Energetic Aspects of Cyclic Pi-Electron Delocalization: Evaluation of the Methods of Estimating Aromatic Stabilization Energies

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Contents

1. Delocalization versus Localization

In quantum mechanics the state of an electron is defined within the frame of probabilistic theory.[1] The electrons of an isolated atom are confined to the space of this atom, which in turn formally reaches to infinity. Following the Heisenberg uncertainty principle even at this very basic atomic level the electrons are delocalized with an uncertainty in their positions, which is inversely proportional to the uncertainty of their momenta.[2] Molecule formation requires bond(s) between two (or more) isolated atoms, which leads to further substantial delocalization over the whole molecular space. Both valence and the inner shell electrons of the system are delocalized, and hence the electron delocalization must be regarded both as general and as the most important phenomenon in chemistry.[3]

To rationalize in a systematic way the large body of experimental work concerning physicochemical properties of the molecules,[4] it is convenient to assume that lone pair and core electrons are localized. It is worth mentioning that some properties are associated with inner electrons, some with valence electrons, and some with unoccupied orbitals. Many properties can be rationalized in this way, such as heats of formation, dipole moments, polarizabilities,

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and magnetic susceptibilities, which can be expressed using additive schemes of empirically devised bond parameters. These parameters are transferrable between molecules. Dewar[5-7] divided molecular properties into two categories: properties that depend collectively on all of the valence electrons and one-electron properties that depend on the electrons occupying specific delocalized molecular orbitals. Only the collective properties show additivity, which results not from bond localization but from additivity of the interactions between the valence electrons.[7] However, it is important to point out that neither bond localization nor electron localization refer to any directly observable property of a system, and consequently they lack any rigorous physical justification. Rather, they are approximate heuristic models and simply suggest that many of the molecules behave as if the bonds in them were localized. Within the concept of bond localization, Cremer[3] clarified that the electrons (or bonds) are localized if the properties of the molecule can be expressed in terms of bond

contributions. In turn, they are considered to be delocalized if the properties of the molecule cannot be rationalized on the grounds of the concept of bond localization.[3] This is the background for a proper understanding of the definition recommended recently by the IUPAC:[8] delocalization is a redistribution of the valence-shell electron density throughout a molecular entity as compared with some localized models (individual atoms in their valence states, separated bonds, or separated fragments). Different topological modes of the electron delocalization include (i) ribbon delocalization of either π- or σ-electrons (i.e. electrons occupying, respectively, π- and σ-orbitals), (ii) surface delocalization of σ-electrons occurring through an overlap of radially oriented σ-orbitals of a cyclic molecule as is the case of cyclopropane, and (iii) volume delocalization of σ-electrons through an overlap of σ-orbitals directed inside a molecular polyhedron.

Concerning the chemical bonding, one of the most popular advanced organic chemistry textbooks (by J. March) defines localized chemical bonding as the bonding in which the electrons are shared by two and only two nuclei, whereas delocalized bonding is considered to be when electrons are shared by more than two nuclei.[9]

The consequences of electron (bond) delocalization are well documented, for example, in a special issue of *Chemical Reviews* devoted to aromaticity (2001),[10] in many subsequent papers,[11,12] and in the papers of this issue of the Journal.

Cyclic π-electron "aromatic" compounds were recognized from an early stage[13,14] as systems in which the nonadditivity of collective properties was the main factor determining their physicochemical behavior.[15] The difference between the actual π-electron energy of a molecular entity (benzene) and the π-electron energy of an analogous hypothetical species with a localized π-system led Pauling and Wheland[16] to the concept of resonance energy in terms of VB theory. This review critically evaluates various models and concepts in the quantitative estimation of cyclic π-electron delocalization from an energetic perspective as applied to aromatic systems, which are regarded as the cornerstone of modern organic chemistry.[17] It is important to briefly note that the effect of aromatic stabilization, while being among the largest deviations from additivity found chemically, is at most a few percent of the total atomization energy for typical aromatic systems.[10a] This in turn causes difficulty in isolating it from other important effects that stabilize/destabilize a molecule.

We might liken this problem to a meal to which some spice was added: although nominally the weight of the spice is small, it is essential for the taste of the food and significantly influences its (other) properties. Despite its leading role, aromatic effects are not an easy task to separate out and quantify, for two main reasons: (i) the "spice-free" meal is unavailable, so any comparison has to rely on an arbitrarily chosen approximate model, which is never perfect and changes from case to case (read: from meal to meal); and (ii) the weights of the spicy meal and its "spice-free" model are very similar, which

makes comparisons difficult.[18] Continuing with the food analogy, skeptics sometimes argue that in the literature "a meal" has also been made of the importance of this topic(!)[19] However, aficionados can (and do) frequently point out that cyclic π-electron delocalization, commonly called aromaticity, is a concept of immense practical importance in chemistry.[20]

2. Aromaticity

Historically, the chemical consequences of increased stability were the main features that distinguished aromatic from other classes of compounds.[21-23] Since the introduction of the concept 140 years ago[22a] it has become one of the most important and most frequently used terms in modern organic chemistry; since 1981, it has been mentioned by some 82000 scientific papers dealing with aromatic properties of chemical systems.[24] Moreover, of ~20 million chemical systems known by the end of the past century, more than two-thirds are considered to be fully or partially aromatic.[17]

As with many other important chemical concepts called by Coulson primitive patterns of understanding in chemistry[25] (e.g. electronegativity, van der Waals radii, Lewis acidity/basicity, molecular diagrams, ionicity), aromaticity is not a directly measurable quantity and can be defined only by convention.[19] It has no precise quantitative and generally accepted definition.[10m,20,26] The concept was originally conceived to explain the stability, type of reactivity, and structure of benzene and benzenoid derivatives. However, changes in structure are not always paralleled by changes in reactivity or other physicochemical properties.[15]

By the 1960s, it was established that a planar, cyclic, fully conjugated π-electron system in its ground state is aromatic if it fulfills three main criteria: energetic, geometric, and magnetic.[27-29] Each of these is discussed in turn below.

2.1. Energetic Criterion

The thermodynamic stability of the system is enhanced with respect to a structurally analogous model system (most often an acyclic system), which has no cyclic π-electron delocalization.

Before going into details, we must point out that energy is a property of matter, which by definition needs some kind of reference state. In most physical situations it is clear and logically associated with the conditions of measurements or theoretical computation. For instance, the ionization potential of an atom (or molecule) is defined as the energy required to move an electron away from an atom (or molecule) to infinity. Two kinds of ionization energies can be distinguished: adiabatic and vertical, depending on whether the resulting ion is in its ground vibrational state or possesses the vibrational energy determined by the instantaneous geometry of the molecule upon ionization.[30] Although definitions in physics are often more abstract, they are also more precise than in chemistry. In chemistry the situation is slightly different — in most cases, a given energetic characteristic needs comparison with some molecular

(atomic) system. For chemists, an individual value of, for example, ionization potential is uninteresting unless this quantity is compared with the value for a well-known or reference chemical system. Then it may serve for interpreting some chemical or physical properties. Another problem is that for more complex interactions it is very difficult to find a reference state that would ideally represent a particular phenomenon, which is free from any "contamination" of various additional interactions.

The quantitative measure of the effect is the resonance energy[16] and more generally the aromatic stabilization energy (ASE).[15,26,31,32] The concept originates from valence bond theory by Pauling[16,33−35] and is often regarded as the most basic criterion of aromaticity,[10a] because it influences the reactivity and much of the physicochemical behavior. The criterion has often been used to explore various hypotheses concerning the chemical behavior of systems considered to be aromatic.[10] The pioneering papers by Pauling and Sherman[13] and then Kistiakowsky et al.[14] made use of the difference in energy between a model Kekulé structure[36] (see Figure 1)
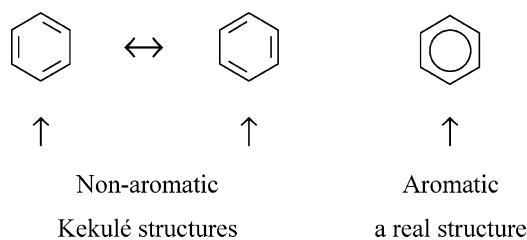

Figure 1. Nonaromatic Kekulé structures[36] and real structure of benzene.

and that of the real molecule. In valence bond theory (VB)[33,37,38] the quantum mechanical resonance energy (QMRE)[39] vertical energy[10s,40,41] and adiabatic energy[40,42,43] are the operational criteria for the extent of electron delocalization.[10s] Within the frame of molecular orbital theory (MO)[44] the concept of resonance energy was first investigated within the Hückel method (HRE)[44] and later substantially developed by Dewar[10p,45] (DRE) and Hess and Schaad (HSRE).[10p,46] Another insight into resonance energy is provided by the models based on graph theory,[47] the most important contributions being the topological resonance energy (TRE)[48] and conjugated circuits model (CCM).[11,49] Many empirical values of resonance energy that derive from heats of reaction[50] (combustion,[13,51] hydrogenation,[14,52] dehydrogenation,[53] tautomeric equilibria,[54−57] etc.) are also available.[4,7,10n,58,59] The application of isodesmic[60] and homodesmotic reactions,[61] using energies from high-level ab initio calculations (replacing the limited-quality semiempirical ones, such as AM1[62] or PM3[63]), accompanied by expanding molecular modeling possibilities[64,65] led to further rapid progress in this field.[10j,15,66]

The main problem in estimating the stabilization energy due to cyclic π-electron delocalization is the choice of an appropriate reference structure (nonaromatic compound or compounds). Even if it is well chosen, the selection is always arbitrary. In consequence, as has been pointed out,[10m] the estimated stabilization energies even for benzene may range by

over 50 kcal/mol! This is due to some ill-conceived choices of reference compound and/or level of theory, often dictated by the earlier availability (or lack of) of experimental data.[32] This point deserves further comment and will be critically discussed later.

2.2. Geometric Criterion

Cyclic bond lengths tend to be intermediate between those typical for single and double bonds.

Importantly, this property is a cooperative effect of both the σ and π orbitals. In the case of benzene, its regular shape is actually a result of the σ-imposed geometric symmetry rather than the π-electrons.[10r,s,39,67] Quantitative descriptors of this effect are the so-called geometrical indices of aromaticity. As with the energetic criterion, they are defined using the difference (in geometry) between a system with full π-electron delocalization and a comparable model nonaromatic Kekulé-like structure with localized double bonds. It has been shown[10m,24,68] that, among the indices based on geometry, the harmonic oscillator model of aromaticity (HOMA) model[69−71] may be considered to be the most reliable.[10a] HOMA is defined as a normalized sum of squared deviations of the individual experimental (or calculated) bond lengths and an optimal bond length, which corresponds to full π-electron delocalization

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum (R_{\text{opt}} - R_i)^2 \qquad (1)$$

where n is the number of bonds taken into the summation and α is an empirical constant chosen to give HOMA equal to 0 for the model nonaromatic systems (e.g. the Kekulé structure) and equal to 1 for a system with all bonds equal to the optimal value R_{opt}. The individual bond lengths are represented by R_i.

In general, the form of the model including heteroatoms is as follows:[69]

$$\text{HOMA} = 1 - \{\alpha(\text{CC}) \sum [R(\text{CC})_{\text{opt}} - R_i]^2 +$$
$$\alpha(\text{CX}) \sum [R(\text{CX})_{\text{opt}} - R_i]^2 + \alpha(\text{CY}) \sum [R(\text{CY})_{\text{opt}} -$$
$$R_i]^2 + \alpha(\text{XY}) \sum [R(\text{XY})_{\text{opt}} - R_i]^2\}/n \quad (2)$$

The values of R_{opt} and α for given types of bonds (CX and XY) are given in Table 1.

Table 1. Parameters of the HOMA Model [R(s) and R(d) Indicate Single and Double Bonds, Respectively; Adapted from Reference 69]

type of bond	R(s) (Å)	R(d) (Å)	R_{opt} (Å)	α
CC[a]	1.467	1.349	1.388	257.7
CN[b]	1.465	1.269	1.334	93.52
CO[c]	1.367	1.217	1.265	157.38
CP[d]	1.814	1.640	1.698	118.91
CS[e]	1.807	1.611	1.677	94.09
NN[f]	1.420	1.254	1.309	130.33
NO[g]	1.415	1.164	1.248	57.21

[a] Based on butadiene-1,3.[72] [b] Based on H_2NCH_3 and $HN=CH_2$.[73] [c] Based on HCOOH monomer.[73] [d] Based on $H_2C=PCH_3$.[73] [e] Based on $S(CH_3)_2$ and $H_2C=S$.[73] [f] Based on $(CH_3)_2C=N-N(CH_3)_2$ and $H_3CN=NCH_3$.[73] [g] Based on $CH_3ON=O$.[73]

Because bond lengths are the most easily accessible structural parameters[62,65,72−76] the HOMA model provides fast and efficient information on aromaticity.[10m,24,68,77] The classic examples where HOMA is superior to other geometry-based models are [6]radialene[24] and perylene[68,78−80] (see Figure 2). In
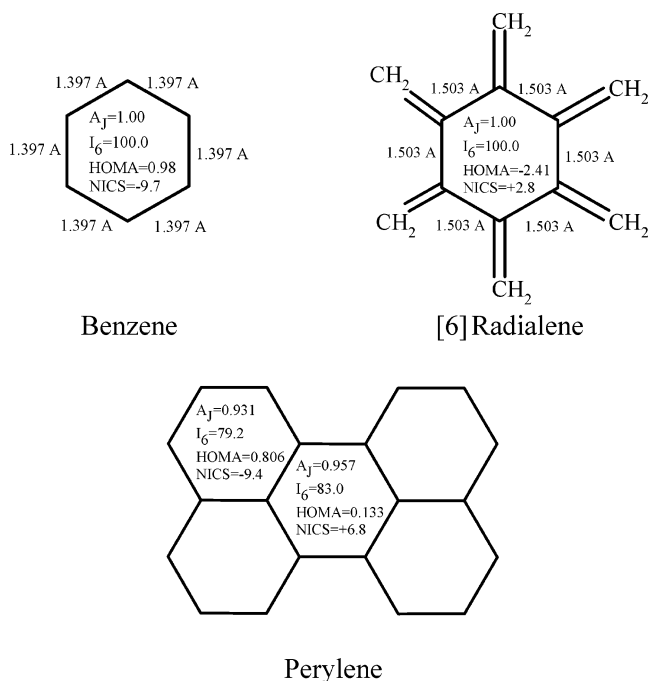

