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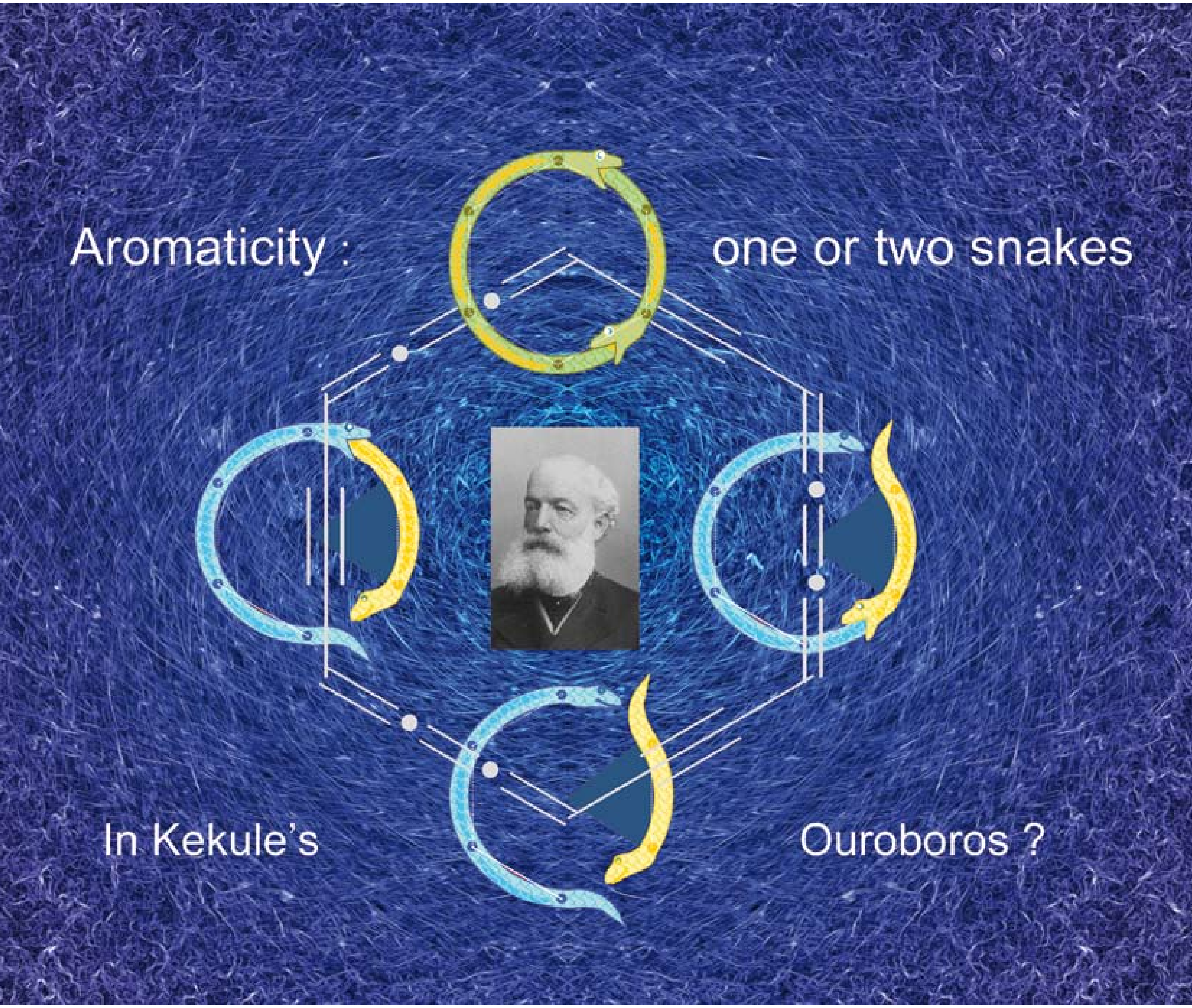

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Evaluating the cyclic π-electron delocalization energy through a double cut of conjugated rings

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The cutting of two bonds of a ring A⬭B allows us to define two closed-shell disconnected fragments A and B, and to evaluate the energy of the A⬭B molecule from the eigenstates of A and B by second-order perturbation theory in the framework of tight-binding/Hückel theory. Diagrammatic arguments allow identification of the properly cyclic π-electron delocalization contribution to the energy, which we denote ε_{cyc}(AB), and which can be simply expressed in terms of the energies of the cyclic molecule, its fragments and of the two singly bridged **A‿B** and **A⁀B** systems. The rules for the selection of suitable A and B fragments are given. The mathematical expression for ε_{cyc}(AB) can be translated into a chemical scheme that defines a new energetic aromaticity index, referred to as aromatic cyclic energy (ACE), which may be simply calculated from five Hückel energies. ACE of neutral and ionic [*N*]annulenes and their ring *carbo*-mers have been estimated, and shown to yield consistent evaluations of aromatic and antiaromatic cyclic energetic effects. A comparison is made with two other indices of aromaticity, Breslow resonance energies and ELFπ values.

1 Introduction

The concept of aromaticity[1] may be envisaged as a qualitative formulation of the connection between the existence of cycles in the molecular graph of a fully conjugated molecule and the properties of the whole molecule. These properties may be intrinsic or static.[2] Structural indices (bond length equalization),[3] specific patterns of electron density,[4] and the electronic energy of the π system,[1] all fall into this class. 6-electron 6-atom rings are stabilized whereas 4-electron 4-atom rings are destabilized, as explained in many basic textbooks. In contrast, other properties such the magnetic NMR chemical shifts and induced ring currents,[5] have been classified as dynamic properties,[2] since the application of an external perturbation, *i.e.* an external magnetic field, is necessary to reveal them.

Returning to the evaluation of (de)stabilization as a measure of (anti)aromaticity, we note that the definition has been much debated and, in fact, a large number of definitions in terms of ideal chemical reactions have been proposed, each of which may lead to a significantly different estimate. Some proposed reaction schemes are: isogyric,[6,7] isodesmic,[8] homodesmotic,[9] hyper-homodesmotic,[10] *n*-isoconjodesmic.[2] To avoid such ambiguities, one may ask whether it would be possible to make a direct evaluation of the ring-specific part of the electronic energy.

To answer that question, this paper therefore describes a general method for the estimation of the cyclic π-electron delocalization energy contribution applicable to any ring. The method proceeds through the partition of the ring A⬭B into two closed-shell fragments A and B, connection of which by two distinct bonds b_1 and b_2 builds the ring under consideration. Assuming that one may define a π-electron Hamiltonian and orthogonal fragment π orbitals on A and B, respectively, the method starts from the zeroth order picture, in which the wavefunction is an antisymmetrized product of ground-state functions of A and B. This zeroth order function gives an optimal treatment of the delocalization inside fragments A and B, without allowing inter-fragment delocalization. The latter effect is introduced by the existence of non-zero hopping integrals for the two bridging bonds between A and B. The inter-fragment delocalization energy appears as a second-order correction and can be decomposed into three components, namely:

(i) a delocalization through bond b_1 only, which would exist in the **A⁀B** open chain system.

(ii) a delocalization through bond b_2 only, which would exist in the **A‿B** open chain system.

(iii) a delocalization involving the two bonds b_1 and b_2.

