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Non-additivity of the static correlation energy of π-electrons in planar molecules as a manifestation of anti/aromaticity[†]

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ABSTRACT: The non-dynamic or static correlation energy of π-electrons, $E(\mathrm{ND})^{\pi}$, was studied in a number of cyclic organic molecules, including various heteroatomic systems, employing CASSCF$^{\pi}$ formalism. It is shown that $E(\mathrm{ND})^{\pi}$ is highly additive in linear polyenes. However, interesting non-additivities are found in anti/aromatic molecules. They are seemingly counterintuitive since $E(\mathrm{ND})^{\pi}$ is smaller in aromatic compounds than in the corresponding open-chain polyenes. The opposite takes place in antiaromatic systems. However, they are easily understood if it is taken into account that the HF HOMO–LUMO gaps are higher in aromatic and lower in antiaromatic molecules compared with reference zig-zag polyenes. The results of the present analysis confirm that anti/aromaticity is an excess or depletion feature, meaning that deviations of $E(\mathrm{ND})^{\pi}$ from additivity are a direct consequence and clear manifestation of anti/aromaticity. It is argued that anti/aromaticity is necessarily a multifaceted phenomenon, since each molecular property probes different portions of the electron density distribution and/or a ladder of the molecular orbital energy levels, thus leading to distinct scales of anti/aromaticity. Each of these scales is useful in its own right. However, the most important scale is based on homodesmotic reactions, since they are directly related to thermodynamic in/stability and consequently to the omnipresent chemical reactivity.

KEYWORDS: antiaromaticity; aromaticity; non-dynamic correlation energy; π-electrons

INTRODUCTION

It is widely recognized and accepted that aromaticity is one of the cornerstones of organic chemistry, with significant implications in biochemistry and inorganic chemistry. This assertion is based on the well known fact that around 50% of all known organic compounds possess aromatic ring(s) and that many molecules of biological importance are aromatic like, e.g. porphyrins and bases of nucleic acids. Notwithstanding its fundamental role in empirical chemistry, the notion of aromaticity has been a stumbling block and a matter of controversy since Kekulé's hypothesis on the structure of benzene,[1] and that has continued until now.[2] The underlying reason is that aromaticity is not an observable property and consequently it cannot be exactly defined. In this respect it resembles another non-observable property, which has also faithfully served chemistry for a number of decades, namely hybridization of atomic orbitals. Hybrid orbitals can be estimated according to several recipes, each of them determining its own scale of the hybridization parameters. However, once a particular criterion is adopted, the computed s- and p-characteristics of local hybrid orbitals provide a consistent picture and rationale for a wide variety of physico-chemical properties of organic molecules.[3] They are local in nature and reflect one of the most fundamental tenets of atoms in molecules—a decrease in symmetry on going from a spherical environment in free atoms to that defined by the local environment encompassing the nearest neighbors. One is therefore tempted to name hybridization as pseudo- or quasi-observable.[3] Similarly, aromaticity cannot be defined in a unique way and yet it is manifested in a number of chemical and physical properties of molecules conditionally termed 'aromatic.' There are, however, two essential differences between hybridization and aromaticity. The latter is a non-local effect embracing the whole molecule or significant fragment(s) of the molecular systems, which are cyclic and planar as a rule, if some special 3D molecules exhibiting aromaticity are put aside. Second, aromaticity is a non-additivity feature

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describing the deviation of the property under scrutiny from the additivity scheme for the same property, which is based either on atoms, chemical bonds or atomic groupings.

Characteristic properties exhibited by cyclic (and polycyclic) aromatic compounds are as follows: (1) they are more stable than acyclic olefinic analogues. The excess in stability is termed the aromatic stabilization energy (ASE) and is usually determined by the hypothetical homodesmotic reactions[4,5] employing, e.g., open-chain polyenes as non-aromatic standards. Different aromaticity scales were developed depending on the choice of non-aromatic gauge molecules. Nevertheless, their results are comparable, thus giving rise to the energetic criterion of aromaticity. It should be pointed out that the energy criterion is the most essential one in chemistry, because energy plays a decisive role in chemical reactivity. Moreover, it employs either total molecular energies (in theoretical calculations) or heats of molecular formation, thus being based on observables. (2) The cyclic bond lengths are intermediate between typical single and double bond distances with a tendency to be equal as in the archetypal benzene. Hence, alternation in bond distances indicates an aromatic defect, which is built in the harmonic oscillator model of aromaticity (HOMA) developed and applied to a large number of carbocyclic and heterocyclic organic compounds by Krygowski and coworkers.[6–12] It consists of two terms: (i) expansion or contraction of the aromatic moiety and (ii) alternation of bond distances. HOMA is a geometric index of aromaticity, which in turn is closely related to the energetic criteria. Needless to say, it is based on measurable bond distances, thus being related in principle to an observable. (3) The magnetic behavior of aromatic compounds has some unusual features, which are used as magnetic probes of aromaticity. For example, the enhancement of magnetic susceptibility (Λ) relative to the combined atom and bond additivity scheme of Pacault *et al.*[13,14] was considered as a signature or fingerprint of aromaticity. Further, according to Benassi *et al.*[15] the magnetic susceptibility component perpendicular to the molecular plane is an even more reliable index than those based on magnetic anisotropy or NMR data.[16] The latter were discussed first by Gready *et al.*[17] and the use of *o*-benzylic coupling constants $^4J(^1H,^1H)$ was recommended as a measure of relative degree of aromaticity.[17] Claramunt *et al.*[18] studied the chemical shifts and coupling constants of 1-substituted pyrazoles by ^1H, ^{13}C and ^{15}N NMR spectroscopy in solution in order to find out how the aromaticity is affected by substituent effects. Recently, a new magnetic criterion has been introduced by Schleyer and co-workers[19–22] called the nucleus-independent chemical shift (NICS). It is calculated at the center of an aromatic ring or, preferably, 1 Å above this center. Undoubtedly, it would be better characterized as the magnetic shielding of a ghost nucleus, which is appropriately placed above the plane of the aromatic ring, but we prefer here to retain the widely adopted terminology. It is more important to point out that a non-observable (aromaticity) is described by another non-observable (NICS), which calls for caution. Nevertheless, NICS is a widely used criterion of aromaticity and it seems that it does give a qualitative insight into the aromatic character of cyclic compounds, although a number of exceptions are also well documented. (4) Finally, there are a number of theoretical indices of aromaticity, which will not be elaborated on here. Instead, we refer to the book by Minkin *et al.*[23] and the special issue of Chemical Reviews published recently.[2]

There are some other facets of aromatic compounds that make them a special class of molecular systems, such as the electrophilic substitution susceptibility, but this cannot be used as a criterion.