Figure 2. Aromaticity indices for benzene, [6]radialene,[24] and perylene.[68,80]

the case of [6]radialene all CC bond lengths are significantly elongated and equal to ~1.503 Å.[24] Both the Bird I_6 model[81] and the Julg A_J model[82] incorrectly predict a fully aromatic character ($I_6 = 100$ and $A_J = 1.0$, respectively). The reason for this shortcoming is that these geometry-based models are defined solely on the basis of the variance of bond lengths[82] or equivalent bond orders.[81,83] No alternation of bond lengths (orders) implies fully aromatic character, as in the case of benzene. In turn, HOMA indicates the nonaromatic character of [6]radialene (HOMA = −2.41)[24] and the fully aromatic character of benzene (HOMA = 0.98), in line with the NICS[12b,84] estimates (NICS = +2.8 ppm and NICS = −9.7 ppm, respectively).[24] Apart from the variance of bond lengths, HOMA additionally takes into account the deviation of the mean bond length from the optimal one, R_{opt}, which can be viewed as an internal standard. It has been shown that it is possible to separate (in an analytical way) the bond elongation factor (the so-called EN term) and bond alternation factor (the so-called GEO term) contributing to the HOMA model

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum (R_{opt} - R_i)^2 = 1 -$$
$$\left[\alpha(R_{opt} - R_{av})^2 + \frac{\alpha}{n}\sum (R_{av} - R_i)^2\right] =$$
$$1 - \text{EN} - \text{GEO} \quad (3)$$

where R_{av} stands for the mean bond length. Formula 3 has been also extended to hetero-π-electron systems with use of a formalism based on the Pauling bond order.[85]

According to the Clar classification of rings in benzenoid hydrocarbons[86] the central ring in perylene is an empty (nonaromatic) ring. HOMA supports this classification (HOMA = 0.133),[68] as does NICS (NICS = +6.8 ppm).[87] The other geometry-based descriptors such as A_J and I_6 show incorrectly that the central ring is more aromatic than the outer ones. Again, the bond elongation factor (not present in the definitions of A_J and I_6) is of fundamental importance.

The model has been successfully applied to the description of cyclic π-delocalization in a variety of carbo-[70,88−91] and heterocyclic systems,[31,71,92,93] benzenoid hydrocarbons[78−80,87,94−97] and their aza derivatives,[98] nonbenzenoid nonalternant hydrocarbons[99−103] and their heteroanalogues,[104,105] spherical systems,[106,107] and Y aromatics.[108] A great advantage of the model is that it can be used to estimate both the local and global aromaticities of a system. The case of dibenzo(*def,i*)naphtho(1,8,7-*v,w,x*)pyranthrene[109] illustrates this point well. The total aromaticity estimated by the HOMA model (using all CC bond lengths) is 0.589. Figure 3 illustrates the
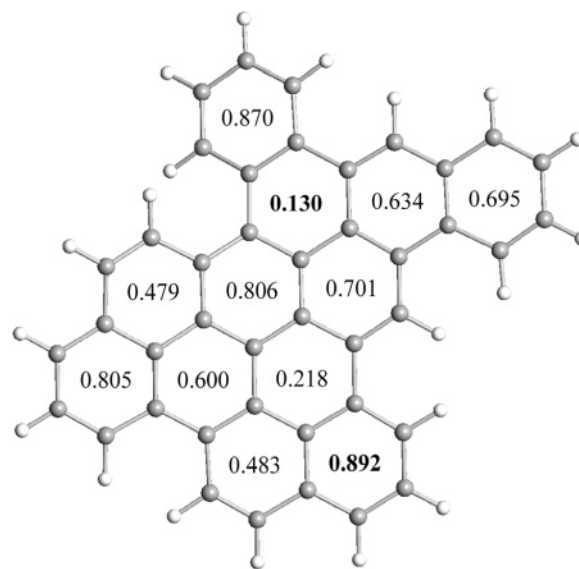

Figure 3. Aromatic character of dibenzo(*def,i*)naphtho-(1,8,7-*v,w,x*)pyranthrene.[109] The numbers in rings indicate the HOMA values.

extent of π-electron delocalization in particular rings. Depending on topological position, HOMA ranges from 0.130 to 0.892.

The free base porphyrin is another example in which the geometry-based descriptor of aromaticity HOMA may be very helpful for interpreting the electronic structure of the system.[110] On the basis of experimental geometries retrieved from the Cambridge Structural Database[76] and supported by ab initio calculations (at the B3LYP/6-31G* level), including the geometry optimizations and calculation of the magnetically based index NICS[84] (at the GIAO-RHF/6-31+G* level), it was found that the most aromatic part of the system is the "internal cross", shown in bold in Figure 4a (HOMA = 0.880, NICS = −16.5 ppm). Two pyrrole rings with NH groups are clearly more aromatic (HOMA = 0.666, NICS = −15.2 ppm) than the other five-membered rings (HOMA = 0.452, NICS = −4.5 ppm). Although the
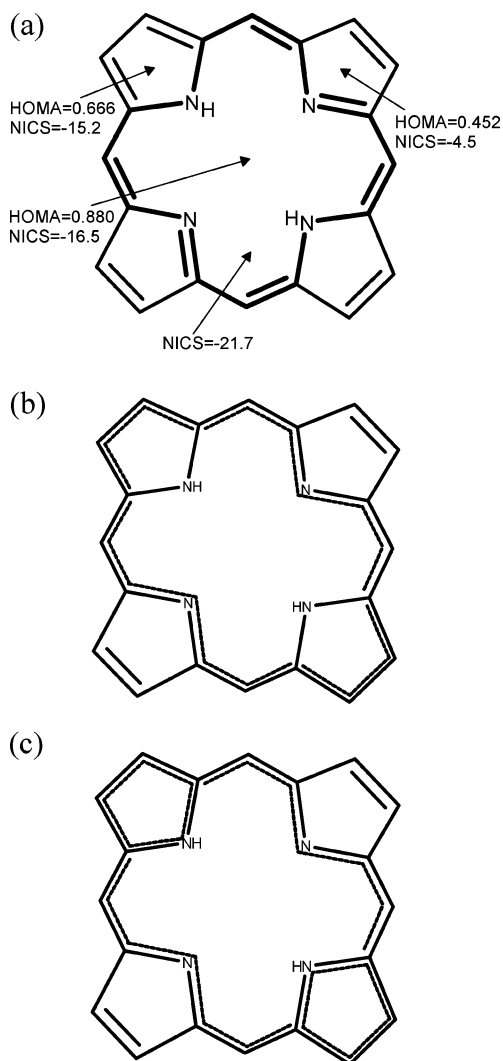
Figure 4. (a) π-Electron structure assessed by descriptors of aromaticity: HOMA and NICS; (b) [18]annulene model of porphyrin; (c) porphyrin as the 22 π-electron macrocycle with two C_2H_2 exocyclic bridges. Reprinted with permission from ref 110. Copyright 1998 Wiley-VCH Verlag GmbH.

Figure 5. Map of π-current density in free-base porphyrin. The diamagnetic circulation is shown anticlockwise. Reprinted with permission from ref 114. Copyright 2002 Wiley-VCH Verlag GmbH.

difference in HOMA may be attenuated due to the uncertainty in the hydrogen positions,[111] both models, HOMA and NICS, agree that the former rings can be considered to be true pyrrole rings, whereas the latter ones have short, localized CC double bonds. On this ground it may be considered that the NH groups are not the inert bridging groups as suggested by the classic [18]annulene model[112] (Figure 4b), but instead they are an integral part of the aromatic system. It has been suggested that a more appropriate description of the porphyrin moiety should be a 22 π-electron macrocycle with two C_2H_2 exocyclic bridges (Figure 4c). Using ipsocentric current-density mapping techniques (a method with a distributed origin for the vector potential, where the induced current density at each point is calculated with that point as origin),[113] Fowler and Steiner[114] visualized the current density in porphyrin induced by a perpendicular magnetic field. Although some details differ,[115] their findings are generally consistent with the results of the HOMA and NICS approaches (see Figure 5).

The interested reader may find earlier reviews on the applications of geometry-based indices of aroma-
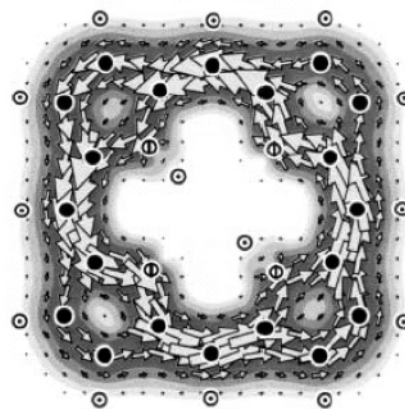
ticity in refs 10m, 24, 116 and in the monograph by Minkin et al.[15]

However, a few critical remarks about the geometry-based models of aromaticity should be made here. First of all, as in the case of energetic descriptors, the reference nonaromatic model systems are arbitrarily chosen. This is clear when one analyzes the variety of systems used as references for single and double bonds (see Table 1).[69] Some of them are conjugated[3] (CC, CO, CP, NN and NO types of bond), whereas the others (CN and CS bonds) are not.

Obviously the geometry-based aromaticity indices, if they are to be applied in a reliable way, need a reliable molecular geometry. However, different experimental techniques such as gas-phase electron diffraction (ED),[72,117] microwave spectroscopy (MW),[118] X-ray and neutron diffraction,[75,119] and occasionally infrared or Raman spectroscopy,[120] as well as theoretical approaches,[62,65] (semiempirical methods,[121] ab initio or DFT with different basis sets), all result in molecular geometries defined in a slightly different way.[122,123] Fortunately, the differences in experimental techniques are often not significant for the purpose of describing aromaticity using geometry-based indices.[10m] However, the quality of theoretical calculations may be of key importance, especially for subtle analyses of small differences in aromaticity.[10m] Recently, Neugebauer and Häfelinger[122] made an extensive analysis of optimized bond lengths using DFT methods[124,125] using 6 functionals (SVWN, Becke88, BLYP, B3LYP, B3PW91, and BhandH)[126] and 10 different basis sets (STO-3G, 6-31G, 6-311G, 6-31G*, 6-31G**, 6-311G(3df,3pd), cc-pVDZ, AUG-cc-pVDZ, cc-pVTZ, AUG-cc-pVTZ).[127] They correlated accurate experimental r_e CC (and CH) distances with corresponding DFT optimized molecular structures. Their regressions can be used to predict accurate experimental r_e equilibrium CC distances for bonds of medium-sized to large molecules and enable the introduction of distance-dependent scaling factors, which allow very accurate predictions of higher basis set geometries using smaller ones. Similar analyses have also been carried out with other functionals (VWN, SLYP, VWN, BP91, ACM)[128] and other types of bonds[129] at the Hartree–Fock (SCF HF) ab initio level.[123] On the other hand, in the case of X-ray or

neutron diffraction the strong intermolecular interactions in the crystal lattice may sometimes be of similar magnitude to intramolecular effects and change the extent of π-electron delocalization.[69,75,130] For instance, it has been shown[131,132] that in phenols the perturbation in the OH group due to the hydrogen bonding not only affects bonds in the closest vicinity but is also transmitted to other bonds in the ring. Depending on the acidity of phenol, the experimental CC bond lengths in the benzene fragment can vary from 1.365 to 1.447 Å.[131] Figure 6 presents the
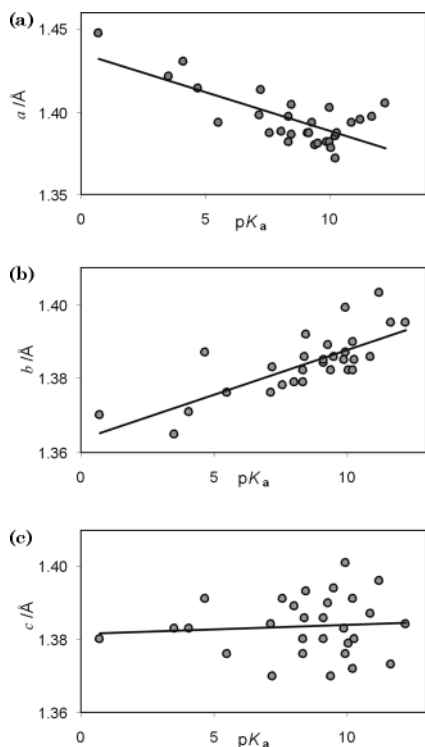
Figure 6. Scatter plots of the mean geometric parameters a, b, c versus the acidity of phenols: (a) a versus pK_a, $cc = -0.736$; (b) b versus pK_a, $cc = 0.763$; (b) c versus pK_a, $cc = 0.072$. Number of data points, $n = 29$. Reprinted with permission from ref 131. Copyright 2004 Polish Chemical Society.

dependencies between the pK_a of complexes of substituted phenols with oxygen and nitrogen bases retrieved from the Cambridge Structural Database[76] and the mean bond lengths of the ring (for enumeration of the bonds see Figure 7).
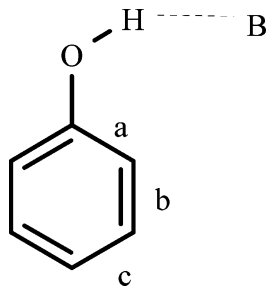

Figure 7. Labeling of geometric parameters used in Figure 6. a, b, and c are the mean values for these kinds of bonds.