It will be shown that it is term (iii) that expresses an energy associated with cyclic circulation of the electrons around the ring. Evaluation of the properly cyclic energy contribution can be performed by this perturbative approach. From the general analytic expression for this correction, a simplified approximate formulation of ε_{cyc}(AB) can be derived, involving the energies of the cyclic molecule and of the moieties resulting

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from single and double cuts of the ring. Making a *double* cut of the ring is therefore *required* for a proper estimate of the cyclic π-electron delocalization energy. This is in line with the intuitive description of a cycle A⬭B: in a cycle A communicates with B by distinct out and return routes (two cuts).

The energy $\varepsilon_{\text{cyc}}(\text{AB})$ can be translated into a chemical scheme defining a new energetic aromaticity index, ACE, which may be simply calculated from five Hückel energies. The ACE of neutral and ionic [*N*]annulenes and their ring *carbo*-mers will be estimated and compared to other energetic and structural aromaticity indices.

2 Double cutting for evaluation of the cyclic π-electron delocalization contribution to the energy

2.1 Principles

By cutting two π bonds of a cyclic conjugated molecule, two independent fragments A and B of a given A⬭B molecule may be defined. The cutting of the P_A–Q_B and R_A–S_B bonds (Fig. 1) is restricted to the π system and may be thus translated into a cancellation of the interactions between the valence 2p_z atomic orbitals of P_A and Q_B on the one hand, and R_A and S_B on the other. These atomic 2p_z orbitals are, respectively referred to as p_A, q_B, r_A and s_B.

In second quantization, the π-electron Hückel Hamiltonian expressed in terms of atomic orbitals *i*, *j*.., the hopping integral β_{ij} and creation and annihilation operators (a_i^+ creates an electron on site *i* and a_j annihilates an electron on site *j*) can be written

$$H = \sum_{i\in \text{AB}} \varepsilon_i a_i^+ a_i + \sum_{ij\in \text{AB}} \beta_{ij}(a_i^+ a_j + a_j^+ a_i) \tag{1}$$

and can be divided into three contributions as:

$$H = H_\text{A} + H_\text{B} + V_\text{AB} \tag{2}$$

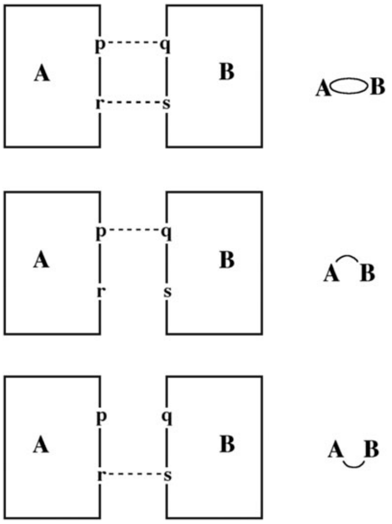


Fig. 1 Illustration of the fragmentation of a cyclic system A⬭B.

where H_A (H_B) is the π Hamiltonian of fragment A (B) of the molecular system. The interfragment operator V_AB is the sum of two on-bond operators:

$$\begin{aligned} V_\text{AB} &= V_{pq} + V_{rs} \\ V_{pq} &= \beta_{pq}(a_p^+ a_q + a_q^+ a_p) \\ V_{rs} &= \beta_{rs}(a_r^+ a_s + a_s^+ a_r) \end{aligned} \tag{3}$$

One may now approach the AB problem from the solutions for the separate fragments:

$$H_\text{A}\Psi_\text{A}^0 = E_\text{A}^0\Psi_\text{A}^0 \text{ and } H_\text{B}\Psi_\text{B}^0 = E_\text{B}^0\Psi_\text{B}^0 \tag{4}$$

where Ψ_A^0 is the antisymmetrized product of the occupied MOs $\varphi_{i\text{A}}$ for system A

$$\Psi_\text{A}^0 = \left|\prod_{i\text{A}} \varphi_{i\text{A}}\bar{\varphi}_{i\text{A}}\right|, \text{ with } H_\text{A}\varphi_{i\text{A}} = \varepsilon_{i\text{A}}\varphi_{i\text{A}}$$

and

$$\Psi_\text{B}^0 = \left|\prod_{i\text{B}} \varphi_{i\text{B}}\bar{\varphi}_{i\text{B}}\right|, \text{ with } H_\text{A}\varphi_{i\text{B}} = \varepsilon_{i\text{B}}\varphi_{i\text{B}} \tag{5}$$

Diagonalization of H_A and H_B also provides antibonding unoccupied MOs and their energies:

$$H_\text{A}\varphi_{i^*\text{A}} = \varepsilon_{i^*\text{A}}\varphi_{i^*\text{A}} \text{ and } H_\text{B}\varphi_{i^*\text{B}} = \varepsilon_{i^*\text{B}}\varphi_{i^*\text{B}} \tag{6}$$

Let us assume that we have a closed-shell system AB and that the fragments A and B are also of closed-shell character. The zero-order energy is then:

$$E_\text{AB}^0 = E_\text{A}^0 + E_\text{B}^0 = 2\left(\sum_\text{occ} \varepsilon_{i\text{A}} + \sum_\text{occ} \varepsilon_{i\text{B}}\right) \tag{7}$$

which is free from any cyclic effect in the A⬭B ring but incorporates exactly all π-electron delocalization effects inside A and inside B.

The second order energy correction $\varepsilon^{(2)}(\text{AB})$, accounts for π-electron delocalization between A and B through charge-transfer (CT) excitations *i*A → *j**B and *j*B → *i**A.

$$\varepsilon^{(2)}_{(\text{AB})} = 2\left(\sum_{i\text{A}}\sum_{j^*\text{B}} \frac{\langle\varphi_{i\text{A}}|V_\text{AB}|\varphi_{j^*\text{B}}\rangle^2}{\varepsilon_{i\text{A}} - \varepsilon_{j^*\text{B}}} + \sum_{j\text{B}}\sum_{i^*\text{A}} \frac{\langle\varphi_{j\text{B}}|V_\text{AB}|\varphi_{i^*\text{A}}\rangle^2}{\varepsilon_{j\text{B}} - \varepsilon_{i^*\text{A}}}\right) \tag{8}$$

The possibility of CT for both α and β electrons is responsible for the factor 2. Each integral in the numerator is the sum of the two integrals involving V_{pq} and V_{rs}, respectively.

$$\begin{aligned} \langle\varphi_{i\text{A}}|V_\text{AB}|\varphi_{j^*\text{B}}\rangle &= \langle\varphi_{i\text{A}}|V_{pq}|\varphi_{j^*\text{B}}\rangle + \langle\varphi_{i\text{A}}|V_{rs}|\varphi_{j^*\text{B}}\rangle \\ &= c_{i\text{A},p\text{A}}\cdot c_{j^*\text{B},q\text{B}}\cdot\beta_{pq} + c_{i\text{A},r\text{A}}\cdot c_{j^*\text{B},s\text{B}}\cdot\beta_{rs} \end{aligned} \tag{9}$$

where $c_{i\text{A},p\text{A}}$ is the coefficient of the atomic orbital p_A in the MO $\varphi_{i\text{A}}$ (and so on). Hence, the numerators involve four terms:

$$\begin{aligned} \langle\varphi_{i\text{A}}|V_\text{AB}|\varphi_{j^*\text{B}}\rangle\langle\varphi_{j^*\text{B}}|V_\text{AB}|\varphi_{i\text{A}}\rangle = {} & \\ \langle\varphi_{i\text{A}}|V_{pq}|\varphi_{j^*\text{B}}\rangle\langle\varphi_{j^*\text{B}}|V_{pq}|\varphi_{i\text{A}}\rangle & \\ + \langle\varphi_{i\text{A}}|V_{rs}|\varphi_{j^*\text{B}}\rangle\langle\varphi_{j^*\text{B}}|V_{rs}|\varphi_{i\text{A}}\rangle & \\ + \langle\varphi_{i\text{A}}|V_{pq}|\varphi_{j^*\text{B}}\rangle\langle\varphi_{j^*\text{B}}|V_{rs}|\varphi_{i\text{A}}\rangle & \\ + \langle\varphi_{i\text{A}}|V_{rs}|\varphi_{j^*\text{B}}\rangle\langle\varphi_{j^*\text{B}}|V_{pq}|\varphi_{i\text{A}}\rangle & \end{aligned} \tag{10}$$