The antipodes of aromatic are antiaromatic compounds. A benchmark for extreme manifestation of antiaromaticity is cyclobutadiene (**CBD**). It has a much higher energy than the corresponding open-chain polyene. Good quality *ab initio* calculations on **CBD** show that its total energetic destabilization relative to 1,3-butadiene is $78.6\,\text{kcal mol}^{-1}$ ($1\,\text{kcal} = 4.184\,\text{kJ}$).[24,25] This is, of course, the sum of the angular strain energy E_S(**CBD**) and antiaromatic destabilization energy of the 4π electron moiety, E_{ad}(**CBD**), where the latter is provisionally ascribed to the π-electron network only. The energy E_S has recently been estimated to be $32 \pm 2\,\text{kcal mol}^{-1}$.[26] Taking this value into account, we derive E_{ad}(**CBD**) to be $46.6 \pm 2\,\text{kcal mol}^{-1}$, which compares with the results of the experimental work of Deniz *et al.*[26] ($55 \pm 11\,\text{kcal mol}^{-1}$) and an earlier G2 study which gave E_{ad}(**CBD**) $= 40.6\,\text{kcal mol}^{-1}$.[27]

It is important to mention that our analysis indicated that there were two types of aromaticity: *endo*- and *exo*-aromaticity,[24] and they should be clearly distinguished. Since these concepts have both conceptual and practical consequences, we shall make a brief comment on the main conclusions. *Endo*-aromaticity of the paradigmatic benzene is related to its deformation propensity provided the topology of the π-electron manifold is preserved. It is well known that the benzene moiety is easily distorted, as shown theoretically by Lipkowitz and Peterson[28] and by Hall.[29] The flexibility of the benzene structural framework is confirmed by x-ray studies, which have shown that its crystal structure at 15 K is not planar.[30] Its moderate chair conformation is caused by weak intermolecular interactions in the range 1–$3\,\text{kcal mol}^{-1}$ according to Kitaygorodsky,[31] indicating a pronounced distortion ability. Similarly, the difference in total energy for the optimized D_{6h} structure of benzene and the hypothetical reference cyclohexatriene is only $5.6\,\text{kcal mol}^{-1}$.[24] Concomitantly, the benzene ring is easily deformed by a judicious choice of substituents[32–38] or by its fusion to small strained ring(s). The latter leads to the well known Mills–Nixon[39–42] or reversed Mills–Nixon[43–45] effects, which in turn have interesting structural and chemical consequences. In particular, a small ring fusion leads to a substantial α,β discrimination in electrophilic substitution reactions.[46–49] *Exo*-aromaticity is related to a hypothetical ring-opening reaction(s) leading to open-chain π-electron fragment(s) as exemplified by 1,3-butadiene. Aromatic stabilization relative to a ring-scission process is completely different from the stabilization energy acting against the ring deformation described above. Analysis of the HF energies satisfying the virial theorem shows that the *exo*-aromaticity has its origin in a decreased $\frac{1}{2}(V_{ee} + V_{nn})$ term, where V_{ee} and V_{nn} are electron–electron and nucleus–nucleus repulsions, respectively. In contrast, *endo*-aromaticity leading to favoured D_{6h} benzene compared with artificially deformed D_{3h} cyclohexatriene is a consequence of a more efficient nucleus–electron attraction V_{ne}.[24] *Endo*- and *exo*-antiaromaticity can be defined analogously.[24] It appears that the transition D_{4h} structure (TS) of **CBD** is a consequence of an enormous increase in the V_{nn} repulsion. In the contrast, its *exo*-antiaromaticity is manifested predominantly in a considerably smaller nucleus–electron attraction V_{ne} term compared with 1,3-butadiene.[24]

A closer look at the π-electron correlation energies in cyclic molecules revealed a seemingly counterintuitive behavior of the non-dynamic or static correlation in anti/aromatic compounds.[24,50] It was the purpose of this work to examine the role of the non-dynamic π-electron correlation energies $E(\mathrm{ND})^{\pi}$ in planar organic molecules in some more detail with particular emphasis on the problem of anti/aromaticity. However, we would like to point out that our aim is not to develop a new criterion of aromaticity, but merely to illustrate the fact that anti/aromaticity is reflected in typical deviations of the $E(\mathrm{ND})^{\pi}$ values from the additivity rule.

METHODOLOGY

The non-dynamic correlation energy of π-electrons, $E(\mathrm{ND})^{\pi}$, is conveniently calculated by the multiconfigurational SCF (MCSCF) method, taking into account the complete active space of π-MOs (CASSCF$^{\pi}$) according to formalism developed by Ruedenberg *et al.*[51] and Roos.[52] The expression is

$$E(\mathrm{ND})^{\pi} = E(\mathrm{HF}) - E(\mathrm{CASSCF})^{\pi} \qquad (1)$$

where we define the correlation energy as a positive magnitude for the sake of convenience, although it is negative by its nature, thus stabilizing the molecular systems. Dunning's cc-pVDZ basis set[53] was used and geometries were optimized at the CASSCF$^{\pi}$/cc-pVDZ level. Hence, Eqn (1) takes the form

$$\begin{aligned} E(\mathrm{ND})^{\pi} &= E(\mathrm{HF/cc\text{-}pVDZ//CASSCF^{\pi}/cc\text{-}pVDZ}) \\ &\quad - E(\mathrm{CASSCF^{\pi}/cc\text{-}pVDZ}) \end{aligned} \qquad (2)$$

A more detailed description of the complete active space calculations involves the specification of the number of active electrons and active molecular orbitals. Concomitantly, CASSCF$(n_1,n_2)^{\pi}$ implies n_1 active (π) electrons and n_2 (π) active MOs. In hydrocarbons we used $n_1 = n_2$ with one notable exception, the cyclopropenyl cation, where $n_1 = 2$ and $n_2 = 3$. The latter implies that one π-MO and a degenerate pair of π^*-MOs are active in the CASSCF$^{\pi}$ procedure. In fluorinated compounds $n_2 = n_1 - 1$ in singly substituted molecules, $n_2 = n_1 - 2$ for double substitution, etc. The same holds for molecules involving O(sp^3) oxygen. A special case is given by nitrogen atoms. We shall distinguish between the two-coordinated sp^2 (planar) nitrogen atoms N(sp^2)$_2$ as in the $=$NH group and three-coordinated planar nitrogens N(sp^2)$_3$ as in the $>$NH fragment belonging to planar five-membered rings. In all other compounds $n_1 = n_2$ as in planar hydrocarbons.