Similar analysis based on the optimized geometries (at B3LYP/6-311+G** level) of complexes of phenol[132]

and *p*-nitrophenol[132,133] interacting with fluoride anion led to the conclusion that the geometry-based index HOMA may range from 0.55 to 1.0 (!) depending on the O...F distance.[132] Figure 8 presents this dependence.
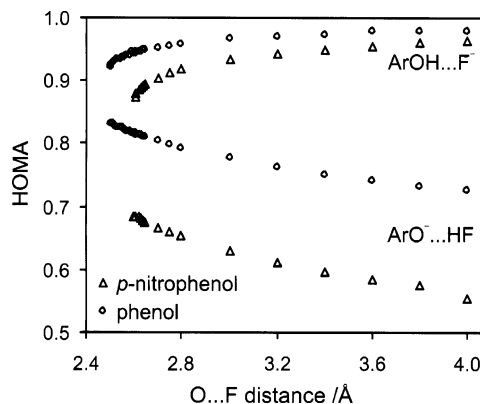

Figure 8. Variation of HOMA values for ArOH···F⁻ and ArO⁻···HF interactions for *p*-nitrophenol and phenol complexes. Reference values of HOMA are 0.989, 0.985, 0.683, and 0.514 for phenol, *p*-nitrophenol, phenolate, and *p*-nitrophenolate, respectively. Reprinted with permission from ref 132. Copyright 2004 American Chemical Society.

The problem of intermolecular interactions affecting bond length alternation (and hence aromaticity) is very complex and is discussed in detail in another review in this issue by Krygowski et al.,[134] devoted to interrelations between H-bonding and π-electron delocalization.

Finally, apart from the variations in geometry-based indices caused by the source of the geometrical data, another very important point should be considered. Bond length equilization (or alternation) does not always correctly indicate the changes in π-electron delocalization! Recently, Fowler et al.[135,136] analyzed the ring currents[113] in cyclooctatetraene systems, tetrakis(bicyclo[2.1.1]hexeno)cyclooctatetraene (D_{4h}), planar cyclooctatetraene (COT) (D_{4h}), tetrakis(cyclobutadieno)cyclooctatetraene (D_{4h}), tetrakis(cyclobuteno)cyclooctatetraene (D_{4h}), and in tub-shaped equilibrium COT (D_{2d}) (see Figure 9). Despite a similar degree of strong bond length alternation in the COT moieties ($\Delta R = 0.153-0.184$ Å), the ring current patterns may be totally different. Following the London[137] expectations of paratropic ring currents in 4n π systems, the tetrakis(bicyclo[2.1.1]hexeno)-cyclooctatetraene[138] (a), the planar COT[139] (b), which is the transition state for tub-to-tub inversion, and the tetrakis(cyclobuteno)cyclooctatetraene[140] (e) all display a strong central paratropic ring current. Relaxation of cyclooctatetraene to its tub-shaped equilibrium geometry (c) has relatively little effect on the bond length alternation ($\Delta R = 0.155$ Å, the same as in the case of planar COT) but completely destroys the delocalized ring current. The π-current density map drawn in the median plane of the molecule shows localized circulations from the four double bonds (two above and two below the plotting plane). In the case of tetrakis(cyclobutadieno)cyclooctatetraene (d), bond length alteration is exactly the same as in the case of (bicyclo[2.1.1]hexeno)-cyclooctatetraene (a), but the π-electron ring current
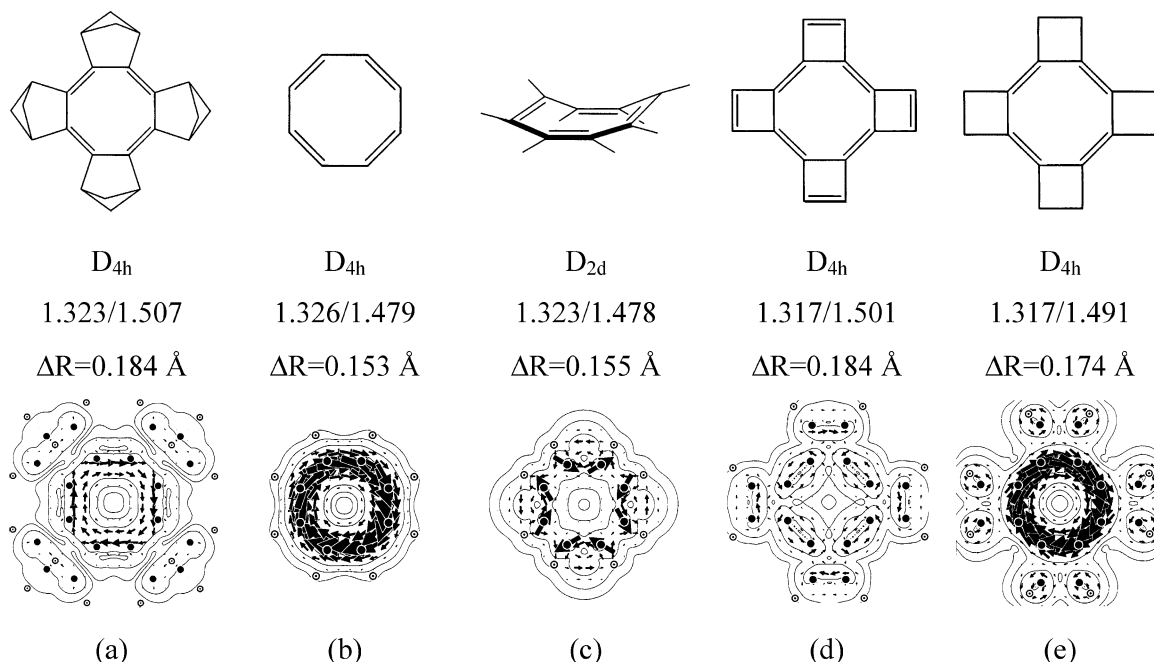
D_{4h}	D_{4h}	D_{2d}	D_{4h}	D_{4h}
1.323/1.507	1.326/1.479	1.323/1.478	1.317/1.501	1.317/1.491
ΔR=0.184 Å	ΔR=0.153 Å	ΔR=0.155 Å	ΔR=0.184 Å	ΔR=0.174 Å
(a)	(b)	(c)	(d)	(e)

Figure 9. Maps of π-current density in (a) tetrakis(bicyclo[2.1.1]hexeno)cyclooctatetraene, (b) planar cyclooctatetraene (COT), (c) tub-shaped COT, (d) tetrakis(cyclobutadieno)cyclooctatetraene, and (e) tetrakis(cyclobuteno)cyclooctatetraene: (●) carbon; (⊙) hydrogen. Except for (c) the nuclear positions are projected in the plotting plane. In (c) the median plane was used as the plotting plane. The current densities induced by a unit magnetic field acting along the principal axis are plotted in a plane 1 Å above that of the central ring. The diamagnetic circulation is shown anticlockwise and the paramagnetic one clockwise. Reprinted with permission from ref 135. Copyright 2002 Wiley-VCH Verlag GmbH.

shows the typical signature of localized double bonds, specifically as a result of the conjugation of the clamping group with the central ring. Obviously, the differences observed in these current maps are not a consequence of differences in bond length alternation. Instead, the switch from localized to delocalized behavior is due to the difference between the electronic structures of the 16 π-electron conjugated tetrakis(cyclobutadieno)cyclooctatetraene and the 8 π-electron cyclooctatetraene system. Similar conclusions for COT were reached independently by Krygowski et al.[24,91]

Localization of the electronic structure of benzene to achieve 1,3,5-cyclohexatriene by annelation with rigid bridges was challenging for many synthetic and computational efforts.[141] Fowler et al.[142] has shown that the choice of a bridge determines whether a diamagnetic ring current sustains. Despite a substantial alternation of the CC bond lengths of the benzene ring in tris(bicyclo[2,1,1]hexeno)benzene (a) (Figure 10), as well as in tris(cyclobuteno)benzene (b) (Figure 10), a strong central diamagnetic ring current is retained, whereas in the case of tris(benzocyclobutadieno)benzene (c) (Figure 10) and tris(cyclobutadieno)benzene (d) (Figure 10), where the bond length alternation in the central ring is comparable, no diamagnetic π-electron ring current is observed. Direct visualization of the current density in maps of highly strained benzenes[143] (annelated by cyclopropa, cyclobuta, and cyclobutadieno clamps) indicates that, despite significant alternation of bonds, only the annulation by unsaturated clamps disrupts the conventional diamagnetic ring current. Similarly as in the case of cyclooctatetraene, the differences in current maps are evidently not a consequence of

differences in bond length alternation. The electronic character of the clamping groups, rather than their role as geometrical constraints, is the decisive factor in whether the central ring current is retained or not. Strong bond length alternation in a ring may be a symptom of either a rigid saturated clamp without significant effect on ring current or a strongly interacting unsaturated clamp which, by pushing the HOMO and LUMO apart, quenches the current.[142]

Very recently, Solà et al.[144] found another limitation of the geometry-based HOMA approach: it finds no aromaticity in the transition state of the Diels−Alder reaction.

On the basis of the philosophy of the HOMA, Matta and Hernàndez-Trujillo[145] and Solà et al.[146] proposed new indices of aromaticity, θ and FLU (aromatic fluctuation index), respectively, where the bond distances were replaced by relevant delocalization indices, in both cases derived from Bader's atoms in molecules (AIM) theory.[147]

2.3. Magnetic Criterion

An external magnetic field perpendicular to the molecular plane induces a diatropic ring current. This current gives rise to a secondary field, which is directed antiparallel with respect to the external field (see Figure 11).[148,149]

Historically, the exaltation of magnetic susceptibility,[137,150−153] its anisotropy,[154−156] and characteristic proton NMR chemical shifts[15,157] were important criteria frequently used in experimental (and theoretical) work. Now, the nucleus-independent chemical shift (NICS) is often considered to be a better criterion.
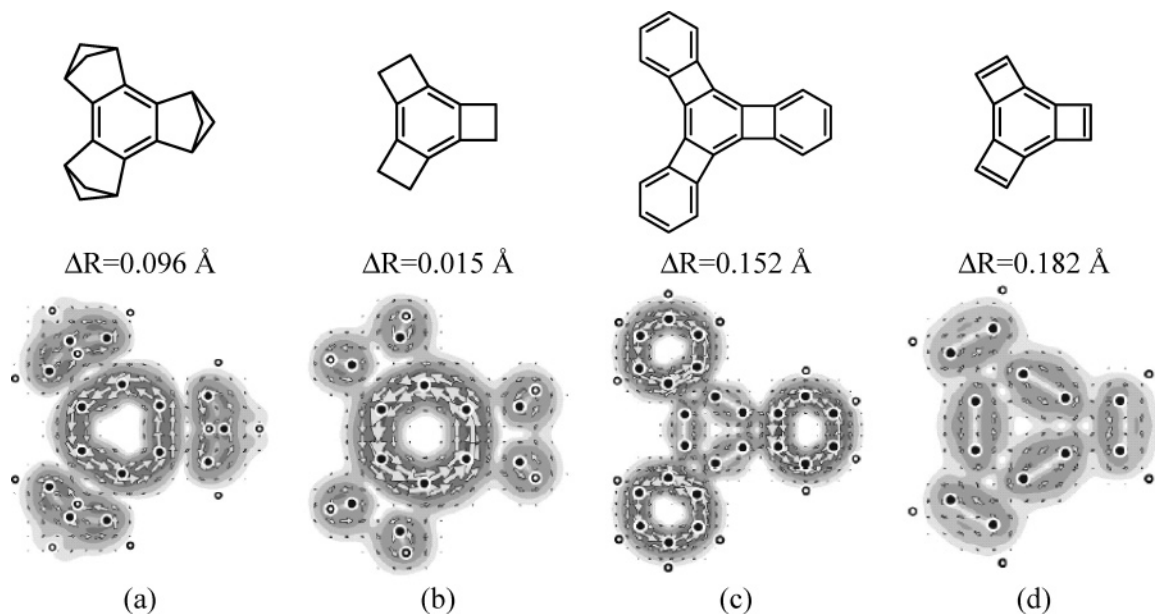
ΔR=0.096 Å   ΔR=0.015 Å   ΔR=0.152 Å   ΔR=0.182 Å

(a)   (b)   (c)   (d)

Figure 10. Maps of π-current density in (a) tris(bicyclo[2.1.1]hexeno)benzene, (b) tris(cyclobuteno)benzene, (c) tris(benzocyclobuteno)benzene, and (d) tris(cyclobutadieno)benzene: (●) carbon; (○) hydrogen. The nuclear positions are projected into the plotting plane, the current densities are plotted 1 Å above the molecular plane. The diamagnetic circulation is shown anticlockwise and the paramagnetic one clockwise. Reprinted with permission from ref 142. Copyright 2001 Royal Society of Chemistry.

External magnetic field Ho
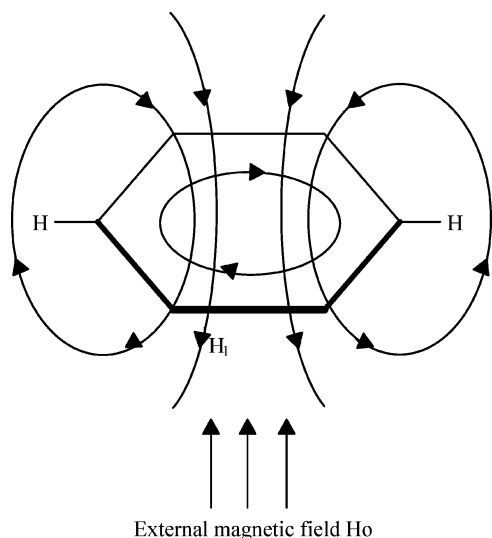
Figure 11. External magnetic field inducing an internal ring current.