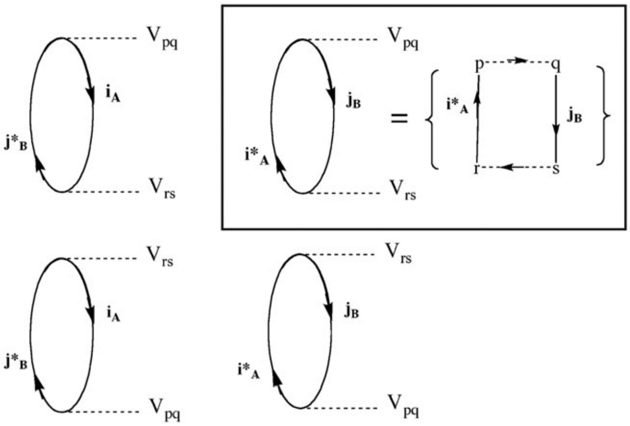


Fig. 2 Feynman diagrams illustrating the cyclic effects of eqn (10).

The first two terms involve back-and-forth charge transfers between $\varphi_{i\mathrm{A}}$ and $\varphi_{j^*\mathrm{B}}$ through a single channel, namely the *p*–*q* or the *r*–*s* bond. The last two terms are ring-specific and can be assigned to cyclic π-electron delocalization as the electron hops from $\varphi_{i\mathrm{A}}$ to $\varphi_{j^*\mathrm{B}}$ through one bond and returns through the other. The third term corresponds to a "true" clockwise circulation around the ring, and the fourth corresponds to a "true" circulation in the opposite sense.

For readers who are familiar with Feynman diagrams,[11] the cyclic effects are pictured in Fig. 2, together with their pictorial transcription. One sees there the electron hop from $\varphi_{i\mathrm{A}}$ on atom *r* to atom *s* in $\varphi_{j^*\mathrm{B}}$ and the return to atom *p* in $\varphi_{i\mathrm{A}}$ from atom *q* in $\varphi_{j^*\mathrm{B}}$. The intra-fragment movement from *r* to *p* and from *s* to *q* is ensured by the intra-fragment delocalization, *i.e.* the simultaneous presence of $\varphi_{i\mathrm{A}}$ at *p* and *r* and of $\varphi_{j^*\mathrm{B}}$ at *q* and *s* atomic orbitals.

Returning to eqn (8) and eqn (10) and in view of our remarks, one may write:

$$\varepsilon^{(2)}(\mathrm{AB}) = \varepsilon^{(2)}(\mathbf{A}\frown\mathbf{B}) + \varepsilon^{(2)}(\mathbf{A}\smile\mathbf{B}) + \varepsilon^{(2)}_{\mathrm{cyc}}(\mathrm{AB}) \qquad (11)$$

$$\text{where } \varepsilon^{(2)}(\mathbf{A}\frown\mathbf{B}) = 2\sum_{i\mathrm{A}}\sum_{j^*\mathrm{B}}\frac{\langle\varphi_{i\mathrm{A}}|V_{pq}|\varphi_{j^*\mathrm{B}}\rangle}{\varepsilon_{i\mathrm{A}}-\varepsilon_{j^*\mathrm{B}}} + \sum_{j\mathrm{B}}\sum_{i^*\mathrm{A}}\frac{\langle\varphi_{j\mathrm{B}}|V_{pq}|\varphi_{i^*\mathrm{A}}\rangle^{\varphi}}{\varepsilon_{j\mathrm{B}}-\varepsilon_{i^*\mathrm{A}}} \qquad (12)$$

is the π-electron delocalization energy between A and B through the *p*–*q* bond, and $\varepsilon^{(2)}(\mathbf{A}\smile\mathbf{B})$ is the π-electron delocalization energy through the *r*–*s* bond. The third term of eqn (11) is the cyclic contribution of the π-electron delocalization to the electronic energy and is then explicitly given by a sum over states, running over all A → B and B → A charge-transfer single excitations:

$$\varepsilon^{(2)}_{\mathrm{cyc}}(\mathrm{AB}) = 4\left(\sum_{i\mathrm{A}}\sum_{j*\mathrm{B}}\frac{\langle\varphi_{i\mathrm{A}}|V_{pq}|\varphi_{j*\mathrm{B}}\rangle\langle\varphi_{j*\mathrm{B}}|V_{rs}|\varphi_{i\mathrm{A}}\rangle}{\varepsilon_{i\mathrm{A}}-\varepsilon_{j*\mathrm{B}}} + \sum_{j\mathrm{B}}\sum_{i*\mathrm{A}}\frac{\langle\varphi_{j\mathrm{B}}|V_{pq}|\varphi_{i*\mathrm{A}}\rangle\langle\varphi_{i*\mathrm{A}}|V_{rs}|\varphi_{j\mathrm{B}}\rangle}{\varepsilon_{j\mathrm{B}}-\varepsilon_{i*\mathrm{A}}}\right) \qquad (13)$$

One may use

$$\varepsilon^{(2)}_{\mathrm{cyc}}(\mathrm{AB}) = 4\left(\sum_{i\mathrm{A}}\sum_{j*\mathrm{B}}\frac{c_{i\mathrm{A},p\mathrm{A}}\cdot c_{j*\mathrm{B},q\mathrm{B}}\cdot c_{i\mathrm{A},r\mathrm{A}}\cdot c_{j*\mathrm{B},s\mathrm{B}}}{\varepsilon_{i\mathrm{A}}-\varepsilon_{j*\mathrm{B}}} + \sum_{j\mathrm{B}}\sum_{i*\mathrm{A}}\frac{c_{j\mathrm{B},q\mathrm{B}}\cdot c_{i*\mathrm{A},p\mathrm{A}}\cdot c_{i*\mathrm{A},r\mathrm{A}}\cdot c_{j\mathrm{B},s\mathrm{B}}}{\varepsilon_{j\mathrm{B}}-\varepsilon_{i*\mathrm{A}}}\right)\beta_{\mathrm{pq}}\beta_{\mathrm{rs}} \qquad (14)$$

The expression for $\varepsilon^{(2)}_{\mathrm{cyc}}(\mathrm{AB})$ in eqn (14) calls for some comments:

(i) As shown in the Appendix, it can be proved that for neutral non-alternant cycles, a zero value of $\varepsilon^{(2)}_{\mathrm{cyc}}(\mathrm{AB})$ is expected.