NICS values in cyclic molecules were calculated 1 Å above the 'center of the ring,' using the GIAO-HF/cc-pVDZ//CASSCF$^{\pi}$/cc-pVDZ method. The 'center of the ring' corresponds to a minimum of the electron density within the ring obtained by Bader's topological atoms in molecules (AIM) analysis. MOLCAS[54] and Gaussian[55] codes were employed in this work.

RESULTS AND DISCUSSION

The gauge non-aromatic polyenes involving relevant heteroatoms are depicted in Fig. 1. Two comments are appropriate here. First, $\mathbf{n}(n_1,n_2)$ or $\mathbf{n\text{-}X}(n_1,n_2)$, ($\mathbf{X} =$ F, O, NH, OH and NH$_2$), denote molecules, whereas n_1 and n_2 within parentheses denote the number of active electrons and active π-MOs, respectively, as usual. Second, the NH$_2$ group in **1-NH$_2$**, **2-NH$_2$** and **3-NH$_2$** is forced to be planar for parametrization purposes, implying that these systems are only model molecules. The calculated non-dynamic correlation energies $E(\mathrm{ND})^{\pi}$ are fitted by an atomic additivity equation:

$$\begin{aligned} E(\mathrm{ND})^{\pi} &= n(\mathrm{C})E(\mathrm{C})^{\pi} \\ &\quad + n[\mathrm{N(sp^2)_2}]E[\mathrm{N(sp^2)_2}]^{\pi} \\ &\quad + n[\mathrm{N(sp^2)_3}]E[\mathrm{N(sp^2)_3}]^{\pi} \\ &\quad + n[\mathrm{O(sp^2)}]E[\mathrm{O(sp^2)}]^{\pi} \\ &\quad + n[\mathrm{O(sp^3)}]E[\mathrm{O(sp^3)}]^{\pi} \\ &\quad + n(\mathrm{F})E(\mathrm{F})^{\pi} + n(\mathrm{H})E(\mathrm{H})^{\pi} \end{aligned} \qquad (3)$$

where we distinguish sp^2 and sp^3 oxygen atoms and two types of sp^2 nitrogen atoms as mentioned above. The corresponding numbers of specific atoms in considered polyenes are denoted by n(X), X = C, N(sp^2)$_2$, N(sp^2)$_3$, O(sp^2), O(sp^3), F and H, whereas the effective non-dynamic π-electron correlations are given as $E(\mathrm{X})^{\pi}$, X = C, N(sp^2)$_2$, N(sp^2)$_3$, O(sp^2), O(sp^3), F and H. The contribution of H atoms arises from their polarization

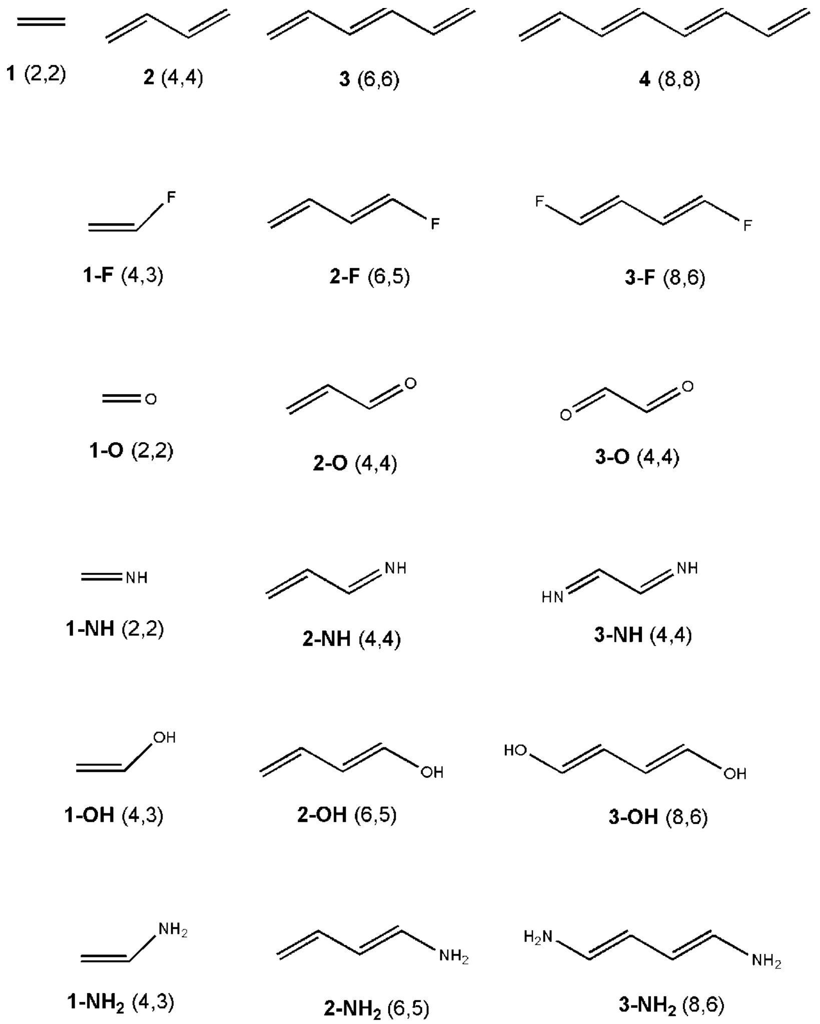


Figure 1. Schematic representation of zig-zag polyenes

function and it is negligible as expected (Table 1). Analogous additivity equations hold for both the HF and CASSCF$^{\pi}$ energies, where the average atomic contributions are denoted by ε and η, respectively:

$$\begin{aligned} E(\mathrm{HF}) = {} & n(\mathrm{C})\varepsilon(\mathrm{C}) \\ & + n[\mathrm{N(sp^2)_2}]\varepsilon[\mathrm{N(sp^2)_2}] \\ & + n[\mathrm{N(sp^2)_3}]\varepsilon[\mathrm{N(sp^2)_3}] \\ & + n[\mathrm{O(sp^2)}]\varepsilon[\mathrm{O(sp^2)}] \\ & + n[\mathrm{O(sp^3)}]\varepsilon[\mathrm{O(sp^3)}] \\ & + n(\mathrm{F})\varepsilon(\mathrm{F}) + n(\mathrm{H})\varepsilon(\mathrm{H}) \end{aligned} \tag{4}$$

