is thus anticipated to act as a π-acceptor toward strong donor substituents such as dithiafulvenes [44]. In contrast, strong acceptor substituents such as carbonyl oxos are anticipated to provide the *carbo*-quinoid with oxidative reactivity. By comparison with the hydroquinone/benzoquinone redox system, the quadrupolar *carbo*-hydroquinone could thus be targeted by reduction of the putative *carbo*-benzoquinone. The *carbo*-meric redox system proved to be viable at the DFT level of theory (Scheme 13) [45], but attempts at preparing derivatives of either components failed hitherto.



Scheme 13 *Carbo*-meric version of benzoquinone/hydroquinone redox system.

En route to the challenging preparation of *carbo*-hydroquinone, the dianisyl phenylogue ether **6c** (R = 4-MeO–C_6H_4) was thus envisioned as a stabilized hexaaryl model thereof [46].

Synthesis of quadrupolar *carbo*-benzenes

Reaction of 2 equiv of 4-anisyl magnesium bromide with pericyclynedione **4** thus afforded the dianisyl-[6]pericyclynediol **3c** as a mixture of stereoisomers in 76 % yield. In view of preventing anisyl-directed polymerization, pericyclynediol **3c** was treated with $SnCl_2$/HCl at low temperature. An etheral solution of **3c** was thus treated with $SnCl_2$/HCl –78 °C, and the temperature was slowly increased up to –40 °C over 1 h. The resulting dark green mixture was then neutralized with aqueous NaOH (1 N at –40 °C), and extracted with diethylether. The combined organic layers were dried and evaporated to dryness, and the residue was purified by column chromatography over silica gel to give several chromophores, two of which could be identified.

The less polar product was a sparingly soluble golden solid (8 %), which on the basis of NMR, MS, IR, and electronic spectra proved to be the targeted dianisyl-tetraphenyl-*carbo*-benzene **6c**. The presence of the *carbo*-benzene macrocycle was confirmed by the characteristic absorption bands in the visible region (λ_{max} = 482 nm and λ = 525, 580 nm) and by the strongly deshielded *ortho*-^{1}H nuclei of the phenyl (δ = 9.46 ppm, d, $^3J_{HH}$ = 7.2 Hz) and anisyl substituents (δ = 9.41 ppm, d, $^3J_{HH}$ = 8.1 Hz). The latter chemical shifts are induced by the strong diamagnetic ring current of the *carbo*-benzene ring, which was shown to be the signature of its magnetic aromaticity.

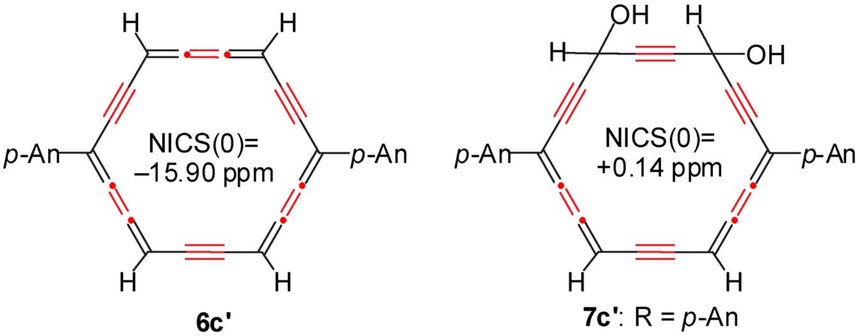
The less polar product was a much more soluble dark green solid (14 % yield). Full characterization by matrix-assisted laser desorption/ionization with time-of-flight mass spectrometry (MALDI-TOF MS) (*m*/*z* = 800.39) and NMR spectroscopy showed that its consisted in a 60/40 mixture of the *meso*/*dl* epimers of a partly reduced [6]pericyclyne macrocycle, which could be resolved by semi-preparative high-performance liquid chromatography (HPLC) techniques. By confrontation with DFT-calculated NMR and UV–vis spectra of the two possible regioisomers, the exact structure was assigned to the cyclohexadiene ring *carbo*-mer **7c** (Scheme 12), where the anisyl substituents are conjugated through two butatriene edges. The absence of a macrocyclic π-ring current in **7c** is revealed by the relative shielding of the *ortho*-^{1}H nuclei of the phenyl ($\delta = 7.93$ ppm, d, $^3J_{HH} = 8.0$ Hz) and anisyl substituents ($\delta = 7.75$ and 7.77 ppm, d, $^3J_{HH} = 9.0$ Hz) as compared to **6c**.