(ii) $\varepsilon^{(2)}_{\mathrm{cyc}}(\mathrm{AB})$ (eqn (14)) was derived from a second-order perturbative expansion. The convergence of a perturbative expansion and the reliability of the low-order corrections depend on the quality of the zeroth order wave function and on the choice of the zeroth order Hamiltonian.

Regarding the role of higher-order corrections, one may notice that the third-order correction is zero since a determinant $\phi_{i\mathrm{A}j^*\mathrm{B}}$ interacts only through V_{AB} with determinants of the type $\phi_{j\mathrm{B}j^*\mathrm{B}}$ or $\phi_{i\mathrm{A}i^*\mathrm{A}}$ which do not interact with ϕ_0. Any further corrections are therefore of fourth order and are expected to be small in comparison to the second-order terms, justifying the truncation at second order.

A simpler formulation of $\varepsilon^{(2)}_{\mathrm{cyc}}(\mathrm{AB})$ can be obtained using the energy of the singly bridged systems $\mathbf{A}\frown\mathbf{B}$ and $\mathbf{A}\smile\mathbf{B}$, which can be approximated by:

$$\begin{aligned} E(\mathbf{A}\frown\mathbf{B}) &= E^0_{\mathrm{A}} + E^0_{\mathrm{B}} + \varepsilon^{(2)}(\mathbf{A}\frown\mathbf{B}) \\ E(\mathbf{A}\smile\mathbf{B}) &= E^0_{\mathrm{A}} + E^0_{\mathrm{B}} + \varepsilon^{(2)}(\mathbf{A}\smile\mathbf{B}) \end{aligned} \qquad (15)$$

Combining $E_{\mathrm{AB}} = E^0_{\mathrm{A}} + E^0_{\mathrm{B}} + \varepsilon^{(2)}(\mathrm{AB})$ and eqn (11), it follows that:

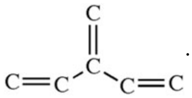
$$\varepsilon_{\mathrm{cyc}}(\mathrm{AB}) = E_{\mathrm{AB}} - E(\mathbf{A}\frown\mathbf{B}) - E(\mathbf{A}\smile\mathbf{B}) + E^0_{\mathrm{A}} + E^0_{\mathrm{B}} \qquad (16)$$

2.2 Criteria for the selection of the best double cut

For large rings, one may imagine various partitions into closed shell fragments A + B or A′ + B′ with $\mathrm{A}\bigcirc\mathrm{B} = \mathrm{A}'\bigcirc\mathrm{B}'$, the pairs of cut π bonds being different. As already pointed above, the validity of the perturbative approach is expected to be better for the partition yielding the lowest zero-order energy.

The best cut should therefore obey first *rule 1* based on the following criterion: the zeroth order energy $E^0_{\mathrm{A}} + E^0_{\mathrm{B}}$ should be as low as possible. In general, this will ensure that the energy differences involved in the denominators of eqn (13) are as large as possible. Thus, partition into two radical systems $\mathrm{A}^\bullet$ and $\mathrm{B}^\bullet$ should be avoided since one would have a singly occupied non bonding MO in $\mathrm{A}^\bullet$ ($\mathrm{B}^\bullet$) and so A → B* (B → A*) charge-transfer excitation energies would be formally zero.

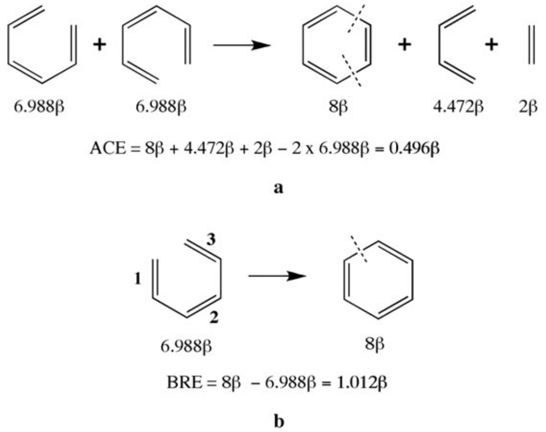
As a consequence of *rule 1*, the choice of the cut for charged species is straightforward. Electronic delocalization between strongly localized bond electron pairs is rather limited in neutral closed-shell molecules (which explains the relevance of the Lewis description of the electronic population), and even in conjugated molecules one obtains a reasonable estimate of the total energy starting from a localized Kekulé-type strongly localized wave function. In contrast, delocalization of charge in conjugated ions is significant. The appropriate cut for ionic species should define the largest possible charged fragment and the smallest possible neutral fragment, *i.e.* for a C_{2n+1} ion, the partition should be into the C_{2n-1} ion and a neutral C_2 fragment.

For double cuts with the same zeroth order energies, $E^0_A + E^0_B = E_{A'}{}^0 + E_{B'}{}^0$ (*e.g.* fulvene, see below), a second criterion, namely minimization of the non-cyclic next-nearest-neighbour interactions between bonds, should be invoked. It is known from perturbative expansions that the energy may be written as a sum of four terms: (i) bond energies, (ii) energies of interaction between nearest-neighbour bonds, (iii) increments accounting for the delocalization of the electrons from one bond to the next-nearest-neighbour bonds (involving back-and-forth movement of the electrons, but free from any cyclic movement), and (iv) higher-order increments arising from non-cyclic delocalization effects, of decreasing amplitudes, plus the cyclic effects. The next-nearest-neighbour increments are non-negligible (0.08β) for linear topologies of three bonds (C═C–C═C–C═C), but zero for a branched topology such as  . In order to identify the properly cyclic contribution to the energy, the difference between the number of non-zero next-nearest-neighbour interactions in both sides of eqn (16) should therefore be made as small as possible. This is *rule II*.

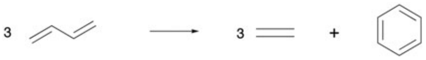
2.3 A new energetic aromaticity measure (ACE)

The properly cyclic π-electron delocalization contribution to the energy, $\varepsilon_{cyc}(AB)$, has been derived from a second-order perturbation treatment. As this energy arises from cyclic delocalization, it seems natural to suggest $\varepsilon_{cyc}(AB)$ as an aromaticity measure that we may call aromatic cyclic energy (ACE). The mathematical expression can be translated into a chemical reaction scheme involving, on the right-hand side, the aromatic molecule and its fragments resulting from the double cutting process, and, on the left-hand side, the acyclic isomers resulting from the corresponding single cuts. This equivalence is illustrated below for benzene (Scheme 1(a)). Only single C–C bonds are broken and the dangling valencies are terminated by H atoms so that the numbers of C–H and C–C bonds are conserved on each side of the chemical equation. Using the same resonance integral β for benzene and its fragments, ACE(C_6H_6) is easily estimated from five Hückel energies (Scheme 1(a))

It may be interesting to compare ACE values with Breslow resonance energy (BRE) values. The latter is an estimate derived from a single fragmentation of the aromatic ring (Scheme 1(b)). BRE is therefore the difference in π energy between the cyclic aromatic molecule and the corresponding acyclic isomer.[12–14]



Scheme 1 (a) Chemical reaction scheme with Hückel energies in β units used for the evaluation of ACE. (b) Breslow resonance energy (BRE) for benzene.



Scheme 2 Simplest homodesmotic ASE for benzene.

It is noticeable that ACE(C_6H_6) is only about half the corresponding BRE(C_6H_6). This difference is easy to understand, as BRE incorporates acyclic electron delocalization between bonds 1 and 3 (Scheme 1(b)), which does not appear in ACE.