and

$$\begin{aligned} E(\mathrm{CASSCF})^{\pi} = {} & n(\mathrm{C})\eta(\mathrm{C}) + n[\mathrm{N(sp^2)_2}]\eta[\mathrm{N(sp^2)_2}] \\ & + n[\mathrm{N(sp^2)_3}]\eta[\mathrm{N(sp^2)_3}] \\ & + n[\mathrm{O(sp^2)}]\eta[\mathrm{O(sp)^2}] \\ & + n[\mathrm{O(sp)^3}]\eta[\mathrm{O(sp)^3}] \\ & + n(\mathrm{F})\eta(\mathrm{F}) + n(\mathrm{H})\eta(\mathrm{H}) \end{aligned} \tag{5}$$

Perusal of the least-squares values obtained for the three types of energies $E(\mathrm{ND})^{\pi}$, $E(\mathrm{HF})$ and $E(\mathrm{CASSCF})^{\pi}$ presented in Table 1 reveals excellent performance of Eqns (3)–(5). For instance, effective non-dynamic correlation energies per atom $E(\mathrm{X})^{\pi}$ reproduce the calculated $E(\mathrm{ND})^{\pi}$ values with an average absolute deviation (*AAD*) of only 0.3 kcal mol^{-1}, whereas the maximum absolute deviation (*MAD*) is 1.0 kcal mol^{-1}. The correlation coefficient R^2 is 0.9996. Effective average energies $E(\mathrm{X})^{\pi}$ are of some interest, because they are small but positive for F atoms and small and negative for sp^3 O atoms and sp^2 three-coordinated N atoms. It appears that $\mathrm{N(sp^2)_3}$ and $\mathrm{O(sp^3)}$ atoms do not contribute to the non-dynamic correlation of π-electrons and in fact they diminish it slightly. Finally, $E(\mathrm{X})^{\pi}$ increases along the triad X = C, $\mathrm{N(sp^2)_2}$ and $\mathrm{O(sp^2)}$.

It should be stressed that both components yielding the non-dynamic correlation energy $E(\mathrm{ND})^{\pi}$, that is, HF and CASSCF$^{\pi}$ energies, conform to the same *mutatis mutandis* additivity rule. Once again performance of the additivity is excellent, as evidenced by very low *AAD* values 0.8 and 1.0 kcal mol^{-1}, respectively, in spite of the great simplicity of Eqns (4) and (5). Obviously, polyenes

Table 1. Atomic weighting factors (effective energy per atom in a molecule) appearing in additivity Eqns (3)–(5) for non-dynamic correlation energy, the total energy obtained by the CASSCF$^{\pi}$/cc-pVDZ method and the total energy at the HF/cc-pVDZ//CASSCF$^{\pi}$/cc-pVDZ level[a]

Atom	$E(\mathrm{ND})^{\pi}_{\mathrm{add}}$ (kcal mol^{-1})	$E(\mathrm{CASSCF})^{\pi}_{\mathrm{add}}$ (a.u.)	$E(\mathrm{HF})_{\mathrm{add}}$ (a.u.)
C	8.57	–37.88687	–37.87320
$N(sp^2)_2$	12.04	–54.46535	–54.44616
$N(sp^2)_3$	–1.34	–54.45633	–54.45846
$O(sp^2)$	13.67	–74.88043	–74.85868
$O(sp^3)$	–0.35	–74.86199	–74.86253
F	0.36	–99.42703	–99.42645
H	0.01	–0.57383	–0.57381
AAD	0.3	0.8 kcal mol^{-1}	1.0 kcal mol^{-1}
MAD	1.0	1.9 kcal mol^{-1}	3.1 kcal mol^{-1}
R^2	0.9996	1.0000	1.0000

[a] $N(sp^2)_2$ and $N(sp^2)_3$ correspond to two- and three-coordinated sp^2 nitrogens respectively.

Table 2. Non-dynamic correlation energy $E(\mathrm{ND})^{\pi}$ of gauge linear zig-zag polyenes calculated by the CASSCF$^{\pi}$ procedure and by the additivity Eqn (3), given in kcal mol^{-1}[a]

Molecule	$E(\mathrm{ND})^{\pi}$	$\Delta E(\mathrm{ND})^{\pi}_{\mathrm{add}}$	$\Delta E(\mathrm{ND})^{\pi}$	$\Delta E(\mathrm{CAS})$	$\Delta E(\mathrm{HF})$
1	17.7	17.2	0.5	0.7	1.3
2	34.8	34.4	0.4	0.7	1.1
3	51.7	51.5	0.2	0.3	0.5
4	68.7	68.7	0.0	–0.2	–0.2
1-F	17.6	17.5	0.1	–0.8	–0.7
2-F	34.8	34.7	0.1	0.3	0.4
3-F	35.0	35.1	–0.1	0.2	0.2
1-O	22.3	22.3	0.0	1.8	1.9
2-O	38.4	39.4	–1.0	–2.0	–3.1
3-O	45.0	44.5	0.5	0.1	0.6
1-NH	20.8	20.6	0.2	1.1	1.2
2-NH	37.6	37.8	–0.2	–0.4	–0.7
3-NH	41.3	41.3	0.1	–0.3	–0.3
1-OH	16.4	16.8	–0.4	–1.9	–2.4
2-OH	34.0	34.0	0.0	0.5	0.4
3-OH	33.9	33.7	0.2	0.7	1.0
1-NH$_2$	15.7	15.9	–0.2	–1.0	–1.1
2-NH$_2$	32.4	33.0	–0.6	–0.5	–1.2
3-NH$_2$	32.1	31.7	0.4	0.8	1.1

[a] Deviations from additivity are defined as follows: $\Delta E(\mathrm{ND})^{\pi} = E(\mathrm{ND})^{\pi} - E(\mathrm{ND})^{\pi}_{\mathrm{add}}$; $\Delta E(\mathrm{CAS}) = E(\mathrm{CASSCF}^{\pi}/\text{cc-pVDZ}) - E(\mathrm{CASSCF}^{\pi}/\text{cc-pVDZ})_{\mathrm{add}}$; $\Delta E(\mathrm{HF}) = E(\mathrm{HF}/\text{cc-pVDZ//CASSCF}^{\pi}/\text{cc-pVDZ}) - E(\mathrm{HF}/\text{cc-pVDZ//CASSCF}^{\pi}/\text{cc-pVDZ})_{\mathrm{add}}$.

provide good non-aromatic systems yielding a convenient scale for estimating exo-anti/aromaticity. A more detailed analysis of deviations from the additivity for all three types of the energy can be made by inspection of Table 2.