The exaltation of magnetic susceptibility is defined as

$$\Lambda = \chi_m - \chi_a \qquad (4)$$

where χ_m and χ_a are the measured (or computed) bulk susceptibility values for a given cyclic conjugated system and for a hypothetical cyclic system with localized double bonds in which the ring current vanishes. Dauben et al.[153,158,159] suggested diamagnetic susceptibility exaltation as the major criterion for aromaticity. Recently, also Schleyer[26,160] proposed that "compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic delocalization may also result in bond length equalization, abnormal chemical shifts, and magnetic anisotropies, as well as chemical and physical properties that reflect energetic stabilization". However, as with the

energetic criterion, the final results depend strongly on the reference model structure, which is usually calculated from additive schemes.[153] For this purpose several sets of parameters have been proposed,[161,162] including approaches based on homodesmotic reactions.[32,33,61] In the case of theoretical investigations, the reliability depends obviously on the level of theory applied, including the treatment of electron correlation effects.[10m,26]

Because the exaltation of magnetic susceptibility depends on the size of a ring in question,[84] Gayoso and Ouamerali[163] proposed to normalize it in this way

$$\rho = k\frac{n\Lambda}{S^2} \qquad (5)$$

where n is the number of π-electrons, S is the area of the ring, and k is the normalization factor referring the ρ values to benzene.

Flygare et al.[154–156] proposed the anisotropy of magnetic susceptibility, defined as a difference between out-of-plane and the average in-plane components of the tensor of magnetic susceptibility, as a criterion of aromaticity

$$\Delta\chi = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) \qquad (6)$$

where χ_{xx}, χ_{yy}, and χ_{zz} are the elements of the diagonalized magnetic susceptibility tensor and z is the out-of-plane axis for the planar molecule.

Although this is attractive because no reference system is needed, in practice the anisotropy of magnetic susceptibility is difficult to apply as a measure of π-electron delocalization; its magnitude is determined by not only ring currents but other effects such as local contributions due to π-bond anisotropy and the anisotropy of CC and CH σ-bond magnetic susceptibility, as well as the anisotropy due to local

paramagnetic currents.[164] For instance, in the case of benzene about half of the anisotropy of magnetic susceptibility is attributable precisely to local contributions.[15,155,165] For these reasons, the anisotropy of magnetic susceptibility should not be considered as a fully reliable indicator of the extent of cyclic π-electron delocalization in the ring.[103] Another suggestion is to use the nonlocal contribution to anisotropy that can be estimated by comparison of the anisotropy of magnetic susceptibility (given by eq 6) and a local contribution calculated for a model localized structure.[166] Again, the reference is of key importance.

The deshielding of outer protons and the shielding of inner ones in aromatic annulenes attributed to diamagnetic ring currents (and an opposite picture for antiaromatic annulenes arising from paramagnetic ring currents) offered an excellent opportunity for devising a scale of aromaticity based on ^{1}H NMR spectra.[15,157] Aromatic protons typically have signals of ~7 ppm or more, whereas olefinic protons resonate at ~5 ppm.[26] The difference is often interpreted using Pople's ring current model (Figure 11).[15,148,167] However, the values of magnetic shieldings depend on many contributions,[164] and the induced diamagnetic ring current (albeit very important) is only one of them. In fact, Schleyer and Wannere[168] have recently shown that the unusual downfield of ^{1}H shielding in benzene (and other arenes) with respect to vinylic protons is not due to the deshielding ring current effects. Instead, factors such as variations in all of the C−C(σ) and the C−H contributions as well as the different π-bond shielding in benzene compared to cyclohexene are decisive! The interested reader is referred to an excellent review by Mitchell on measuring aromaticity by NMR.[10i]

The NICS is a theoretical concept that has helped to stimulate interest in aromaticity and at the same time led to great progress in understanding many aspects of cyclic systems with delocalized (or localized) electrons including rings,[169] clusters,[10b,170] transition states,[171] excited states,[172] transition metal complexes,[173] homoaromatic,[10d,171f,174,175] twist systems,[176] and three-dimensional ones,[177] such as, for example, spherical species.[95,178] According to the Institute for Scientific Information (Philadelphia),[179] by the end of 2004 over 600 papers cited the original 1996 Schleyer *J. Am. Chem. Soc.* paper.[84] Why? Because the NICS criterion of aromaticity is simple and efficient. Originally it has been defined as the negative value of the absolute shielding computed at the geometric center of a ring system. Now it is also calculated at other points,[110] inside or around molecules. A great advantage of the model is that no reference structures, nor increment schemes and calibrating reactions, are needed. Rings with negative NICS values qualify as aromatic, and the more negative the NICS value, the more aromatic are the rings. Consequently, an antiaromatic system has NICS > 0. Because the local effects of σ-electron structure may significantly influence the NICS values, calculation of NICS 1Å above the ring (where local contributions diminish relative to the ring current effects)[180] and more recently dissected NICS[181]

was recommended. Because the magnetic response properties are tensors[157] and the trace (being the sum of three diagonal components) for a number of reasons may be very different,[12a] most recently Schleyer[12b] recommended the component corresponding to the principal axis perpendicular to the ring plane, NICS$_{zz}$, as a preferred measure for the characterization of the π-system. The tensor components have also been used earlier by Wiberg in his review to describe antiaromaticity in monocyclic conjugated carbon rings.[10j]

One of the disadvantages of NICS is that it is a local descriptor of aromaticity, although some attempts have been made to use it globally.[66a] As with the other magnetically based indices of aromaticity, NICS is size-dependent, and, moreover, its absolute value depends on the level of theory applied.[84] This causes difficulties in direct comparisons of aromaticity in very different systems.[182] Another shortcoming is that NICS is a wholly theoretical concept and a nonmeasurable property.[12a] Despite this, NICS is undoubtedly a valuable and popular tool for the assessment of aromaticity, and the interested reader is referred to the comprehensive review on the topic by Schleyer et al.[183]

The other extremely useful tool provided by theory is magnetic field induced current density maps. Recently they were reviewed by Gomes and Mallion[10l] and Lazzeretti.[12a,157] Although the maps are less useful for quantitative assessment of aromaticity,[184] they visualize diatropicity more directly than any other qualitative or quantitative tool[12a,185] and are valuable instruments for interpreting the large out-of-plane component of the magnetic susceptibility tensor in aromatics. Current density maps illustrated in a conventional way as usually lack information concerning the electron flow perpendicular to the molecular plane, although this can also be shown.[186] The ipsocentric technique[113] involving continuous transformation of origin of current density in a diamagnetic zero formulation[187] is the state-of-the-art technique. By recovering chemical intuition they have been paramount in resolving many long-standing controversies in organic chemistry.[12f,h,l,m,114,135,136,142,143,188,189] A few examples are presented in Figures 5, 9, and 10.

In competition with energetic stability, magnetic criteria are often considered to be the fundamental criteria of aromaticity.[26] Apart from the paper devoted to NICS,[183] three others discuss the relationships between magnetic properties and π-electron delocalization.[190−192]

2.4. Reactivity Criterion

Aromatic compounds generally undergo electrophilic substitution reactions (so-called aromatic substitution) more easily than they do addition.[9,193] In other words, they exhibit a tendency to retain their initial π-electron structure.[194] However, this criterion is not a property of the ground state of a system but depends on the difference in energy between the ground state and a transition state toward an intermediate. More precisely, unlike thermodynamic stability, which is a unique property of the ground state,

kinetics depends on energies of the ground state, transition states, and also intermediate states, with the possibility of various subsequent reactions leading to stable products. This illustrates the difficulties of formulating a general and quantitative aromaticity criterion based on reactivity, although a few theoretical attempts (mostly for benzenoid hydrocarbons) have been made.[66a,171h,195] Electrophilic substitution reactions are more typical for aromatic compounds than addition reactions. However, the increasing tendency to addition within the series of linear polyacenes is well-known: beginning with anthracene, the 1,4-addition process becomes more important, and in pentacene it is dominant.[20] For fullerenes the substitution is not defined, but the addition reactions are familiar.[10c,26] In such compounds, cyclic π-electron delocalization is possible, which potentially leads to quite different physicochemical properties.

Because the relationship between the change of resonance energy and free energy of activation (or its equivalent) depends on the type of reaction, various models of reactivity[66a,195] have limited applications and can be used only for simple cases. Moreover, they depend strongly on the level of theory used.[20]

Reactivity is closely related to the HOMO and LUMO energies. The idea of the absolute hardness[196] (half the HOMO/LUMO gap)[197] and relative hardness[198] (the difference between the hardness of a molecule and some hypothetical reference structure) is commonly used as a criterion of chemical reactivity and stability.[199] Good relationships between hardness and resonance energy for five-membered heterocyclic rings,[199] benzenoid hydrocarbons,[200] and other hydrocarbons have been found.[201]

It should be emphasized that reactivity, despite being a non-ground-state property, is a very important criterion for aromaticity. Following the most recent proposal, we consider as fully aromatic those cyclic π-electron systems that follow all of the features (energetic, geometric, magnetic, reactivity) of aromatic character, whereas those which follow some but not all of them are partly aromatic.[20] If only the first three criteria are considered, then cyclic π-electron delocalization should be the description applied, instead of aromaticity.

2.5. Some Other Remarks on Aromaticity

A key criterion for aromaticity is the Hückel $4N + 2$ rule,[202] which states that cyclic (planar) π-electron systems with $(4N + 2)$ π-electrons are more stable than those containing $4N$ π-electrons (N is an integer). Despite the qualitative formulation, it has stimulated research in synthetic organic chemistry and theoretical organic chemistry in the intervening decades.[203] Antiaromatic cyclobutadiene (four π-electrons), aromatic benzene (six π-electrons), and antiaromatic (planar) cyclooctatetraene (eight π-electrons) are the most typical examples. Fulvene is strongly π-electron accepting, whereas the ring in heptafulvene is a strongly π-electron-donating system. Therefore, as shown in Figure 12, electron-donating/accepting substituents stabilize fulvene and heptafulvene, respectively. In line with this picture Havenith et al.[188t] nicely documented the diamagnetic
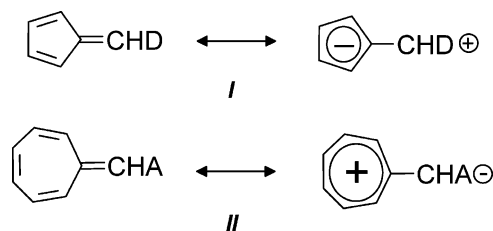
Figure 12. Illustration of the Hückel rule for the fulvene (I) and heptafulvene (II) derivatives. Reprinted with permission from ref 99. Copyright 1995 Slovak Academy of Sciences.

ring current both for the BH_2^- analogue of fulvene and for the NH_2^+ analogue of heptafulvene, along with the island patterns of localized bond-centered circulations for the parent fulvene and heptafulvene systems (see Figure 13). Stępień et al.[101,102] found
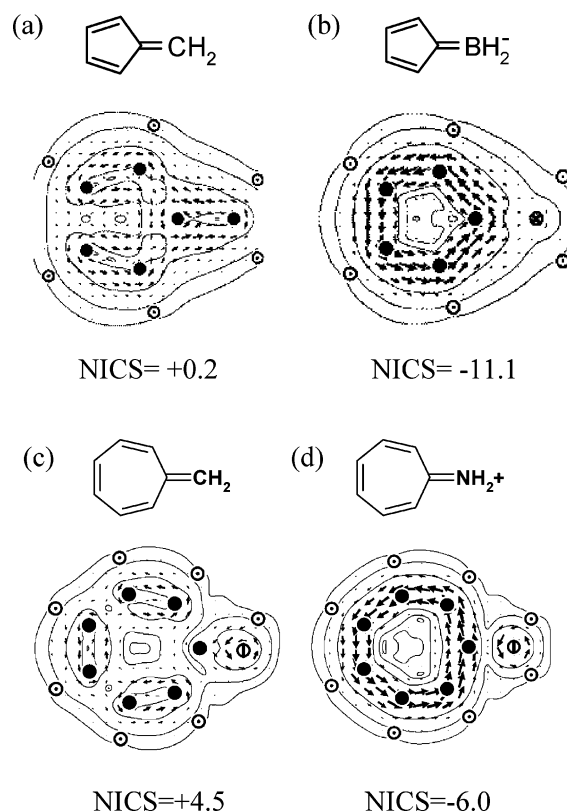
Figure 13. Maps of π-contributions to current density for (a) fulvene, (b) BH_2^- analogue of fulvene, (c) heptafulvene, and (d) NH_2^+ analogue of heptafulvene. The current densities induced by a unit magnetic field normal to the molecular plane are plotted in a plane 1 Å above that of the ring, with contours denoting the modulus of the current density and vectors representing in-plane projections of current. Diamagnetic (diatropic) circulation is shown anticlockwise and paramagnetic (paratropic) circulation clockwise. Reprinted with permission from ref 188t. Copyright 2002 Royal Society of Chemistry.

excellent relationships between the variation of cyclic π-electron delocalization (ASE, HOMA, and NICS) in mono-6-substituted fulvenes and the nature of the substituent, in line with these expectations. Figure 14 presents these plots. Similar dependencies were also found for heptafulvenes.[103]

A direct relationship[204] with the thermodynamic stability of neutral monocyclic conjugated species is
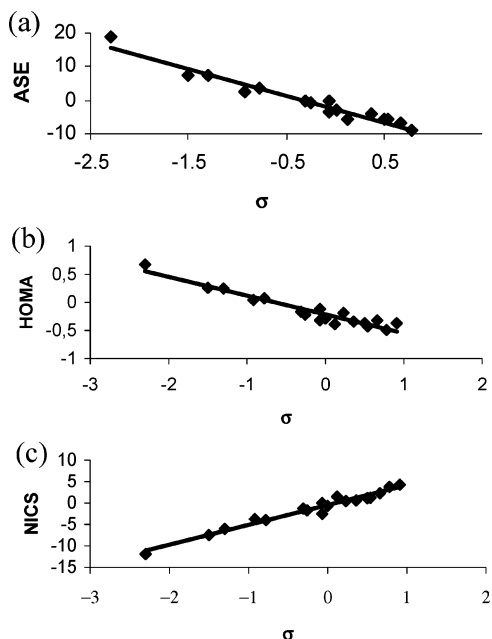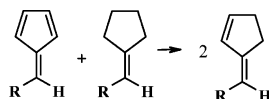
(a)   (b)

Figure 16. Structures of (a) cycl[3.3.3]azine and (b) pyrene.

dominant factor determining their stabilities. For polycyclic systems the rule can be formulated in a general way using graph-topological approaches,[207] which consider various types of circuits.