ACE may also be considered as an aromatic stabilization energy (ASE) calculated from the homodesmotic[9] reaction Scheme 1(a). This is not the usual scheme for the calculation of ASE of benzene.[15] ACE is slightly lower than the ASE corresponding to the simplest homodesmotic reaction (Scheme 2) which amounts to 0.584β.[16] Again, this may be assigned to the equalization of the delocalization between nearest-neighbour bonds in Scheme 1(a) (ACE), but not in Scheme 2 (homodesmotic ASE).

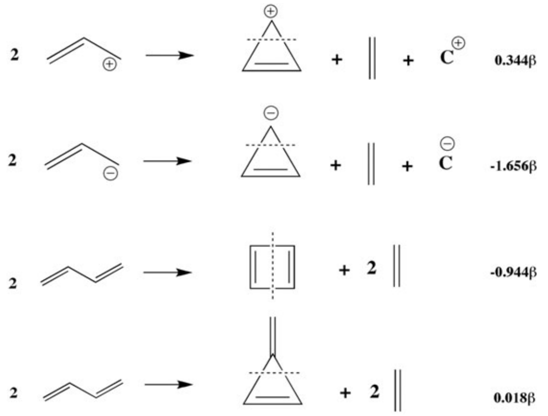
3 Application to [*N*]annulenes and their ring *carbo*-mers

3.1 [*N*]annulenes and selected isomers.

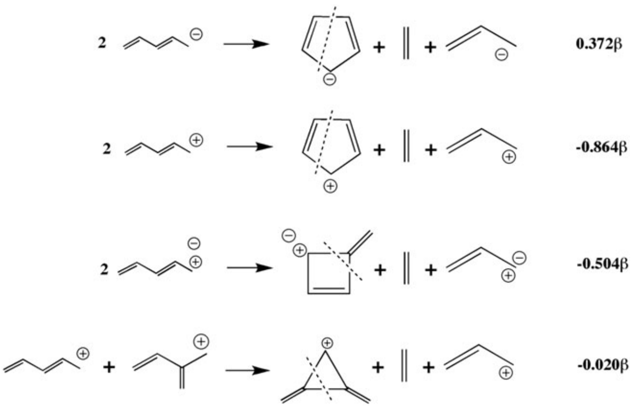
The same double cutting process was applied to the smallest [*N*]annulenes ($3 \leq N \leq 22$) and selected isomers. The corresponding ACE values are presented in Scheme 3, Scheme 4, Scheme5 and Scheme 6 and Table 1.

***N* = 3.** For $C_3H_3^+$ ($C_3H_3^-$), the fragmentation is uniquely to ethylene and a C^+ (C^-) ion (Scheme 3). The $C_3H_3^+$ cation ($C_3H_3^-$ anion) is thus predicted to be strongly aromatic (resp. anti-aromatic).

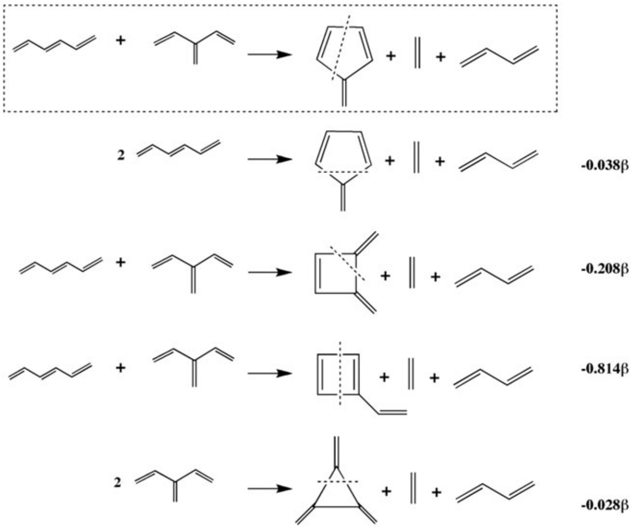
***N* = 4.** C_4H_4. There are again unique partitions for anti-aromatic cyclobutadiene (−0.944β) and the essentially non-aromatic methylene cyclopropene. The value of 0.018β estimated for the latter is small, though it still deviates from the zero value expected for neutral non-alternant cycles. The deviation of ACE from zero is an indication of the size of the high-order contributions that are left out of the second-order treatment.



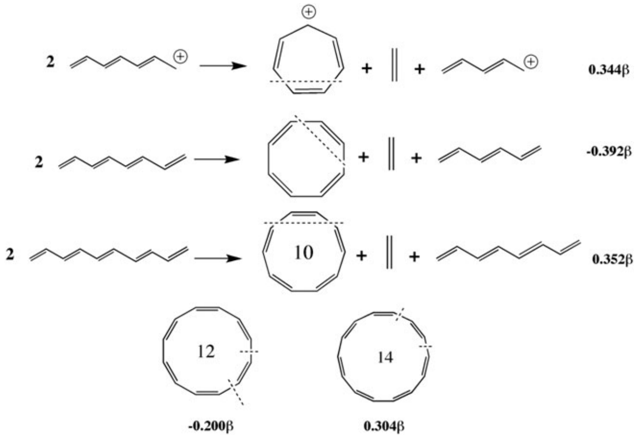
Scheme 3 ACE for the [3]- and [4]annulenes and methylene cyclopropene.



Scheme 4 ACE for [5]annulenes and some selected isomers.



Scheme 5 ACE for selected isomers of benzene. The partition appearing in the dotted frame is to be rejected, according to *rule II*.



Scheme 6 ACE for the [*N*]annulenes, $N = 7–14$

***N* = 5.** From *rule I*, requiring the more extended charge delocalization in the ionic fragment, the best partition of $C_5H_5^-$ ($C_5H_5^+$) yields the allyl anion (cation) and ethylene. Two inequivalent fragmentations into ethylene and an allyl cation (anion) may be considered for the four-membered ring isomer of $C_5H_5^+$, namely the 3-methylene cyclobutene cation (anion). From *rule II*, requiring the minimization of acyclic next-nearest-neighbour interactions, the fragmentation depicted in Scheme 4 is selected.

The three-membered ring isomer is the dimethylene cyclopropyl cation. It may be cut either into butadiene + C^+ cation

Table 1 BRE and ACE (in β units) for the first [*N*]annulenes, $N = 3–22$ and some selected isomers

Compound		BRE/β	ACE/β
[*N*]annulene C_NH_N			
$C_3H_3^+$		1.172	0.344
$C_3H_3^-$		−0.828	−1.656
C_4H_4		−0.472	−0.944
$C_5H_5^-$		1.008	0.372
$C_5H_5^+$		−0.228	−0.864
C_6H_6		1.012	0.496
$C_7H_7^+$		0.934	0.344
C_8H_8		0.140	−0.392
$C_{10}H_{10}$		0.888	0.352
$C_{12}H_{12}$		0.336	−0.200
$C_{14}H_{14}$		0.844	0.304
$C_{18}H_{18}$		0.812	0.266
$C_{22}H_{22}$		0.814	0.278
***carbo*-[*N*]annulene $C_{3N}H_N$**			
$C_9H_3^-$		0.888	0.314
$C_{12}H_4$		0.336	−0.200
$C_{15}H_5^+$		0.826	0.272
$C_{18}H_6$		0.812	0.266
$C_{21}H_7$		0.796	0.244
C_4H_4 isomers			
$C_3H_2(CH_2)$	Methylene cyclopropene	0.49	0.018[a]
$C_5H_5^+$ isomers			
$C_4H_3(CH_2)^{+(-)}$	3-Methylene cyclobutene cation (or anion)	0.132	−0.504
$C_3H(CH_2)_2^+$	Dimethylene cyclopropenyl cation	0.614	−0.020
C_6H_6 isomers			
$C_5H_4CH_2$	Fulvene	0.478	−0.038[a]
$C_4H_2(CH_2)_2$	3,4-Dimethylene cyclobutene	0.308	−0.208
$C_4H_3(CHCH_2)$	Vinylcyclobutadiene	−0.298	−0.814
$C_3(CH_2)_3$	3-Radialene	0.4	−0.028[a]
C_8H_8 isomers			
$C_7H_6CH_2$	Methylene cycloheptatriene	0.470	−0.062[a]