Representative cyclic molecules studied here are presented schematically in Fig. 2. The computed $E(\mathrm{ND})^{\pi}$ energies are compared with the additivity estimates in Table 3. At first sight, counterintuitive behavior of $E(\mathrm{ND})^{\pi}$ is apparent: the aromatic compounds possess lower non-dynamic π-electron correlation energies than the corresponding open-chain polyenes, whereas the opposite holds for antiaromatic systems. Hence, $\Delta E(\mathrm{ND})^{\pi} = E(\mathrm{ND})^{\pi} - E(\mathrm{ND})^{\pi}_{\mathrm{add}}$ is positive for the latter and negative for the former molecules. However, this is easily explained by examining the HF HOMO–LUMO gaps in benzene and **CBD**. They are, in comparison with the corresponding zig-zag polyenes (1,3,5-hexatriene and 1,3-butadiene, respectively) higher for benzene by 2.2 eV and lower for **CBD** by 1.9 eV. Taking into account that 1 eV = 23.06 kcal mol^{-1}, it is obvious that $E(\mathrm{ND})^{\pi}$ will be lower and higher in benzene and **CBD**, respectively, compared with the additive values.

It is of some interest to compare our results with the corresponding NICS values given in Table 3. At this point some preliminaries are necessary, because it is very important to stress that some researchers believe in aromaticity as a one-dimensional property. This would imply that the hierarchy of the aromatic compounds should be the same for all criteria of aromaticity. Obviously, this is not possible, because each molecular property probes one particular region of the molecular electron density distribution and/or arrangement of MO energies, assuming that the independent single particle picture applies. Consequently, aromaticity is differently manifested in various properties, not to mention criteria based on non-observables. It follows as a corollary that

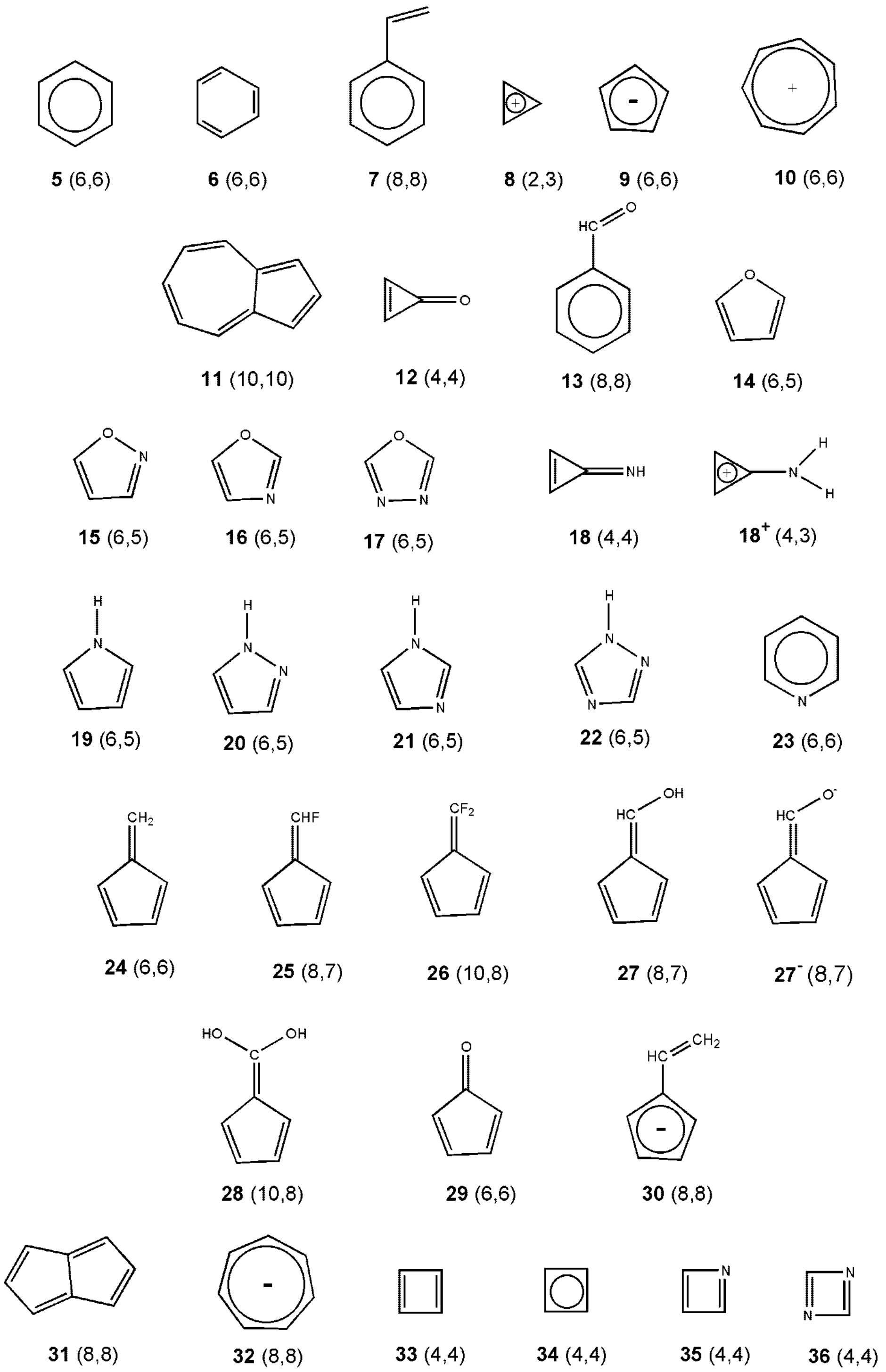


Figure 2. Schematic representation of cyclic and bicyclic planar molecules considered in the present study

non-additivity for various molecular features is sometimes different, thus leading to several distinct ladders of aromaticity. This is exactly the outcome of a recent statistical study by Cyrański *et al.*[56] which confirmed some earlier conclusions about this problem.[57–61] Therefore, a close semblance between $\Delta E(\mathrm{ND})^{\pi}$ and NICS is not expected and indeed it does not occur. Qualitative accordance is observed in some cases, however, as the rest of this discussion will show. Let us also emphasize that the static correlation energy of π-electrons $\Delta E(\mathrm{ND})^{\pi}$ is also not an observable. It is a portion of the total molecular energy being in addition dependent on the choice of active electrons and molecular orbitals. It is gratifying that the latter can be usually made in a natural self-evident way. The second point to be made is that the aromatic stabilization can be reduced essentially to the