Using the atoms-in-molecules (AIM) theory of Bader,[147] Solà et al. have recently invented an electronically based indicator of aromaticity called the para-delocalization index (PDI).[208] It is defined as the average of all delocalization indices (DI)[209] between para-related carbon atoms in a six-membered ring. The DI value between atoms A and B, $\delta(A,B)$, is obtained by double integration of the exchange correlation density over the basins of atoms A and B, which in turn are defined from the zero-flux gradient condition in $\rho(r)$:[209]

$$\delta(A,B) = -\int_A \int_B \Gamma_{XC}(\vec{r}_1,\vec{r}_2) \, d\vec{r}_1 \, d\vec{r}_2 -$$
$$\int_B \int_A \Gamma_{XC}(\vec{r}_1,\vec{r}_2) \, d\vec{r}_1 \, d\vec{r}_2 =$$
$$-2\int_A \int_B \Gamma_{XC}(\vec{r}_1,\vec{r}_2) \, d\vec{r}_1 \, d\vec{r}_2 \quad (7)$$

δ provides a quantitative measure of the number of electrons delocalized or shared between atoms A and B.[209,210] The PDI is therefore clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity. Unsurprisingly, this theoretical model has been successfully applied to describe π-electron delocalization in many chemical species such as polycyclic aromatic hydrocarbons,[208] carbazole derivatives,[12i] fullerenes,[211] and open shell systems.[212] Most recently it has been used to study the relationship between aromatic stabilization and substituent resonance effects, with good relationships between PDI and substituent constants.[88] The theoretical quantification of electron delocalization in aromatic molecules by means of AIM[147] and electron localization function ELF[213] topological approaches is the topic of another review in this issue.[214]

3. Resonance Energy

As already mentioned, the resonance energy (RE)[16] concept was born in the 1930s within the concept of valence bond (VB) theory. Independently, two successful experimental approaches at that time by Pauling and Sherman[13] and by Kistiakowsky et al.[14] resulted in an enormous body of subsequent experimental and theoretical work. The latter has been mostly realized within the framework of molecular orbital theory (MO), leading to great variety of expanding methodological possibilities. Historically, the most important steps involve the Hückel resonance energy (HRE),[44] Dewar resonance energy

Figure 14. Dependencies between ASE (a), HOMA (b), and NICS (c) versus substituent constants (σ_p^+ and σ_p) for mono-6-substituted fulvenes. The correlation coefficients $cc = 0.979$ (a), $cc = 0.960$ (b), and $cc = 0.982$ (c). ASE[102] is defined as follows:

where R = H, CH$_3$, OCH$_3$, NH$_2$, NMe$_2$, F, CMe$_3$, OH, O$^-$, CF$_3$, COCH$_3$, CONH$_2$, SiMe$_3$, B(OH)$_2$, NO$_2$, CN, NO, CCH. Reprinted with permission from ref 101. Copyright 2001 Elsevier Science.
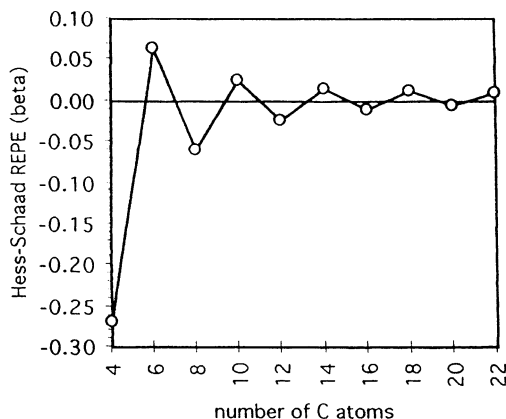
Figure 15. Resonance energies per π-electron, REPE (in units of β) for the conjugated monocyclic hydrocarbons using the Dewar−de Llano reference structure with eight bond types and the Hückel computational method. Reprinted with permission from ref 10p. Copyright 2001 American Chemical Society.

shown in Figure 15. It should be stressed that originally the rule applies to monocyclic systems, and its application to polycyclic systems can lead to confusion. For example, cycl[3.3.3]azine (Figure 16a) has 14 π-electrons, but is known as antiaromatic.[205] In turn, pyrene (Figure 16b) having 16 π-electrons is a system commonly considered to be aromatic.[95,206] The rule also loses its applicability for highly charged species, because the electrostatic interactions are the

(DRE),[10p,45] and Hess−Schaad resonance energy (HSRE).[10p,46] Nowadays the isodesmic[60] and especially the homodesmotic[61] approaches are widely considered to be the most sophisticated methods for estimating the extra stability due to cyclic π-electron delocalization. Because the RE is well-defined within VB theory, the aromatic stabilization energy (ASE) is much more general and therefore has gained wider acceptance.

3.1. Valence Bond Approach

Let Ψ_o be the correct wave function for a given case. A fundamental principle of quantum mechanics states that the energy value W_o calculated quantum mechanically with the correct wave function Ψ_o for the normal state of the system is lower than that calculated with any other wave function Ψ that might be proposed; as a consequence, the actual structure of the normal state of a system is that one, of all conceivable structures, that gives the system the maximum stability.[33] In the simplest case: if structures I and II represent the normal state of the system under study, then the theory states that the more general function $\Psi = c_I\Psi_I + c_{II}\Psi_{II}$ is also a possible wave function for the system and the ratio c_{II}/c_I is chosen in the way to minimize the energy of the system. If the ratio is neither small nor large, it means that the state is described by both structures I and II (in combination). The structure of such a system is not exactly intermediate between the two structures, I and II, because as a result of resonance (mixing) it is stabilized by the "resonance energy". The system is described as "resonating" between structures I and II. To be precise, the extra stability of the system relative to structure I or II (whichever is the more stable) is called the resonance energy. The more general case involves more structures, and the wave function may be formed by linear combination of the wave functions Ψ_i corresponding to the N structures

$$\Psi = \sum_i^N c_i\Psi_i \qquad (8)$$

where the c_i coefficients are found by minimization of the energy. Benzene can be represented by the 2 most stable valence bond Kekulé structures, 3 Dewar benzene structures, and 170 ionic structures as shown in Figure 17.[215]

Detailed VB calculations for benzene indicate that the Dewar structures make only very small contributions (<6−7% each)[216] to the overall stabilization of the ground state. Explicit calculations indicate, however, the great importance of ionic structures and show that all of these configurations mix with the ground state.[217] The resonance energy (the so-called vertical resonance energy, VRE[10s] (previously denoted in the literature as quantum mechanical resonance energy, QMRE[39,218]) is defined as the difference between the actual VB energy of the molecule and the VB energy calculated for the most stable single contributing structure having the same geometry. In the case of benzene, this involves the energy difference between 1,3,5-cyclohexatriene (with the same
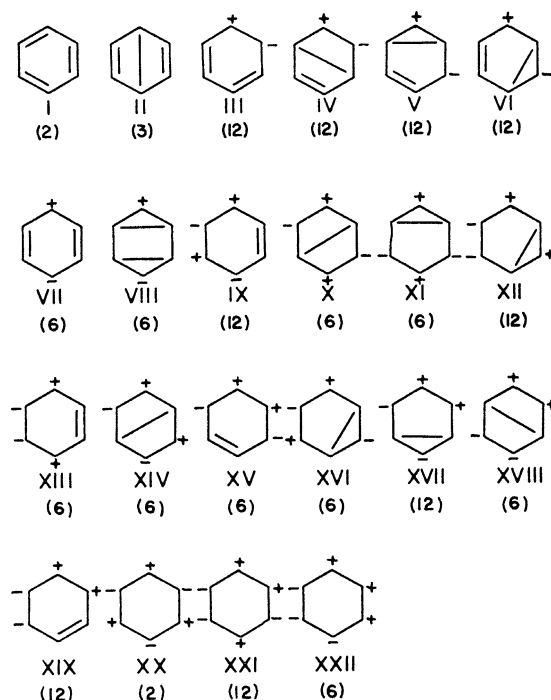

Figure 17. Valence bond representation of benzene and the number of equivalent structures. Reprinted with permission from ref 215. Copyright 1974 American Chemical Society.

geometry as benzene) and benzene. The estimated values of VRE for a few species (including also a few transition states) are presented in Table 2.

Table 2. Vertical Resonance Energies for Delocalized Species Based on HF/6-31G Calculations,[39,218] Using the Method in Reference 40 (Given in Kilocalories per Mole). Adapted from ref 10s

system	VRE	system	VRE
N_4	45	N_6	103
P_4	25	P_6	44
C_4H_4	30 (22[222])	C_6H_6	85 (55,[219] 62,[a] 63,[41] 65[b])
Si_4H_4	18	Si_6H_6	42
H_6	119	C_8H_8	49

[a] Using CASSCF projection into the space of Kekulé structure. [b] Using bond-distorted orbitals where semidelocalization is permitted only to the centers that are formally bonded in the Kekulé structure. Following Shaik et al.[10s] this method leads to more realistic values than those produced by removing the constraints over the sites of semidelocalization.

A great advantage of the VRE concept is that these values are an intrinsic property of a system. However, as can be deduced from Table 2 all of the systems have appreciably high VREs, which makes it difficult to apply this idea. For instance, the H_6 and N_6 transition states have substantially bigger values of VRE than benzene, whereas the cyclobutadiene and planar cyclooctatetraene have approximately one-third and half of the VRE of the benzene value. In general, unstable species are characterized by large values of VRE and, importantly, the aromatic $4N + 2$ π-electron analogues of benzene have considerably higher values than the $4N$ π-analogues of cyclobutadiene.[10s,218] The largest differences in VRE, however, occur for aromatic and antiaromatic species with an odd number of atoms and mixed-valence

situations.[10s] Moreover, the absolute values may vary considerably (e.g. by 30 kcal/mol for benzene[40,219]), due to the different numbers of structures and types of atomic orbitals used in actual VB calculations.

The underlying reason for the quite substantial values of VRE values is that they generally correspond to the energy contribution made by electron delocalization as a whole and not to the part of it represented solely by the cyclic π-electron delocalization.[15] To quantify the thermodynamic stability/instability of a cyclic molecule, most of the VRE energy is frequently referred to a polyene (most often hexatriene or butadiene) with the same number of π-conjugative interactions as the relevant polygon. This leads to the Dewar resonance energy (DRE),[10p,45] which is widely considered as the most common standard resonance energy.[15] The Hess cycle for relating the DRE to VRE for benzene is shown in Figure 18.[10s]
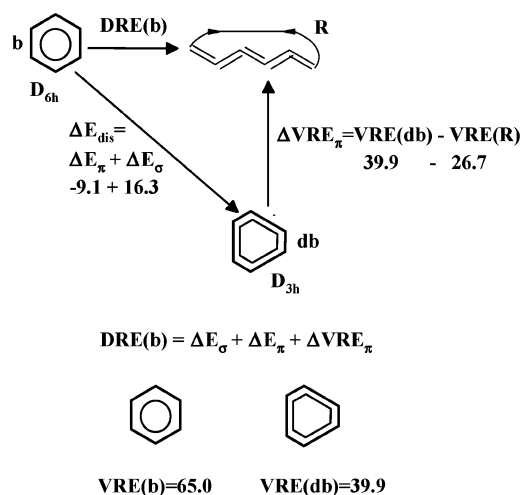
Figure 18. Hess cycle for relation of the Dewar resonance energy (DRE) with vertical resonance energy (VRE) for benzene. Vertical resonance energy values for benzene (b), distorted benzene (db) and reference structure (R) are denoted VRE(b), VRE(db) and VRE(R), respectively.[10s]

Initially benzene (denoted b) is distorted to give a species db (distorted benzene), which possesses a VRE [VRE(db)] of 39.9 kcal/mol (Figure 18). It is apparent that this species maintains a degree of delocalization as a result of the large vertical energy of D_{6h} benzene. Due to the opposing σ- and π-components, the distortion energy ΔE_{dis} (b → db) is relatively small (7.2 kcal/mol). The difference between the VRE(db) of distorted benzene and the VRE(R) of the reference structure (polyene) [VRE(db) − VRE(R) = 13.2 kcal/mol] completes the cycle. The estimated DRE value for benzene (VBSCF/6-31G level)[10s] of 20.4 kcal/mol is in good agreement with experimental estimates based on heat of formation (see the section devoted to isodesmic and homodesmotic reactions). A similar thermocycle for cyclobutadiene leads to a value of −70 kcal/mol,[10s] which is in good agreement with the recent estimate of Deniz et al.[220] (−87 ± 11 kcal mol). The important reasons for the so large negative resonance energy are the imbalanced ring strain energy (−32 kcal/mol)[220] in comparison to the linear reference polyene structure and the face-to-face π−π-interac-

tion (−25 kcal/mol),[10s] which is present in the Kekulé structure[221] but not in the reference system. If these factors are accounted for, then the estimated value of RE is much smaller, but in line with Hückel expectations, still negative (DRE = −13 kcal/mol).