[a] Non-alternant cycles, where the true aromatic cyclization energy is expected to be zero

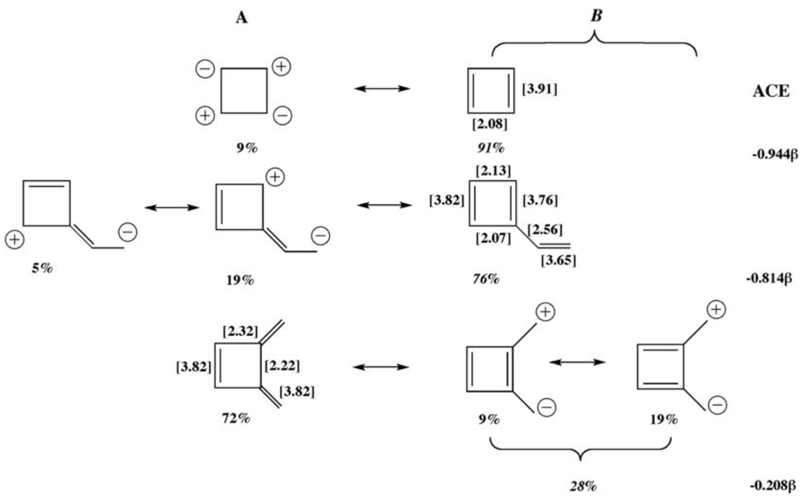


Fig. 3 Lewis structures weighted by ELF analysis (ELF scaled populations in brackets). B3PW91/6-31G** level of calculation. The weights of structures B (italic) are linearly correlated to the corresponding ACE values (bold).

or into ethylene + allyl cation. By *rule I*, the latter partition is selected.

***N* = 6.** C_6H_6. Benzene was already discussed above (Scheme 1(a)). Two inequivalent fragmentations of fulvene (the five-membered ring isomer of benzene) into ethylene and butadiene may be envisaged. By *rule II*, the second one is the best (Scheme 5). The deviation of ACE (fulvene) from the expected zero value is again related to non-negligible high-order contributions.

By *rule II*, the best partition of 3,4-dimethylene cyclobutene (a four-membered ring isomer of benzene) yields ethylene and butadiene and corresponds to a large positive ACE value (β being of course negative) (Scheme 5). Only one fragmentation is possible for vinylcyclobutadiene, yielding an ACE value of -0.814β that is unsurprisingly close to that of the cyclobutadiene parent.

[3]radialene is the cross-conjugated isomer of benzene. The unique partition into ethylene and butadiene yields an ACE value close to the expected zero value. This is in good agreement with ring-current analysis.[17]

From the comparison of Scheme 4 and Scheme 5, it is noticeable that the aromaticity of the four-membered rings may vary within a wide range depending on the total charge and on the endo- or exocyclic position of the conjugated double bonds. This aspect has already been investigated for three-membered cycles such as [3]radialenes.[18]

ACE of vinylcyclobutadiene is close to that of the cyclobutadiene parent, whilst the values for 3,4-dimethylene cyclobutene and 3-methylene cyclobutene cation are indicative of lower antiaromaticity. This can be related to the resonance picture of Fig. 3 where the weight of the cyclobutadiene Lewis structure B is variable: the larger the weight of the B structure, the larger the antiaromaticity. These weights can be estimated by *ab initio* or DFT calculation using the electron localization function (ELF). ELF analysis of the above compounds was performed at the B3PW91/6-31G** level. The relative weights of the Lewis structures can be estimated from the populations of the ELF basins.[19] The weights of the cyclobutadiene Lewis structures B (right side of Fig. 3) are in good agreement with the corresponding ACE values.

***N* = 7–14.** ACE values of larger [*N*]annulenes, $N = 7$–14, are reported in Table 1 and depicted in Scheme 6 with reaction schemes.

3.2 *Carbo*-[*N*]annulenes

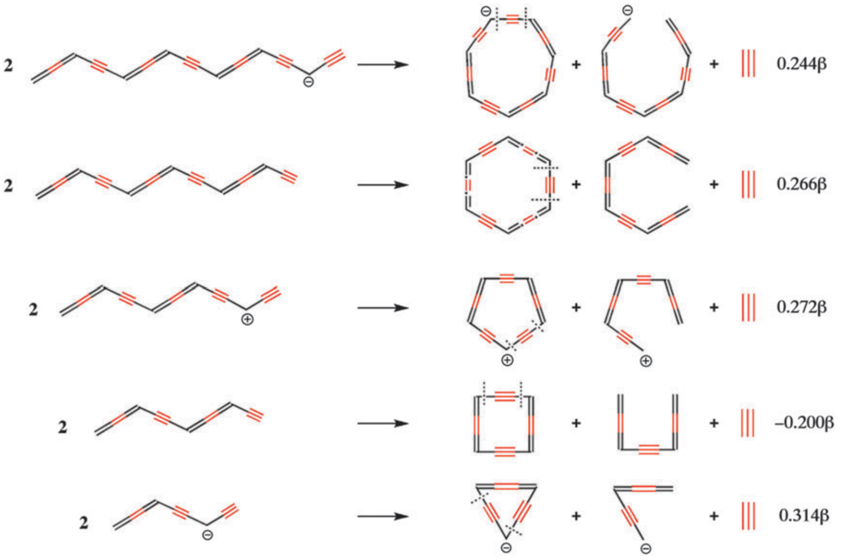
ACE was further investigated for *carbo*-[*N*]annulenes, $N = 3$–7. The out-of-plane π_z aromaticity of [*N*]annulenes ($3 \leq N \leq 6$) has been shown to be preserved in their ring *carbo*-mers, as judged on the basis of the Breslow resonance energy (BRE).[14,20] It appears attractive to test ACE on this series involving sp hybridized carbon atoms in the aromatic ring. The previously reported series has been completed here by $C_{21}H_7^-$ ($N = 7$).[14] The structure of D_{7h} symmetry calculated at the B3PW91/6-31G** level exhibits C–C bond length (1.372 Å, 1.240 Å) close to the one obtained at the same level of calculation for *carbo*-benzene $C_{18}H_6$ (1.369 Å, 1.239 Å).[20]

ACE values describing the out-of-plane π_z aromaticity of *carbo*-[*N*]annulenes are identical to those of the corresponding [3*N*]annulenes. ACE values are given in Table 1 and are depicted on Scheme 7. They are in good agreement with the previous classification of the series in terms of out-of-plane aromaticity. $C_9H_3^-$ is the most aromatic while the aromaticity of *carbo*-benzene is close to the one of *carbo*-cyclopentadienylium but lower than the one of benzene.[2]

3.3 Comparison with Breslow resonance energy

As already outlined, ACE is lower than BRE but is expected by construction to be closer to the 'true' cyclisation energy. A closer examination shows that indeed both indices are linearly correlated (Fig. 4) in the case of cyclic compounds of Table 1:

However, the C_3H_3 cation (and anion) do not conform to this linear correlation. Their ACE value(s) may be biased because they result from fragmentations involving C^+ (C^-), and therefore fail to satisfy rule I.