Prolonged treatment of a sample of pure **7c** with $SnCl_2$/HCl cleanly produced the *carbo*-benzene **6c**, thus showing that **7c** is an intermediate in the reductive aromatization of **3c**. Aromatization of hexaoxy-[6]pericyclynes indeed requires three steps, each of them being characterized by a two-electron reduction potential of a 1,4-dioxy-but-2-yne edge. Isolation of **7c** as major product thus suggests that while the second reduction would be favored with respect to the first one (the mono-butatriene product was not detected), the third reduction is relatively disfavored. Whereas aromaticity of **6c** could be *a priori* considered as a thermodynamic driving force for the final reduction step [47], the reduction of two conjugated edges adjacent to the anisyl substituents could thus be kinetically favored (at –40 °C) through the stabilization of the corresponding *carbo*-cationic intermediates.

The availability of both chromophores **6c** and **7c** provides a new key for a close analysis of the aromaticity of **6c**: the macrocyclicity of the π-conjugation in **6c** is indeed "minimally" interrupted in **7c** on single π-system and on a single edge only. A further analogy between **6c** and **7c** making them "structurally as close as possible except the macrocyclic π-topology" is provided by the quasi-quadrupolar character of both **6c** and **7c** (the dipole moment of **7c** is indeed of 0.68 D only). The redox equation "**7c** + $H_2 \rightarrow$ **6c** + 2 MeOH" is thus a relevant scheme for an accurate ASE estimate of **6c**. Using the zero-point corrected energies, calculation at the B3PW91/6-31G** level affords a significantly negative ASE_{DFT} value:

$$ASE_{DFT} = \Delta H°(0\ K) = ZPE(\mathbf{6c}) + 2\ ZPE(MeOH) - ZPE(\mathbf{7c}) - ZPE(H_2) = -42.85\ kcal/mol$$

Beyond the energetic criterion, the magnetic criterion shows that the *carbo*-benzene ring of **6c** is strongly aromatic while the *carbo*-cyclohexadiene ring of **7c** is definitely not. The conclusions brought by the relative magnetic shielding values (see above) are indeed confirmed by comparison of the calculated NICS values [1b] at the centroids of the rings for models **6c'** and **7c'** of **6c** and **7c**, respectively (Scheme 14): whereas **6c'** exhibits the classical diatropic signature of *carbo*-benzenes (NICS(**6c'**) = –15.90 ppm), its precursor **7c'** does not (NICS(**7c**) = +0.14 ppm).



Scheme 14 Models of the quadrupolar *carbo*-benzene **6c** (*left*) and *carbo*-cyclohexadiene **7c** (*right*) (see Scheme 12), illustrating (on the basis of the NICS(0) values [1b]) that the magnetic aromaticity of a *carbo*-benzene ring vanishes in the corresponding *carbo*-cyclohexadiene ring.

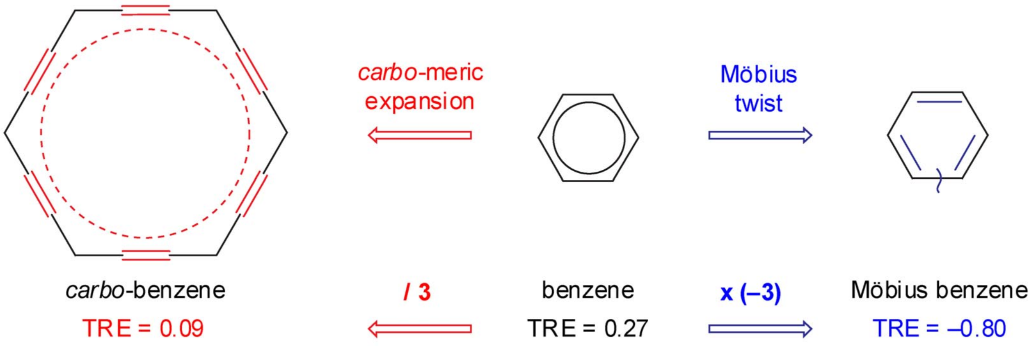
Inspection of the complementary structural criterion of aromaticity was hitherto hampered by a lack of suitable crystals of **6c** and **7c** for X-ray diffraction analysis. Insights into their structural features were thus gained by detailed analysis of their calculated structure at the B3PW91/6-31G** level. The structural aromaticity of the *carbo*-benzene ring is thus locally revealed by the relative fixation of the butatriene bonds in **7c** (sp^2–sp = 1.357, 1.355 Å, sp–sp = 1.249 Å) as compared to **6c** (sp^2–sp ≈ 1.380 Å, sp–sp ≈ 1.235 Å). Although the *carbo*-cyclohexadiene ring adopts a twist conformation, **7c** preserves significant conjugation between the butatriene units (with a dihedral angle of 18.1°), and between each butatriene and the adjacent anisyl ring (with a dihedral angle of 7.1°). This conjugation is ultimately responsible for the intriguing chromophoric properties of **7c**. Indeed, diluted solution of **7c** in various solvents ($CHCl_3$, CH_2Cl_2, Et_2O, pentane, toluene,…) display spectacular dichromism [48], oscillating between a turquoise-blue color for short optical paths and a bright purple color for deeper paths. The absorption spectrum of **7c** displays two sharp left-shouldered bands of equal intensities at 437 and 602 nm, that are accurately reproduced by ZINDO calculations (λ_{calcd} = 615, 433 nm). Detailed analysis by reference to previously reported data [48] shows that the dichromism phenomenon is due to the sharpness of the bathochromic band and to the complete transparency from 650 nm to the end of the visible region (700 nm).