The amount of literature on VREs is vast, and the interested reader may consult a few excellent reviews.[10r,s,37,219,222,223]

3.2. Experimental Approaches

Heats of combustion and hydrogenation were initially used to estimate the energetics of cyclic π-electron delocalization. Heats of combustion allowed Pauling and Sherman[13] to calculate the heat of atomization (via the heat of formation) of benzene and to compare this value with the sum of bond energies of a hypothetical reference (cyclohexatriene) with the CC bonds taken from ethane and ethene and the CH bonds from methane:

$$\text{RE} = -\Delta H_a^o(\text{benzene})_g - [3E(\text{C=C}) + 3E(\text{C−C}) + 6E(\text{C−H})] \quad (9)$$

In eq 9 $\Delta H_a^o(\text{benzene})_g$ is a heat of atomization of gaseous benzene; $E(\text{C=C})$ is the energy of the double bond estimated from the heat of atomization of ethene (the energy of C−H taken from methane), $E(\text{C−C})$ is the energy of the single bond estimated from the heat of atomization of ethane (the energy of C−H taken for methane), and $E(\text{C−H})$ is the energy of the C−H bond estimated from the heat of atomization for methane.

The estimated RE calculated in this way is 36 kcal/mol, in perfect agreement with the value obtained not long after by Kistiakowsky and co-workers[14] on the basis of the hydrogenation enthalpies of benzene and cyclohexene. The hydrogenation energy of benzene (to cyclohexane) is equal to 49.8 kcal/mol. Under the same conditions the hydrogenation energy of an "isolated" C=C bond in cyclohexene is 28.6 kcal/mol. The reference structure for benzene is composed of three "isolated" double bonds. In other words, the hydrogenation energy of three cyclohexene molecules should be compared with that of benzene, suggesting RE = 36 kcal/mol. Figure 19 illustrates this procedure.[10n,52]

Despite the coincidental numerical agreement between the approaches by Pauling and Sherman[13] and Kistiakowsky et al.,[14] it is important to note that the estimated stabilization energies in both cases are perturbed by many additional effects, which are due to (i) the limited precision and accuracy of the experimental data and (ii) the choice of a reference structure. Most obviously, factors such as unbalanced strain and changes of hybridization, conjugation, and hyperconjugation effects may be a source of a substantial error in the latter case.[224] Apart from hydrocarbons, thermochemical measurements lack in generality, because the combustion products of many heterocycles are ill-defined. Although experimental errors in heats of combustion are somewhat larger than in the case of hydrogenation, the problems with
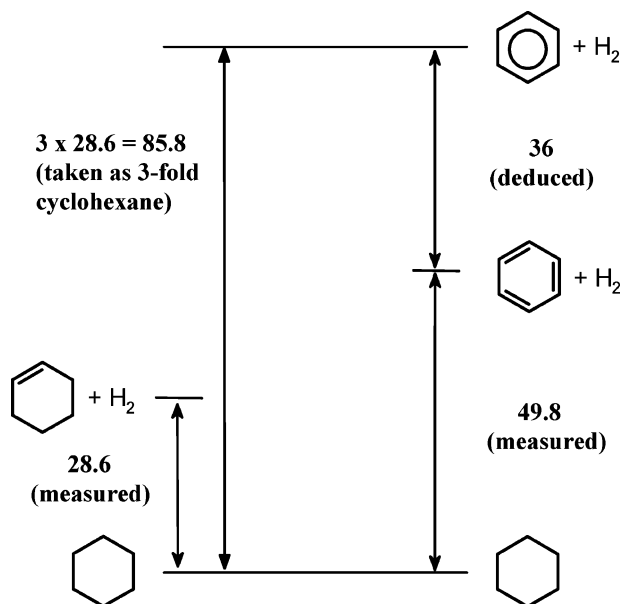
Figure 19. Heats of hydrogenation to assess the aromaticity of benzene.[10n,52]

quantitative hydrogenating of many heterocycles also means that the latter method lacks generality.[10n]

Three important schemes of increments were development by Laidler,[225] Allen,[226] and Benson and Buss.[227] Cox and Pilcher[50a] have demonstrated their equivalence given appropriate algebraic transformations. The interested reader may find extensive tables of RE data based on heat of formations and heat of hydrogenations in the classic book by Wheland[228] and critical analysis of these approaches in the monographs by Cox and Pilcher[50a] and Lewis and Peters[52] and in the Garratt book on aromaticity[229] as well as in an excellent review by George[4] and in a more recent one by Cohen and Benson.[230]

The assignment of particular values of bond energies for given types of bond, as proposed by Pauling and Sherman,[13] is obviously crucial for the magnitude of the estimated resonance energies. By their nature they are always a matter of choice and, hence, depend on reference systems, but the scheme adopted by Cox and Pilcher[50a] is widely accepted to be satisfactory, because it takes next-nearest-neighbor interactions into account with a great diversity of functional groups. Table 3 presents the energies of CC and CH bonds for hydrocarbons.[4] Comparisons of the energies calculated by the additive scheme with the experimental atomization energies of polycyclic hydrocarbons led to stabilization energies due to the cyclic π-electron delocalization effect. These values are collected in Table 4. Two sets of REs are the consequence of two possible arbitrary energies of reference for C_d–C_d types of bonds, as critically discussed by George.[4] These latter values are likely to be the lower and upper limits of bond energy for this kind of bond.[4]
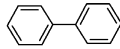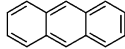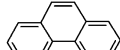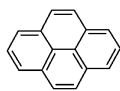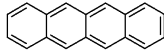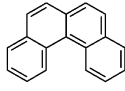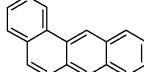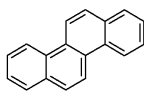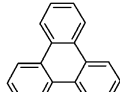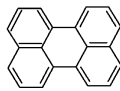
The estimated values of RE_I are definitely too large. For instance, benzene is stabilized by 48.7 kcal/mol, whereas the Dewar resonance energy based on *trans*-butadiene as reference is much smaller and equals 23.9 kcal/mol.[231] The most recent reliable estimate of the stabilization energy of benzene is ~32 kcal/mol,[66d,232a] in line with the RE_{II} value. On the other hand, in the series of linear acenes from benzene to tetracene, the value of RE_I/π increases, which is evidently in contrast with the decrease in the chemical stability of these systems[229,233] supported by Clar's qualitative sextet concept[86,234,235] and recent MO calculations. The problem of the stability of linear acenes has recently attracted considerable theoretical interest[10t,66a,94,236,237] and will be discussed later in this chapter.

The RE_{II}/π scale reflects changes of stability in a more reliable way, but among $C_{18}H_{12}$ isomers it designates triphenylene (not chrysene) as the most aromatic. Tetracene has the lowest RE_{II}/π in the $C_{18}H_{12}$ set, but its value is still evidently overestimated as compared with the RE_{II}/π for anthracene. Both RE_I and RE_{II} agree that the angular acenes are more stabilized than the linear ones.

Another gratifyingly successful approach based on calorimetric data is the group additivity method by Cohen and Benson.[230] A group is defined as "a polyvalent atom (with ligancy of ≥ 2) in a molecule together with all of its ligands".[238] On the basis of enthalpy increments both the heats of formation of the cyclic conjugated (aromatic) system and the reference structure can be constructed from a specified number and type of structural units. Although the component additivity as a method in general has no conceptual flaws,[230,239] the databases used are nevertheless neither refined nor extensive enough to provide the enormous number of components that would be necessary to calculate thermochemical properties for all organic compounds. Table 5 presents selected group additivity values for conjugated olefins and aromatics.

Cyrański et al.[94] applied group additivity values due to Cohen and Benson's method[230] to estimate aromatic stabilization energies of linear (and angular) acenes, showing that in both cases the aromatic stabilization energies per π-electron (ASE/π) decrease rapidly from 3.49 (benzene) to 1.72 (heptacene), as does the HOMA (geometry-based) measure of aromaticity (see Table 6, columns 2 and 8). Figure 20a shows this dependence[94] for linear acenes. On the other hand, Schleyer has argued that the SEs per π-electron do not decrease significantly along the acene series.[66a] Unfortunately, one of the Cohen Benson C_d–$(C_d)_2$ increments critical for the analysis

Table 3. Bond Energy Terms (Laidler Parameters) for Hydrocarbons (in Kilocalories per Mole) Taken from Cox and Pilcher[50a]

type of bond[a]	energy	type of bond[a]	energy
E(C–C)	85.48	E(C–H)$_p$	98.19
E(C$_b$–C)	88.91	E(C–H)$_s$	92.27
E(C$_d$–C)	90.07	E(C–H)$_t$	96.53
E(C$_d$–C$_d$)	89.12[4]	E(C$_d$–H)$_2$	101.19
E(C$_d$–C$_d$)	94.66[4]	E(C$_d$–H)$_1$	100.53
E(C=C)	133.0	E(C$_b$–H)	100.53

[a] C, C$_d$, and C$_b$ denote carbon atoms in the following structural environments: paraffin, olefin, and benzene (aromatic). (C–H)$_p$ (C–H)$_s$, and (C–H)$_t$, denote the C–H bond in a CH$_3$, CH$_2$, or CH group, respectively, the other bond(s) being to paraffinic carbon. (C$_d$-H)$_1$, (C$_d$-H)$_2$, etc., denote the C–H bond in olefins where there are one and two hydrogen atoms, respectively, bound to the olefinic carbon atom.

Table 4. Resonance Energies and RE per π-Electron (RE$_I$/π and RE$_{II}$/π) for Benzene and Polycyclic Hydrocarbons (in Kilocalories per Mole) [Calculated from ΔH_a^o Data with E(Cd−Cd) = 89.12 and 94.66 for RE$_I$ and RE$_{II}$, Respectively; Original Data of RE$_I$ and RE$_{II}$ Taken from Reference 4]

Compound	Formula	Structure	RE$_I$	RE$_I$/π	RE$_{II}$	RE$_{II}$/π
Benzene	C_6H_6		48.7	8.12	32.0	5.33
Naphthalene	$C_{10}H_8$		85.8	8.58	52.6	5.26
Biphenyl[a]	$C_{12}H_{10}$		102.5	8.54	63.8	5.32
Anthracene	$C_{14}H_{10}$		120.0	8.57	70.2	5.01
Phenanthrene[a]	$C_{14}H_{10}$		126.4	9.03	76.6	5.47
Pyrene	$C_{16}H_{10}$		155.8	9.74	94.9	5.93
Tetracene	$C_{18}H_{12}$		158.8	8.82	92.3	5.13
3,4-Benzphenanthrene[a]	$C_{18}H_{12}$		163.4	9.08	96.9	5.38
1,2-Benzanthracene[a]	$C_{18}H_{12}$		162.6	9.03	96.1	5.34
Chrysene[a]	$C_{18}H_{12}$		167.2	9.29	100.7	5.59
Triphenylene[a]	$C_{18}H_{12}$		168.8	9.38	102.3	5.68
Perylene[a]	$C_{20}H_{12}$		186.9	9.35	109.3	5.47

[a] Corrections included for steric hindrance: biphenyl, 1.4; phenanthrene, 0.7; 3,4-benzphenanthrene, 4.4; 1,2-benzanthracene, 0.7; chrysene, 1.4; triphenylene, 2.1; perylene, 1.4 kcal/mol.

is based only on a single, inappropriate compound (azulene), and hence the value of 4.6 kcal/mol is questionable. In fact, Benson revised his data and suggested a value of 8.6 kcal/mol[240] as more appropriate, whereas Schleyer finally refined it as 12.3 kcal/mol.[66a] This resulted in an increase in SE/π along the acene series (see Table 6, column 3), in line with the estimated stabilization energies based on isodesmic reactions involving cyclohexene and cyclohexadiene as a cyclic conjugated diene (see Table 6, column 4). These references are far more appropriate standards for SE estimation of cyclic benzenoid hydrocarbons than the often employed *s-trans*-butadiene and ethylene,[10t] but do not compensate for strain and hybridization effects of the central bridging CC bond, which changes from acene to acene. This may substantially affect the findings. The estimated changes in energies correlate well with the

sum of NICS (see Figure 20b), but both of these values are extensive parameters, so the relationship is statistically biased,[241] and one should be cautious in drawing conclusions from it. It should be noted that recent reliable estimates of stabilization energies based on isomerization reactions[66d] proved that the SE/π of naphthalene is significantly smaller than that of benzene, in line with the analyses of Wiberg[236] (Table 6, column 5) and Slayden and Liebman[10t] (Table 6, column 6). Recently, Grossman et al.[242] have also shown a progressive decrease of SE/π values from benzene to tetradecacene using isodesmic reaction schemes.[60c] In fact, Wiberg suggested[236] that the linearly annelated systems may be thought of as being formed by adding a four-carbon diene fragment across a C−C bond that has a low π-bond order, leading to relatively little stabilization. It should be re-emphasized that creditable values of estimated

Table 5. Cohen−Benson Group Additivity Values for Conjugated Olefins and for Aromatic Systems (Given in Kilocalories per Mole)[a]

Type of increment	Description	Value	Type of increment	Description	Value
C_d-(C_d)(H)		6.78	C_{BF}-$(C_{BF})(C_B)_2$		5.53
C_d-$(C_d)_2$		4.6	C_{BF}-$(C_{BF})_2(C_B)$		4.34
C_B-(H)		3.29	C_{BF}-$(C_{BF})_3$		-0.54

[a] C_d, C_B, and C_{BF} specify the doubly bonded carbon atom, the carbon atom in a benzene ring, and the carbon atom at the junction of two rings, respectively.[230] Adapted from ref 94.