Scheme 7 ACE of *carbo*-[*N*]annulenes ($N = 3$–7): out-of-plane aromaticity.

In the Breslow reaction scheme (as illustrated in Scheme 1(b) for benzene), there is one nearest-neighbour interaction more in the ring than in the acyclic reference. This results in an overestimation of the cyclic π-electron delocalization energy by the typical delocalization energy between nearest-neighbour bonds, which is about 0.5β according to a second-order perturbative estimate. The π typical energy per bond in a long polyene tends to 0.63β Both latter values are indeed close to the 0.575β value obtained in the above correlation. BRE can therefore be expected to overestimate energetic aromaticity by a constant of about this magnitude. It is also noticeable that in the case of non-alternant cycles, ACE performs much better than BRE. Unlike the latter, it takes values close to zero.

Fig. 5 illustrates the smooth behaviour of ACE for aromatic as well for antiaromatic large [*N*]annulenes. Similar trends have been reported for other energetic aromaticity indexes[21] and for the ring currents in large [$4n + 2$] annulenes.[22]

ACE performs therefore better than BRE, which does not converge to zero for infinite [*N*]annulenes.

3.4 Comparison with ELFπ

Recently, Santos *et al.* defined a new aromaticity scale based on the separation of the electron localization function (ELF) into σ and π contributions.[23] The partial ELF (σ or π) value for which the separation of the localization domains of the fully unsaturated ring occurs, is chosen as the (σ or π) aromaticity index. Benzene (ELFπ = 0.91) lies almost at the top of this aromaticity scale ranging from zero to one (ELFπ ≈ 1.00 is attained for the cyclopropenyl cation). *Carbo*-benzene, with ELFπ*z* = 0.86, appears to be slightly less aromatic than its parent molecule.[2] It is interesting to compare ACE values with the corresponding ELFπ values since both indices are expected to describe π-aromaticity. ELFπ values of some [*N*]annulenes and their ring *carbo*-mers are reported in Table 2 and illustrated in Fig. 6. A good linear correlation of both indices is achieved once ACE is scaled by the ratio of the

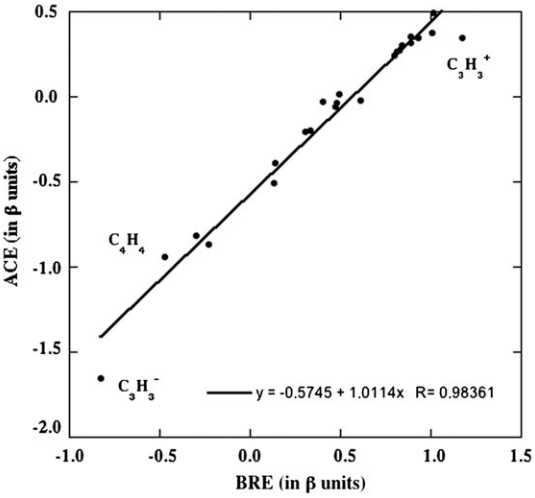


Fig. 4 Comparison of ACE and BRE for cyclic compounds of Table 1.

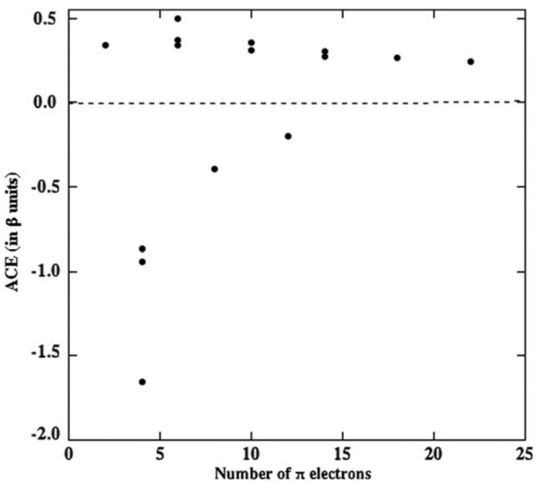


Fig. 5 ACE profile of [*N*]annulenes depending on the number of π electrons.

Table 2 Comparison of ACE with ELF of [*N*]annulenes and their *carbo*-mers

Compound	ACE/β units	ACE*$Nc/Ne\pi/\beta$ units	ELF π
$C_3H_3^+$	0.344	0.516	1.00
$C_3H_3^-$	−1.656	−1.242	—
C_4H_4	−0.944	−0.944	0.11
$C_5H_5^-$	0.372	0.310	0.82
$C_5H_5^+$	−0.864	−1.080	—
C_6H_6	0.496	0.496	0.91
$C_7H_7^+$	0.344	0.401	0.94
C_8H_8	−0.392	−0.392	0.35
$C_{10}H_{10}$	0.352	0.352	0.89
$C_{12}H_{12}$	−0.200	−0.200	—
$C_{14}H_{14}$	0.304	0.304	—
$C_9H_3^-$	0.314	0.283	0.80
$C_{12}H_4$	−0.200	−0.200	0.44
$C_{15}H_5^+$	0.272	0.291	0.895
$C_{18}H_6$	0.266	0.266	0.86
$C_{21}H_7$	0.244	0.233	0.836

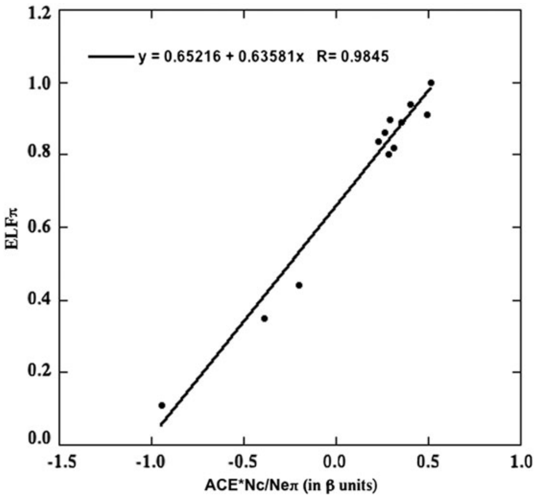


Fig. 6 Correlation of scaled ACE of [*N*]annulenes and their *carbo*-mers with corresponding ELFπ.

number of carbon atoms of the ring (*N*c) to the number of π-electrons (*N*eπ).

4 Extension to *ab initio* or DFT level of calculation

Two possible extensions of this work at the *ab initio* or DFT calculation level may be envisaged. The first might involve an *ab initio* transcription of the above Hückel approach, and the second would rely on the ACE chemical reaction scheme.

4.1 *ab initio* transcription of the Hückel approach

In the first approach, we would consider the cyclic molecule only in its equilibrium geometry and define first a set of π valence MOs, both bonding and antibonding. This could be accomplished in two different ways, either by a π Complete Active Space Self Consistent Field (CASSCF) calculation on the ground state, or by calculating the upper multiplet with all π-electrons with parallel spins. The latter solution may in principle be performed with the exact Hamiltonian or in a density functional theory approximation. In practice, the highest multiplet is too high in energy and the SCF process is expected to converge to spurious solutions.