Table 3. Non-dynamic correlation energy $E(\mathrm{ND})^{\pi}$ obtained by the CASSCF$^{\pi}$ formalism and by the additivity rule for some cyclic molecules, in kcal mol^{-1}, with NICS values (in ppm) for comparative purpose[a]

Molecules	$E(\mathrm{ND})^{\pi}$	$E(\mathrm{ND})^{\pi}{}_{\mathrm{add}}$	$\Delta E(\mathrm{ND})^{\pi}$	NICS	ΔE(CAS)	ΔE(HF)
5	45.5	51.5	−6.0	−12.4	−18.9	−24.9
6	45.1	51.5	−6.4	−11.0	−12.9	−19.3
7	63.2	68.6	−5.4	−11.8	−15.8	−21.3
8	14.8	25.7	−10.9	−15.7	215.8	204.9
9	31.8	42.9	−11.1	−13.7	29.2	18.1
10	41.0	60.1	−19.1	−10.8	153.2	134.0
11	82.2	85.8	−3.6	−7.5[b]; −17.7[c]	9.2	5.6
12	28.7	39.4	−10.7	−10.5	58.7	48.0
13	66.1	73.7	−7.6	−12.3	−21.5	−29.2
14	32.6	34.0	−1.4	−10.8	5.6	4.1
15	35.4	37.4	−2.0	−11.2	28.1	26.1
16	34.7	37.4	−2.7	−10.1	0.8	−2.0
17	37.7	40.9	−3.2	−10.2	12.1	8.9
18	29.6	37.7	−8.1	−9.9	65.8	57.6
$\mathbf{18}^{+}$	11.5	24.4	−12.9	−13.4	187.2	174.2
19	31.0	33.0	−2.0	−11.8	−3.3	−5.3
20	33.9	36.5	−2.6	−12.7	5.3	2.6
21	33.2	36.5	−3.3	−11.8	−7.0	−10.3
22	35.4	39.9	−4.5	−12.2	0.8	−5.3
23	47.9	54.9	−7.0	−12.0	−14.1	−21.2
24	51.7	51.5	0.2	−4.3	11.2	11.3
25	51.4	51.8	−0.4	−5.1	10.4	9.9
26	50.6	52.2	−1.6	−5.8	5.6	3.9
27	48.9	51.1	−2.2	−6.5	8.7	6.5
$\mathbf{27}^{-}$	45.9	51.1	−5.2	−12.3	−1.3	−6.6
28	46.1	50.8	−4.7	−7.6	0.2	−4.5
29	57.2	56.6	0.6	2.0	9.8	10.3
30	46.3	60.1	−13.8	−12.4	24.9	11.1
31	72.0	68.6	3.4	12.6[d]	33.7	37.0
32	51.7	60.1	−8.4	—	52.4	44.0
33	43.6	34.3	9.3	24.2	75.3	84.6
34	74.0	34.3	39.7	—	81.8	121.4
35	45.1	37.8	7.3	18.1	74.5	81.7
36	43.9	41.2	2.7	13.2	70.5	73.1

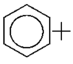
[a] Deviation from additivity are defined as in the footnote to Table 2.

[b] NICS value calculated 1 Å above the center of the seven-membered ring in azulene.

[c] NICS value calculated 1 Å above the center of the five-membered ring in azulene.

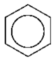
[d] NICS value calculated 1 Å above the center of each of the rings in pentalene.

independent particle features. Consider the following homodesmotic reaction:



$$+3[\mathrm{H_2C{=}CH_2}] = 3[\mathrm{H_2C{=}CH{-}CH{=}CH_2}] - E_{\mathrm{as}}(\mathbf{5}) \tag{6}$$

where the aromatic stabilization is defined as a positive magnitude and denoted by E_{as}. Equation (6) defines the aromatic stabilization up to the triple π-electron delocalization energy in *trans*-1,3-butadiene. Experimentally, $E_{\mathrm{as}}(\mathbf{5})$ is 21.6 ± 1.5 kcal mol^{-1},[62] as obtained from the measured enthalpies of formation $\Delta H_{\mathrm{f}}{}^{\circ}$. Theoretical MP4(SDTQ)/6–31G* calculations[63] including the basis sets superposition error yield $E_{\mathrm{as}}(\mathbf{5}) = 21.35$ kcal mol^{-1}, in excellent agreement with experiment. Employing our additivity Eqns (4) and (5), we can recast Eqn (6) into



$$- 6[\varepsilon(\mathrm{C}) \text{ or } \eta(\mathrm{C})] - 6[\varepsilon(\mathrm{H}) \text{ or } \eta(\mathrm{H})] = -E_{\mathrm{as}}(\mathbf{5}) \tag{7}$$

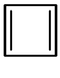
illustrating that the atomic additivity is equivalent to the concept of homodesmotic reactions. Average atomic energies ε and η given in Table 1 yield $E_{\mathrm{as}}(\mathbf{5})$ of 24.9 and 18.9 kcal mol^{-1} for HF/cc-pVDZ//CASSCF(6,6)$^{\pi}$/cc-pVDZ and CASSCF(6,6)$^{\pi}$/cc-pVDZ, respectively. It follows that the aromatic stabilization at the HF level is close to the exact value, being higher by only 3.5 kcal mol^{-1}. Counterintuitive as it is, the CASSCF(6,6)$^{\pi}$ model, which includes the non-dynamic π-electron correlation, yields $E_{\mathrm{as}}(\mathbf{5})$ lower than the exact value by 2.5 kcal mol^{-1}. The latter is obviously recovered by the dynamic correlation of all valence electrons, since a full calculation should in principle give the exact value. Therefore, the contribution of the dynamic correlation of all valence electrons to the aromatic character of benzene is 2.5 kcal mol^{-1}. Since the influence of the σ-electrons on the dynamic correlation is decisive for obvious reasons, this finding underlines an important role of the σ-framework, i.e. it acts in the right direction as far as the stability of aromatic compounds is concerned. We shall come back to this point later. As to the role of π-electrons, we can say with confidence that the contribution of $E(\mathrm{ND})^{\pi}$ to the *exo*-aromatic stabilization is small and negative. Nevertheless, it can serve for diagnostic purposes in identifying aromaticity, albeit only in a qualitative sense, as the present results show.