Table 6. Computed Stabilization Energies (SE) (in Kilocalories per Mole): Total Values and per π-Electron (in Boldface), NICS (in Parts per Million) (Defined as the Sum of NICS for Particular Rings, Calculated in the Molecular Plane and 1 Å above), and HOMA for Linear Acenes[66a]

system	SE/π^a	SE/π^b	SE/π^c	SE/π^d	SE/π^e	ΣNICS(X) X = 0/X = 1[f]	HOMA
benzene	20.9/**3.49**	20.9/**3.49**	32.8/**5.47**	36/**6.0**	21.5/**3.59**	−8.8/−10.6	0.991
naphthalene	26.1/**2.61**	41.5/**4.15**	59.8/**5.98**	60/**6.0**	32.8/**3.28**	−17.8/−21.6	0.811
anthracene	31.2/**2.23**	62.0/**4.43**	83.7/**5.98**	80/**5.7**	41.4/**2.96**	−26.7/−32.9	0.718
tetracene	36.4/**2.02**	82.5/**4.58**	104.8/**5.82**	99/**5.5**	51.5/**2.86**	−36.0/−44.4	0.668
pentacene	41.4/**1.88**	103.0/**4.68**	127.6/**5.80**	117/**5.3**		−42.2/−56.1	0.628
hexacene	46.5/**1.79**	123.5/**4.75**	153.9/**5.91**			−54.8/−67.6	0.629
heptacene	51.6/**1.72**	144.0/**4.80**	175.5/**5.85**			−64.9/−79.7	0.624

[a] Calculated using original Cohen−Benson group additivity values[230] (see ref 94). [b] Based on increments for conjugated olefins, C_d−(C_d)(H) 6.78 and C_d−$(C_d)_2$ 12.3 kcal/mol (see ref 66a). [c] Computed by isodesmic reaction: n 1,3-cyclohexadiene + trans-perhydroacene = acene + n cyclohexene (n = 3, 5, 7, ...) using B3LYP/6-311+G** + ZPE energies (see ref 66a). [d] Based on B3LYP/6-311G** energies and assumed SEs of benzene and naphthalene: SE = ΔE − SE$_{benzene}$ + 2SE$_{naphthalene}$ (see ref 236). [e] Using isodesmic reaction $C_{(2p)}H_{(2q)}$ + (3p−2q) $H_2C=CH_2$ = (2p−q) $H_2C=CHCH=CH_2$ (see eq 18 and ref 66a). [f] NICS at IGLO/TZ2P//B3LYP/6-311+G**.

stabilization energies and the hypotheses based on them intrisically depend on a proper definition of reference structure(s).

Parametrizing the distribution of bonding energy at the equilibrium geometry of a polyatomic molecule offers an alternative approach for obtaining information about strain and aromatic effects. Several consistent relationships between bond lengths and bond energies have been devised[77,79,107,232a,243] (i) using simple models of chemical bonds introduced by Pauling[85] and by Johnston and Parr,[244] (ii) by developing bond-based parametrized models of atomization energies,[107,243c] and (iii) through approaches based on the atoms-in-molecules formalism.[147]

Krygowski et al.[77,79] combined the Johnston and Parr bond order−bond energy formula with the Pauling bond order−bond length relationship to obtain an empirical formula (eq 10), which reproduces the experimental heats of formation of hydrocarbons providing that the precise molecular geometries are known.

$$BE_i = 87.99 \exp[2.255(1.553 - R_i)] \quad (10)$$

Table 7 presents a comparison of experimental heats of formation from atoms and the equivalent values calculated with use of the eq 10 for nine benzenoid hydrocarbons.
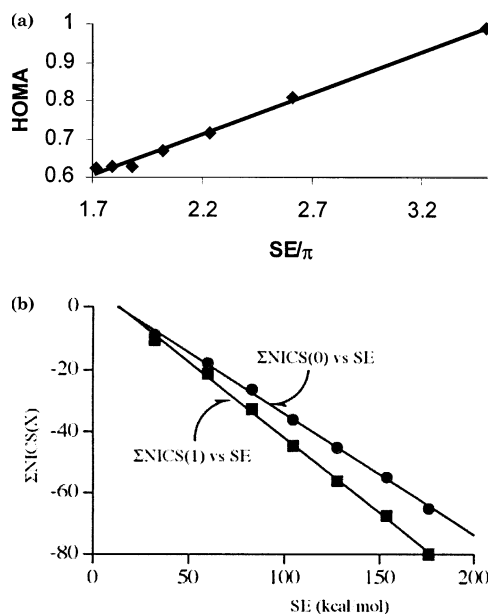

Figure 20. (a) Linear dependence of HOMA index (Table 6, column 8) on the Cohen−Benson SE/π (Table 6, column 2).[94] Correlation coefficient cc = 0.997. (b) Dependence of SE (Table 6, column 4) of acenes versus the total NICS(0) and NICS(1) sums (Table 6, column 7). Correlation coefficient cc = 0.998. Figure 20b reprinted with permission from ref 66a. Copyright 2001 American Chemical Society.

Table 7. Estimated and Experimental Values of Heat of Formation from Atoms (in Kilocalories per Mole)[a]

compound	estimated HF	experimental HF[50b]
benzene	1320.6	1320.6
naphthalene	2100.8	2093.8
anthracene	2868.4	2863.9
phenanthrene	2861.8	2869.5
tetracene	3592.4	3638.8
chrysene	3664.4	3643.9
triphenylene	3647.3	3641.2
3,4-benzophenanthrene	3646.6	3638.8
pyrene	3227.8	3207.7

[a] The CH bond energy was assumed as 100.53 kcal/mol (see Table 3). Adapted from ref 79.

Exner and Schleyer[243a] have shown that the C−C bond energies predicted by the Grimme model[243b] based on the AIM approach are also very well-represented by a single exponential function of bond length (see Figure 21). Moreover, this formula is in
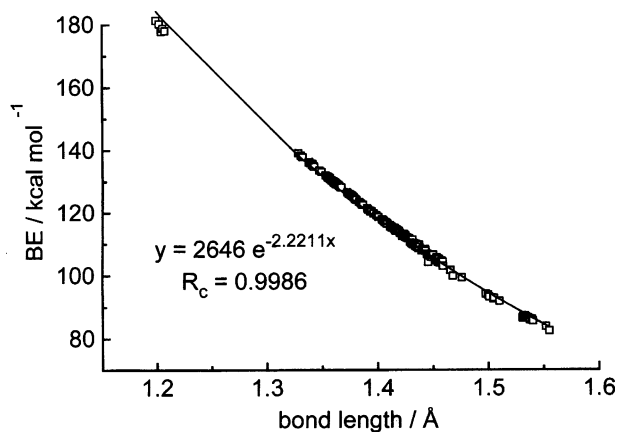
Figure 21. Dependence between the BEs and bond length of 202 CC single, aromatic, double, and triple bonds. Reprinted with permission from ref 243a. Copyright 2001 American Chemical Society.

perfect agreement with the empiricically derived formula by Krygowski et al.[79]

$$BE_i = 2646 \exp(-2.221 R_i) = 84.06 \exp[2.221(1.553 - R_i)] \quad (11)$$

However, only an approximate exponential dependence of CC bond energy with bond length was obtained by Howard[232a] when a set including also nitrogen heteroatom compounds was considered. She pointed out that generally it is unlikely that even CC bond energies can be parametrized as a single-valued function of the bond length, and therefore such models are intrinsically limited in accuracy, even for hydrocarbons. In fact, a three-parameter model does significantly improve the accuracy with which atomization energies of benzenoid hydrocarbons are reproduced.[243c]

Although these kinds of approaches were applied successfully to various chemical problems,[77,245] a closer analysis of CC bond energies provides unrealistic values of aromatic stabilization energies even for benzene. For instance, on the basis of the Krygowski et al.[79] model and the MP2/6-311G** bond lengths for benzene (1.399 Å), single and double CC

bonds in *trans*-butadiene (1.460 and 1.345 Å, respectively) and the single and double CC bonds in *cis*-butadiene (1.472 and 1.344 Å, respectively), the corresponding bond energies are 124.5, 108.5, 140.6, 105.6, and 141.0 kcal/mol, respectively. This leads to SEs of benzene of 0.3 or 7.2 kcal/mol (with either *trans*- or *cis*-butadiene as a reference, respectively). These values are definitely too low! Furthermore, as pointed out by Exner and Schleyer[243a] and by Grimme[243b] the BE method does not describe anions, cations, or open shell species with chemical accuracy, and the changes in bond length due to strain rather than conjugation may lead to unreliable bond energies. Explicitly including heteroatoms is also far from trivial,[243a] so the BE approach is not as general as one might hope. More about bond lengths as general indicators of π-electron delocalization was discussed in the section devoted to geometric aspects as a criterion for aromaticity.

Returning to the case of linear acenes, the inner rings exhibit greater diatropic ring current than the outer ones, as shown on the π-electron ring current density maps (see Figure 22).[113a−c] This correlates well with the regular progressions of HOMA[66a,94] and NICS values[66a,94] toward the higher values of each indicator along the series. The extent of the progressions and the absolute magnitudes of the aromaticity descriptors are much-debated in the literature.[20,66a,94,146,246] Contrary to this comprehensive picture the sums of BE for rings show a progressive decrease approaching the central fragments. This is definitely incorrect and supports the Exner−Schleyer conclusion that use of bond energies is an oversimplified model which reflects largely a property of the σ-electron density, whereas the π-electron density plays a minor, only slightly modifying, role.[243a]

Another way of estimating stabilization energies from bond lengths is provided by the harmonic oscillator stabilization energy (HOSE) model of Krygowski et al.[247] and modified by Bird.[81i] Originally, HOSE was defined as a negative value of energy necessary to deform the real molecule into its Kekulé (or resonance) structure with localized single and double bonds of typical lengths:

$$E_{\text{def}} = -\frac{1}{2}\left[\sum_{r=1}^{n_1}(R_r' - R_o^s)^2 \times k_r' + \sum_{r=1}^{n_2}(R_r'' - R_o^d)^2 \times k_r''\right] \quad (12)$$

R_r' and R_r'' stand for the lengths of π-bonds in the real molecule, whereas n_1 and n_2 are the numbers of the corresponding formal single and double bonds in the ith canonical structure, respectively. In the process of deformation the n_1 bonds corresponding to the single bonds in the ith canonical structure are lengthened, whereas the n_2 bonds corresponding to the double bonds in the ith canonical structure are shortened to the reference bond lengths R_o^s and R_o^d, respectively. The force constants (k_r) follow the assumption $k_r = a + bR_r$.

On this basis, Bird[81i] defined the individual bond energy $E_i = F(R_o^s$ or $R_o^d - R_i)^2 (a - bR_i)$ with empirical parameters a, b, and F (see Table 8), which reproduces the RE of benzene (taken as 38.4 kcal/
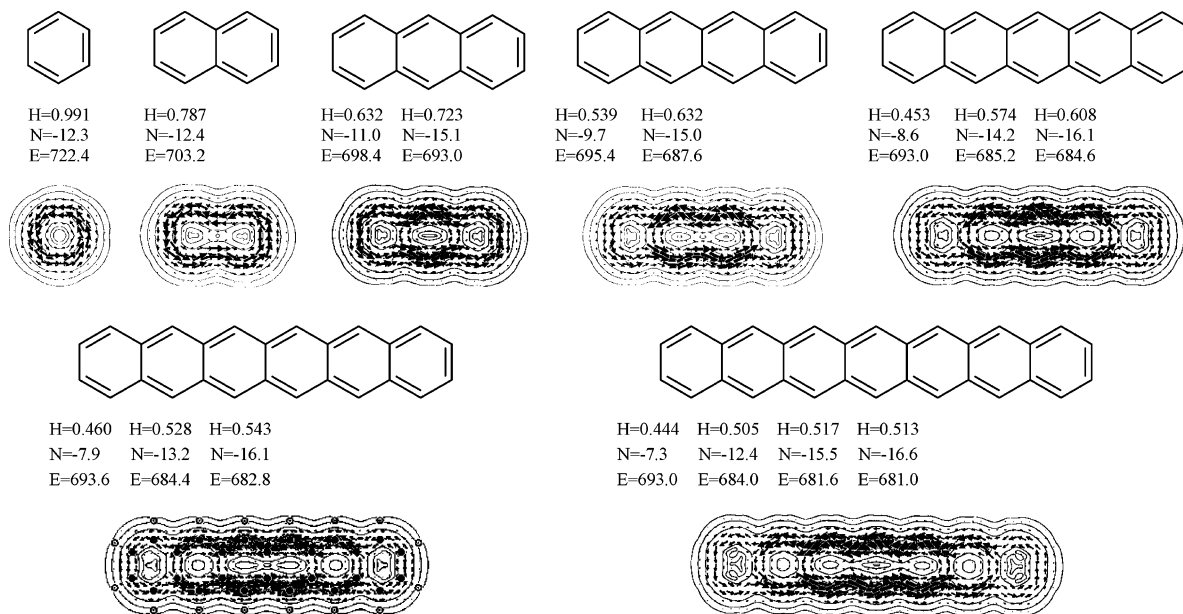
H=0.991 H=0.787 H=0.632 H=0.723 H=0.539 H=0.632 H=0.453 H=0.574 H=0.608
N=-12.3 N=-12.4 N=-11.0 N=-15.1 N=-9.7   N=-15.0 N=-8.6   N=-14.2 N=-16.1
E=722.4 E=703.2 E=698.4 E=693.0 E=695.4 E=687.6 E=693.0 E=685.2 E=684.6

H=0.460 H=0.528 H=0.543   H=0.444 H=0.505 H=0.517 H=0.513
N=-7.9   N=-13.2 N=-16.1   N=-7.3   N=-12.4 N=-15.5 N=-16.6
E=693.6 E=684.4 E=682.8   E=693.0 E=684.0 E=681.6 E=681.0

Figure 22. HOMA, NICS(1), and BE for acenes[94] (denoted H, N, and E) and maps of π contributions to the current density.[113a−c] Current densities induced by a unit magnetic field normal to the molecular plane are plotted in a plane 1 Å above that of the ring, with contours denoting the modulus of the current density and vectors representing in-plane projections of current. Diamagnetic (diatropic) circulation is shown anticlockwise. Reprinted (except hexacene) with permission from ref 113a. Copyright 1996 Wiley. Hexacene reprinted with permission from ref 113b. Copyright 2001 American Chemical Society.