In both cases, one has defined an optimal set of valence MOs which may be transformed into a set of π orthogonal atom-centered orbitals (OAO). The CAS may be expressed in the basis of the corresponding orthogonal valence bond (OVB) determinants, written as antisymmetrized products of the core by products of *n* π OAOs. One may rewrite the CASCI matrix in the basis of the OVB determinants. This matrix will be equivalent to that of a Pariser–Parr–Pople full CI matrix. If one puts to zero the matrix elements between the determinants that are coupled by a charge-transfer operator $\beta_{pq}(a_p{}^+a_q + a_q{}^+a_p)$, one cuts the effect of the circulation on the bond *pq*, and one obtains the energy of an open structure in the geometry of the closed ring, with an untouched σ system. Suppressing the interactions on both the *pq* and the *rs* bonds one obtains the energy of a doubly cut π-system. This would be the *ab initio* transcription of our above Hückel development. Such deletions of off-diagonal matrix elements have been used recently in a similar context by Bao and Yu, although they also perform an apparently undesirable subsequent geometry optimization.[24]

4.2 ACE chemical reaction scheme

The energy of the reaction depicted in Scheme 1(a) to define ACE (benzene) was estimated above in the Hückel framework. It may also be estimated at the *ab initio* or DFT level. The most stable all-*trans* conformation of hexatriene of C_{2h} symmetry was used to calculate ACE for benzene at the B3PW91/6-31G** level.

Table 3 compares various ASE for benzene calculated at the B3PW91/6-31G** level. In agreement with the results obtained within the simple Hückel framework, ACE is comparable to but slightly lower than the other ASE, such as the isogyric and homodesmotic ASE already reported at this level of calculation.[7] It is, however, very close to the hyper-homodesmotic ASE value, which is expected to give a good quantification of the aromaticity, and moreover,

Table 3 Comparison of various ASE for benzene calculated at the B3PW91/6-31G** level

ASE type	Reaction scheme	ASE/kcal mol^{-1}	ASE$_{ZPE}$/kcal mol^{-1}
Isogyric	Hexatriene → Benzene + H_2	−17.9	−23.0
Homodesmotic	3 Butadiene → Benzene + 3 ethylene	−23.5	−24.6
ACE	2 Hexatriene (C_{2h}) → Benzene + butadiene + ethylene	−21.1	−21.5
Hyper-homodesmotic	3 hexatriene (C_{2h}) → Benzene + 3 butadiene	−19.9	−20.0
		−22.5[b]	−19.3[a]

[a] Calculated at B3LYP/6-311+G** level, from ref. 15. [b] Experimental value, from ref. 15.

is in good agreement with the corresponding experimental data.[15]

5 Computational details

Most of the arguments and quantitative illustrations make use of the simple Hückel method. In the DFT calculations (Fig. 3 and Fig. 6 and section 4.2), geometries were optimized under symmetry constraints whenever possible at the B3PW91/6-31G** using Gaussian03.[25] Vibrational analysis was performed at the same level of calculation as the geometry optimization in order to check that a minimum was obtained on the potential energy surfaces and to extract zero-point corrections. ELF analysis was performed with the TopMoD program.[26]

6 Conclusions

The concepts of (anti)aromaticity were originally introduced in relation to the larger (in)stability of fully conjugated ($4n + 2$)-membered or ($4n$)-membered hydrocarbon rings. These concepts has been extended to heterocycles and charged species, and supported by many criteria. However the basic interpretation is energetic. The π-electronic energy should exhibit a specific delocalization term, which is connected to the cyclic circulation of the π electrons around the ring. The present paper has proposed a method to trace and evaluate this specific energy contribution.

It may be relevant here to refer to the famous dream of Kekulé, envisioning the benzene ring as the mythological Ouroboros snake. The Breslow resonance energy is consistent with this single snake picture, while our aromatic cyclic energy suggests the ring as two snakes, each swallowing the tail of the other.

We actually have considered the ring as built from a double bridge between two closed-shell conjugated fragments. A simple second-order perturbative approach has enabled us to identify the part of the inter-fragment delocalization energy that reflects the clockwise and anti-clockwise circulation of the electrons through the two bridging bonds. This development, which establishes a direct connection with the ring current, yields a very simple relation where the properly cyclic contribution is obtained as the difference between the energy of the ring A⬭B plus that of the doubly cut system A + B minus the energies of the singly cut systems, $\mathbf{A}\frown\mathbf{B}$ and $\mathbf{A}\smile\mathbf{B}$. We have called the resulting evaluation of the cyclic energy contribution ACE.

The method might be applied at the *ab initio* level by deletion of off-diagonal elements of the Fock matrix, but we have tested its relevance in the simple topological Hückel model. The results are very consistent and correlate nicely with other aromaticity indices, energetic or related to the electron density. The ACE definition may be translated into a new homodesmotic aromatic stabilization energy, which has been estimated at the DFT level for benzene.

Rules have been formulated to decide for the best double cutting. They are based on rational criteria, the sum of the energies of the fragments should be as low as possible. Our proposal eliminates the non-cyclic part of the inter-fragment energy which is present in the Breslow resonance energy (BRE). In an optimal evaluation of the cyclic energy, the non cyclic delocalization energy between next-nearest-neighbour double bonds (which are small) should vanish. We have proposed to minimize their influence in the choice of the double cutting, without suppressing them entirely. Further work will show how to eliminate this small defect.

7 Appendix

It will be shown that $\varepsilon^{(2)}_{\text{cyc}}(\text{AB})$ is expected to be zero for neutral non-alternant (*i.e.* odd) cycles. Let us focus on the relative contributions of A → B and B → A charge-transfer effects, which appear, respectively in the first and second sums of eqn (14). Let us also recall that an alternant hydrocarbon is such that one may divide its sites in two subsets (o and *) such that the nearest neighbours of any site o (*) all belong to class * (o). If the fragments A and B are both alternant hydrocarbons, and if the bonds p–q and r–s are symmetrically related in the AB system, the two sums have the same amplitude but may either reinforce or cancel. By the pairing theorem,[27] the occupied and virtual MO energy levels of an alternant hydrocarbon take equal and opposite values and the coefficients of virtual MOs are obtained from those of the corresponding occupied MO by changing the signs for all sites of one subset. Returning to the partition scheme of Fig. 1, if p and r belong to the same subset, then $c_{i\text{A},p\text{A}}c_{i\text{A},r\text{A}} = c_{i^*\text{A},p\text{A}}c_{i^*\text{A},r\text{A}}$ whereas if p and r belong to different subsets, $c_{i\text{A},p\text{A}}c_{i\text{A},r\text{A}} = -c_{i^*\text{A},p\text{A}}c_{i^*\text{A},r\text{A}}$. The same holds for atoms q and s. In eqn (14), it is therefore apparent that the two sums will add if *either* the bridging atoms belong to the same subset in both fragments *or* p and q belong to distinct subsets in both fragments. Conversely, they will cancel if the bridging atoms belong to the same subset in one fragment and different subsets in the other. The latter case is related to neutral non-alternant cycles, for which a zero value of $\varepsilon^{(2)}_{\text{cyc}}(\text{AB})$ is therefore expected.

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