Let us commence with the aromatic six-membered rings. In the series **5**, **6**, **7**, **13** and **23** all compounds should be about equally aromatic by both $\Delta E(\mathrm{ND})^{\pi}$ and NICS criteria. A small but hardly significant increase could be expected in benzaldehyde (**13**). Five-membered rings **14**–**17** and **19**–**22** should be considerably less aromatic than benzene according to the $\Delta E(\mathrm{ND})^{\pi}$ diagnostic, but almost as aromatic as benzene if the NICS criterion is applied. The ultimate answer could be given only by the homodesmotic reactions. Particularly aromatic should be the cyclopentadienyl anion **9**, which is in harmony with an earlier finding that cyclopentadiene and its derivatives are a strongly acidic compounds.[64–66] Substituted fulvenes are interesting, since the parent compound **24** is non-aromatic according to $\Delta E(\mathrm{ND})^{\pi}$ and HOMA,[11,12] in contrast to NICS, which predicts an appreciable amount of aromaticity (Table 3). Single and double substitution at position C(6) by F or OH groups increases the aromatic character of the five-membered ring, which is reflected by all three indices $\Delta E(\mathrm{ND})^{\pi}$, NICS and HOMA.[11,12] A particularly strong aromatization effect is found in monosubstituted $\mathrm{CH_2^-}$ (**30**) and $\mathrm{O^-}$ (**27**$^-$) derivatives. However, the NICS prediction is that **27**$^-$ and **30** are equally aromatic, whereas both $\Delta E(\mathrm{ND})^{\pi}$ and HOMA indicate that **30** is by far the most aromatic fulvene. We are inclined to conclude that NICS results should be treated with caution here.

Let us focus on the cationic systems **8**, **10** and **18**$^+$. The cycloheptatrienyl cation **10** should be extremely aromatic according to $\Delta E(\mathrm{ND})^{\pi}$ calculation, whereas it should exhibit lower aromaticity than benzene by the NICS criterion. Our prediction is, however, corroborated by the experimental hydride transfer energy and CCSD(T)/6–311 + G*//CCD/6–311 + G* calculations of Wiberg,[67] both of which indicate that the cycloheptatrienyl cation **10** is stabilized by about 50 kcal mol^{-1}. This is in harmony with Hückel's $4n + 2$ rule, and additionally by its stabilization, which is substantially larger than that in benzene. We note in passing that our calculations give a planar geometry of D_{7h} in agreement with IR, Raman, ^{1}H NMR and x-ray measurements.[67] It follows that perhaps NICS values between charged and neutral species should not be compared. Further, it appears that cyclopropenyl cation **8** should be more aromatic than benzene. This is corroborated by the G2 study of Glukhovtsev *et al.*[68] employing a homodesmotic reaction, which indicated stabilization in **8** as high as 59.1 kcal mol^{-1}. Our experience indicates that charged species generally exhibit higher resonance effects and aromatization stabilization than the comparable neutral molecules. This is in line with recent calculations which have shown conclusively that protonation of some imino groups attached to planar molecular backbones could trigger a very strong aromatization effect in three-, five- and six-membered rings,[69–72] and that the sequential aromatic domino effect might lead to extremely powerful organic superbases.[69–72] By the same token, the protonated cyclopropeneimine **18**$^+$ is highly aromatic by both $\Delta E(\mathrm{ND})^{\pi}$ and NICS indices. A characteristic increase in aromaticity is observed on going from the parent base **18** to its conjugate acid **18**$^+$, as expected. The MP2(fc)/6–311 + G**//HF/6–31G* calculations based on homodesmotic reactions have shown that the conjugation and cationic resonance energy in **18** and **18**$^+$ are 15.7 and 30.3 kcal mol^{-1}, respectively[70]. An additional interesting charged compound is the cycloheptatrienyl anion **32**. Recent B3LYP/6–31G* calculations have shown that **32** has a very small singlet–triplet gap between –1.0 and –2.6 kcal mol^{-1}.[73] The triplet is more stable and planar with D_{7h} symmetry, whereas the singlet assumes a non-planar deformed structure. We are interested here in the planar singlet state of **32** as obtained by the CASSCF$^{\pi}$ calculations, which show that the constrained planar structure is a regular D_{7h} heptagon, exhibiting significant aromatic character, thus violating the Hückel $4n\pi$ rule. It is likely that Hückel rules do not always apply in charged species. One should mention, however, that the NICS value (42.9 ppm)[73] for a non-planar singlet indicates its strong antiaromaticity. It should be noted in this connection that the heptaphenylcycloheptatrienyl anion was synthesized and that it was a singlet.[74] More involved calculations employing more flexible basis sets and a higher level of theory would be desirable. In concluding this section, it is worth noting that cyclopropenone (**12**) should be more aromatic than **18**, implying strong participation of resonance coupling between the singly bonded oxygen anion substituent and the cyclopropenyl cation ring in the total wavefunction. This is in line with the aromatic stabilization of 23.5 kcal mol^{-1} obtained by MP2(fc)/6–311+G**//HF/6–31G* calculation.[50]

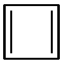
Bicyclic azulene (**11**) and pentalene (**31**) are aromatic and antiaromatic, respectively, in agreement with the generally accepted opinion. It is noteworthy that the NICS value for a five-membered ring is much lower (–17.7) than that for a seven-membered ring (–7.5 ppm), implying a substantially higher aromatic character of the former ring. The $\Delta E(\mathrm{ND})^{\pi}$ calculation indicates, on the other hand, moderate overall aromatic stabilization. This is in accordance with HOMA indices.[6]

Cyclobutadiene (**CBD**) is antiaromatic, as evidenced by a positive $\Delta E(\mathrm{ND})^{\pi}$ value. It is of interest to examine the relative influence of the HF and the electron correlation energies on the antiaromaticity of **CBD**. The corresponding homodesmotic reaction is



$$+ 2[\mathrm{H_2C{=}CH_2}] = 2[\mathrm{H_2C{=}CH{-}CH{=}CH_2}] + E_{\mathrm{td}}(\mathbf{33}) \qquad (8)$$

where the total destabilization is also defined as a positive magnitude. Reducing eq. (8) by the atomic additivity scheme, one obtains:



$$- 4[\varepsilon(\mathrm{C}) \text{ or } \eta(\mathrm{C})] - 4[\varepsilon(\mathrm{H}) \text{ or } \eta(\mathrm{H})] = E_{\mathrm{td}}(\mathbf{33}) \qquad (9)$$