Further studies of the fascinating couple of chromophores **6c** and **7c** are in progress and will be communicated in due course. It is henceforth worth noting that dianisyl-*carbo*-benzene *p*-$(4\text{-MeO-}C_6H_4)_2C_{18}H_4$ is the central ring *carbo*-mer of dianisyl-benzene, a stronger quadrupolar fluorophore than its terphenyl parent [49]. A rationale for the fluorescence properties of these terphenyl derivatives is based on the decrease of the local aromaticity of rings upon UV light-induced co-planarization [50]. Although the tetraphenyl derivative **6c** proved to be only very weakly fluorescent, conjugation with methoxy auxofluors could be a guideline for the design of other *carbo*-benzene derivatives with valuable photophysical properties.

CONCLUSION

The concepts of Möbius conversion and ring *carbo*-merization are symmetric in terms of qualitative effects on the Hückel rule. They have been addressed along different lines, which meet at two points regarding quantitative topological aromaticity.

i. If the sp-C_2 units of *carbo*-mers are considered as pseudo-rings, as it is allowed in chemical graph theory, formal consideration of the "Möbius version" of this units allows to calculate TRE values of conjugated cycloalkynes which are slightly different from those of the corresponding cycloalkenes. The discrimination has been illustrated for *carbo*-[*n*]annulenes and corresponding [3*n*]annulenes.
ii. The topological aromaticity of benzene is *divided by 3* in *carbo*-benzene, while it is *multiplied by –3* in "Möbius benzene" (Scheme 15) [51]. These two relationships also hold approximately for other annulenic species with an even-membered ring and even-type substituents only (see eq. 11 and ref. [52]). 3 is also the approximate factor of the ring size expansion upon *carbo*-merization.



Scheme 15 Quantitative parallel between the variations of topological aromaticity by twisting (*right*) and expanding (*left*) the ring content.

Whereas TRE is the abolute energetic measure of aromaticity in the topological limit (at the constant or variable β HMO level [23]), an ab initio version remains to be devised for real molecules [28a]. Moreover, although the tedious graph-theoretical calculation of TRE values is much simplified by considering the Hückel and Möbius molecular forms in eq. 14, a chemical RE scheme of TRE is still missing. Alternatively, an easy-to-calculate approximate TRE might also be defined from the empirical eqs. 12 and eq. 13, giving the acyclic reference energy E^{ac} in terms of the Hückel and Möbius energies (see Supplementary Information), but their values, though quite good, should remain less exact than those of TRE [9,10] and other topological approaches [53]. Efforts for improving chemical interpretation, calculation and use of TRE are in current progress. Parallel experimental investigations of *carbo*-benzenic chromophores provide a source of inspiration for extending and understanding the domain of nonclassical aromatic systems [54].

SUPPLEMENTARY INFORMATION

Analytical expressions of REs for [2*m*]annulenes. Variation of the cyclobutadiene TRE through the variable β HMO method. HMO calculations of the TRE of Hückel and Möbius ring (data for Fig. 5, eqs. 12 and 13b). Calculation of the TRE of *carbo*-cyclobutadiene. Calculation of the TRE of the *carbo*-cyclopentadienylium cation. Calculation of the TRE of *carbo*-benzene. Supplementary Information is available online (doi:10.1351/PAC-CON-09-11-07).

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