The results obtained for $E_{\mathrm{td}}(\mathbf{33})$ by the HF/cc-pVDZ//CASSCF(4,4)$^{\pi}$/cc-pVDZ and CASSCF(4,4)$^{\pi}$/cc-pVDZ models are 84.6 and 75.3 kcal mol^{-1}, respectively. Surprisingly, the Hartree–Fock $E_{\mathrm{td}}(\mathbf{33})$ is in excellent agreement with experiment ($\Delta\Delta H_{\mathrm{f}} = 86$ kcal mol^{-1}).[26] Substracting the experimental angular strain energy[26] of 32 ± 2 kcal mol^{-1} from $E_{\mathrm{td}}(\mathbf{33})$, the antiaromatic destabilization energy $E_{\mathrm{ad}}(\mathbf{33})$ is found being 52.6 ± 2 and 43.3 ± 2 kcal mol^{-1} for the HF and CASSCF(4,4)$^{\pi}$ models, respectively. The former value compares well with the 55 kcal mol^{-1} attributed to genuine antiaromaticity.[26] It appears that antiaromaticity is well described within the independent electron HF picture, whilst the influence of non-dynamic π-electron and dynamic all-valence electron energies practically cancels out. For example, $E(\mathrm{ND})^{\pi}$ for **CBD** decreases antiaromatic destabilization by 9 kcal mol^{-1}, whereas the dynamic correlation apparently increases it by 12 kcal mol^{-1}. It is interesting that the interplay of $\Delta E(\mathrm{ND})^{\pi}$ and $\Delta E(\mathrm{D})$ is again antagonistic, just as in the case of aromatic benzene. A particularly high deviation from additivity is found in **CBD**(TS). One could argue that the HF function is inappropriate as a reference in this case, but in our opinion it is exactly the CASSCF function, which improves upon the HF approximation in general, yielding in this way the non-dynamic correlation (i.e. the static correlation correction) energy. It should be pointed out that the calculation of NICS in **34** is not possible for the HF wavefunction, since it has the wrong symmetry. Finally, inclusion of nitrogen atoms into the **CBD** ring diminishes antiaromaticity, as evidenced by compounds **35** and **36**.

To summarize, it has been conclusively shown that anti/aromaticity is reflected in deviations of the non-dynamic π-electron correlation energy $E(\mathrm{ND})^{\pi}$ from the additivity rule. The deviations differ in sign for aromatic and antiaromatic compounds, being close to zero in non-aromatic cyclic systems. Hence they can be used as a diagnostic tool. However, $\Delta E(\mathrm{ND})^{\pi}$ can provide only qualitative information about anti/aromaticity, since both aromatic stabilization and antiaromatic destabilization relative to the corresponding linear polyenes are predominantly determined by the HF energies.

CONCLUSION

The Hartree–Fock and CASSCF$^{\pi}$ energies of linear zig-zag polyenes exhibit remarkable additivity in terms of average atomic energies. As a consequence, the non-dynamic correlation energy of π-electrons $E(\mathrm{ND})^{\pi}$ is also additive. In contrast, $E(\mathrm{ND})^{\pi}$ is non-additive in cyclic planar π-systems as a rule. The deviations $\Delta E(\mathrm{ND})^{\pi} = E(\mathrm{ND})^{\pi} - E(\mathrm{ND})^{\pi}_{\mathrm{add}}$ are negative for aromatic and positive for antiaromatic compounds. Since $E(\mathrm{ND})^{\pi}_{\mathrm{add}}$ reproduces the non-dynamic π-electron energy of open-chain polyenes, such a behavior of anti/aromatic cyclic molecules is seemingly counterintuitive. However, this feature is easily understood if the HF HOMO–LUMO gaps are taken into account in, e.g., benzene and **CBD**. It appears that they are higher in benzene and lower in **CBD** compared with reference linear zig-zag polyenes. The overall contribution of the total correlation energy of all valence electrons to the aromatic stabilization of benzene is positive (see above). Since the contribution of σ-electrons to the dynamic correlation is obviously larger than that of π-electrons, it follows that the σ-electron framework has important role in determining aromaticity. This finding lends additional support to the claim of Shaik and co-workers[75–79] that π-electrons are distortive in aromatic molecules, whereas the opposite should hold for the antiaromatic molecules. Specific σ–π partitioning and calculations of Jug and Köster[80] also underpin this assertion. Non-additivity of $E(\mathrm{ND})^{\pi}$ provides one more piece of evidence that anti/aromaticity is an excess/depletion feature, which is characteristic of many molecular properties. It should be strongly emphasized that each of these properties defines its own scale of anti/aromaticity. Hoffman *et al.*[81] rightly pointed out that 'no single property exists, whose measurements could be taken as a direct, unequivocal measure of aromaticity,' implying that a multitude of ladders of anti/aromaticity is possible. This conclusion is perfectly clear, because each molecular property probes different parts of the electron density distribution in molecules and/or arrangement of the MO levels. The multifaceted nature of anti/aromaticity is evidenced by, *inter alia*, an analysis of the paradigmatic cyclobutadiene and benzene, which has shown that it is possible to define two types of de/stabilization leading to *endo*- and *exo*-anti/aromaticity.[24] Their physical origin is completely different (see above). The *endo*-aromaticity is important in order to understand the properties of deformed aromatic moieties produced on fusion to small ring(s) or substituted by various substituents, termed Mills–Nixon[39–45] or AGIBA (angular group-induced bond alternation),[32–38] respectively. The *exo*-aromaticity describes the aromatic stabilization relative to open-chain polyenes as exemplified by Eqns (6) and (7). Finally, it should be mentioned that any of the anti/aromaticity scales based on a particular molecular property is useful in its own right, but that employing homodesmotic reactions is the most important as far as chemistry and chemical reactivity are concerned. Alternatively, one can use the additivity rules for the HF and electron correlation energies developed earlier[24,50] and employed here. Inclusion of the total electron correlation energy of all valence electrons in a large variety of anti/aromatic molecules would be of interest. This work is in progress.

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