Table 8. Empirical Constants to Bird's Modification of the HOSE Model. Adapted from Ref 81i

type of bond	R_o^s (Å)	R_o^d (Å)	F	a ($\times 10^4$) Pa	b ($\times 10^4$) Pa
CC	1.533	1.337	85.94	44.39	26.02
CN	1.474	1.274	62.19	43.18	25.73
CO	1.449	1.250	62.33	57.10	35.51

mol) and 44.9 kcal/mol for the RE of 1,3,5-*s*-triazine. When more than one Kekulé form is possible, a separate energy is calculated for each of them and the energies are then summed according to the following expression:

$$\text{RE} = nE_i \left(\frac{\dfrac{1}{E_i}}{\displaystyle\sum_{i=1}^{i=n} \dfrac{1}{E_i}} \right) \quad (13)$$

Table 9 presents selected values of RE for heterocycles. Apart from the parametrization problems arising from the standard values of single and double bonds taken from nonconjugated systems (e.g. ethene and ethane), empirical scaling factors and simplified corrections for strain, etc., additional problems appear when many resonance structures have to be considered.[77] The original HOSE model is the most efficient if one takes into account a reasonable (i.e. not too large) number of canonical structures; otherwise, the errors of parametrization may significantly bias the findings. Obviously, the discrepancies between the estimated data and the experimental values are also due to the quality of the experimental bond lengths, but this factor has just been discussed. Another problem that arises when the experimental values of resonance energies are analyzed is that

Table 9. Resonance Energies (in Kilocalories per Mole) from Bird's Modification of the HOSE Model[81i] Compared with Experimental Data[81i,200,251]

compound	RE	RE$^{\text{exptl}}$	compound	RE	RE$^{\text{exptl}}$
pyridine	44.1	43.3	imidazole	34.9	40.0
pyrimidine	40.1	40.6	indole	73.3	73.8
pyrazine	38.8	40.9	isoindole	62.5	62.4
pyridazine	43.9^a	33.5	benzimidazole	75.1	78.9
1,2,4-triazine	40.4^a		carbazole	113.5	111.7
1,2,4,5-tetrazine	39.2^a		acridine	101.1	108.3
1,3,5-triazine	44.9	44.9	phthalazine	87.4	80.1
quinoline	81.6	81.0	phenazine	100.3	110.3
isoquinoline	82.6	81.0	cinnoline	83.4	69.8
quinozaline	74.8	76.5	phenanthridine	108.5	119.6
pyrrole	31.8	34.8	benzo[*h*]quinoline	110.9	122.7

^{a} Values of 37.2 kcal/mol (pyridazine), 31.2 kcal/mol (1,2,4-triazine), and 24.5 kcal/mol (1,2,4,5-tetrazine) if the nitrogen−nitrogen bond contributions are excluded.

these values depend strongly on the reference structure used. Recent estimates for pyridine reveal 31[248]−33[66d] kcal/mol of aromatic stabilization based on cyclic references. Within a similar methodological approach[249] the values for pyrimidine, pyrazine, pyridazine, and *s*-triazine are 32.6, 32.0, 26.1, and 24.8 kcal/mol (at the MP3/6-31G* level), respectively. On the other hand, the reliable ASEs for pyrrole and imidazole based on heterocyclic reference systems are 20.6 and 18.8 kcal/mol (at B3LYP/6-311+G** level, see Table 17), respectively.[31] If acyclic reference systems are used, the stabilization energies are lower: 19.8 kcal/mol for pyridine, 15.5 kcal/mol for pyridazine, and 21.5 kcal/mol for benzene[250] (at B3LYP/6-31G* level, see reaction 15 in Table 13 and the Table 16). This is definitely far from the "experimental values"[200,251] given in Table 9.[81i] Moreover, the ordering of resonance energies given therein is inconsistent with expectations based on reliable homodesmotic model reactions.[31,66d,248−250]

3.3. Theoretical Approaches

Historically, the determination of resonance energy was first carried out within the framework of the Hückel molecular orbital (HMO) theory. The RE was defined as the difference between the π-electron energy of a given conjugated molecule (E_π) and the energy of a reference system viewed as a set of nonresonating double bonds forming the hypothetical Kekulé-type structure[44]

$$\text{HRE} = -\,[E_\pi - n_{C=C}(2\alpha + 2\beta)] \qquad (14)$$

where $n_{C=C}$ is the number of double bonds in the reference structure, whereas α and β are the coulomb and resonance integrals, respectively. Although the HRE correlates incidentally with experimental delocalization energies in a set of benzenoid hydrocarbons,[1] generally the model is well-known as an unreliable representation of resonance energy.[10p,15,44,46,252] The highly unstable pentalene (HRE = 2.46β) has a Hückel resonance energy nearly identical to that of the cyclopentadienyl anion (HRE = 2.47β), and both are significantly higher than the value for benzene (HRE = 2.00β). On the other hand, among the annulenes, all of them (except cyclobutadiene) are estimated as aromatic, as summarized in Figure 23.
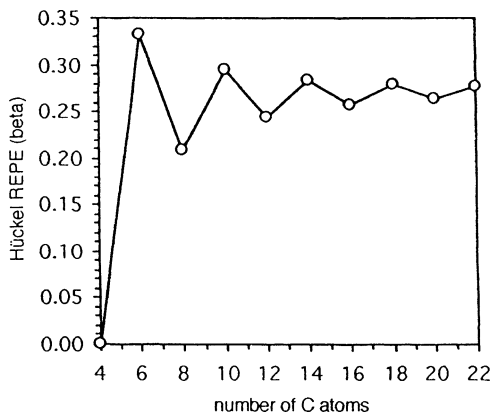
Figure 23. Hückel delocalization energies per π-electron, REPE (in β units), for the conjugated monocyclic hydrocarbons. Reprinted with permission from ref 10p. Copyright 2001 American Chemical Society.

This clearly incorrect description results from both (i) the unsuitable reference structure as discussed by Hess and Schaad[10p] and (ii) the simplified method of calculation. The application of the method can be nowadays justified only for very large systems. Even these estimates should be considered as truly preliminary and tested against more reliable models.

Great progress began with the work by Dewar et al.[45,253] Using the Pariser–Parr–Pople π-electron method[254] they found that the bond energies of acyclic polyenes are additive. This energy additivity of acyclic conjugated compounds has been later evidenced, confirmed, and interpreted by ab initio analyses at various levels of theory.[223a,255,256] The Dewar resonance energy (DRE) was then defined as the difference between the atomization enthalpies of a given conjugated molecule (ΔH_a) and the hypothetical cyclic polyene (ΔH_a^{add}) constructed from linear polyenes with the number of π- and σ-bonds equal to that in a given molecule

$$\text{DRE} = \Delta H_a - \Delta H_a^{add} \qquad (15)$$

where ΔH_a is the calculated heat of atomization of a given conjugated molecule and ΔH_a^{add} is the heat of atomization for the reference structure. For hydrocarbons the above formula can be rewritten as

$$\text{DRE} = \Delta H_a^M - (n_1 E_{C-C} + n_2 E_{C=C} + n_3 E_{C-H}) \quad (16)$$

where n_i is the number of a given bond type.

The DRE using the original computational approach was a topic of a *Chemical Review* paper by Schaad and Hess.[10p] The C—C single bonds in polyenes obviously have significant π-character and, unlike in the Hückel model, all of them are taken into account in the estimation of resonance energies. The Dewar idea of referring the stability of a given system to a polyene (most often hexatriene or butadiene) with the same number of π-conjugative interactions as in a polygon gained wide acceptance. This approach led to the invention of isodesmic[60] and later homodesmotic reactions,[61] which are commonly regarded as providing the most sophisticated measure for the description of the "extra" stabilization found on ring closure. For instance, for annulenes and benzenoid hydrocarbons the reaction schemes can be written in the form of eq 17[60c,61c] and eq 18,[60c,257] respectively.

$$C_{(2p)}H_{(2p)} + p\,CH_2{=}CH_2 = p\,CH_2{=}CH{-}CH{=}CH_2 \qquad (17)$$

$$C_{(2p)}H_{(2q)} + (3p - 2q)\,CH_2{=}CH_2 = \\ (2p - q)\,CH_2{=}CH{-}CH{=}CH_2 \quad (18)$$
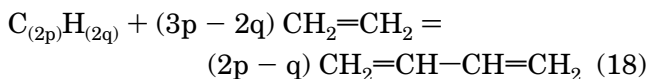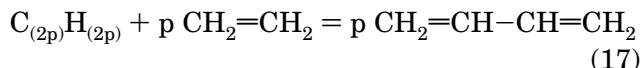
The energies of substrates and products can be obtained either from quantum chemical calculations or, less frequently, from experimental (empirical) data based on calorimetric measurements. Table 10

Table 10. Dewar Resonance Energies (in Kilocalories per Mole) for Polycyclic Aromatic Hydrocarbons[10t] (See also Table 6, Column 6)

system	RE	RE/π
benzene	21.5	3.6
phenanthrene	47.3	3.4
chrysene	60.7	3.4
triphenylene	60.2	3.3
benz[*a*]anthracene	54.8	3.0
benzo[*c*]phenanthrene	54.1	3.0
pyrene	59.6	3.7
perylene	69.1	3.5
coronene	99.9	4.2

Table 11. Hess–Schaad π-Electron Energies (in β) for Eight Topologically Different Types of Bonds. Adapted from Ref 46

type of bond	E^π	type of bond	E^π
H$_2$C=CH	2.0000	C=C	2.1716
HC=CH	2.0699	HC—CH	0.4660
H$_2$C=C	2.0000	HC—C	0.4362
HC=C	2.1083	C—C	0.4358

Table 12. Hess−Schaad Resonance Energies (in β) for Benzenoid Hydrocarbons[46,259a]

system	HSRE	HSRE/π	system	HSRE	HSRE/π
benzene	0.39	0.065	chrysene	0.96	0.053
naphthalene	0.55	0.055	picene	1.17	0.053
anthracene	0.66	0.047	triphenylene	1.01	0.056
tetracene	0.75	0.042	pyrene	0.81	0.051
pentacene	0.84	0.038	perylene	0.97	0.048
phenanthrene	0.77	0.055	coronene	1.28	0.053

presents the data for selected benzenoid hydrocarbons.[10t]

Although the Dewar approach is often considered as the standard RE, reactions 17 and 18 are not unique, and the reader may consult a great variety of approaches for estimating the aromatic stabilization energy of benzene in Table 13. This aspect will be discussed in some detail later. The DREs have been calculated for a broad range of systems including both polycyclic and heterocyclic compounds[32,249,250] and correlated with structural, magnetic, and reactivity criteria.[15] For instance, Ciosłowski[258] has shown that for benzenoid hydrocarbons the RE values reflect well the stability (SI) defined as

$$SI = K^{2/N} \quad (19)$$

where K is the number of Kekulé structures and N is the number of carbon atoms.

Applying the additivity rule[46] Hess and Schaad used the simple HMO method to show that much more detailed differentiation of bond energies corresponding to their local environment/topology is needed, because the energy of an acyclic polyene depends on its branching.[259] They classified the bonds in acyclic polyenes into eight types depending on the number of attached hydrogens and formal CC bond character. The values for five types of carbon−carbon double bonds and three types of carbon−carbon single bonds presented in Table 11 were obtained by a least-squares fitting procedure involving the Hückel π-energies of a set of 40 acyclic compounds.[46] The HSRE is defined as

$$HSRE = E_\pi - \sum_i n_i E_i \quad (20)$$

where E_π is the π-electron energy of a given cyclic system (calculated within the frame of the HMO method), E_i is the energy of a given (i) type of bond (see Table 11), and n_i stands for its number.

In determining the above values, eight types of bond energies could not be obtained from the set of six linear equations constructed alone. Hess and Schaad therefore found it necessary to assign numerical values of 2β for two types of bonds ($H_2C=CH$ and $H_2C=C$).[46] Because these values are somewhat arbitrary, this choice invariably biases the findings. In fact, the parametrization based on localized molecular π-orbitals (π-LMO) leads to slightly different resonance energy values.[260] Despite these flaws, Hess and Schaad presented a great collection of resonance values for benzenoid hydrocarbons,[46,259a,b] nonalternant hydrocarbons,[46,252,259c] annulenes,[259f] and hetero-π-electron systems.[204a,259d,e] For the purpose of comparison of the resonance energies of molecules of different size, the normalized quantity (resonance per electron) REPE has been introduced.[46] Table 12 presents selected data for benzenoid hydrocarbons, whereas Figure 15 shows the plot for the conjugated monocyclic hydrocarbons. Benzene has the highest value of HSREPE in the set, and in the series of linear acenes a progressive decrease is observed, correlating with their stabilities. This point was discussed earlier. The angular polyacenes have significantly higher values of HSRE (or HSREPE) than their linear analogues, which was confirmed by advanced ab initio analyses.[94,236] On the other hand, unlike the Dewar-based values (see Table 10) the HSREs suggest that both pyrene and coronene are less aromatic than benzene, which is in line with chemical experience and intuition. Finally, the predicted stabilities of annulenes (see Figure 15) follow expectations based on the Hückel $4N + 2$ rule.[202] It is clear that the successful application of this scheme within such an unsophisticated (and topologically natured) method as HMO highlights the great importance of the correct choice of the reference structure!
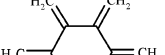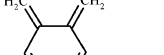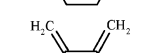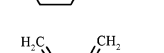
Another insight into RE is obtained from graph-topological approaches.[47] Two types of models have arisen as important: the topological resonance energy (TRE) developed by Trinajstić et al.[48,261] and Aihara;[262] and the conjugated circuit model (CCM)[49] of Randić. In TRE a characteristic polynomial is constructed for the reference structure with only the acyclic Sachs graphs[263] for the given molecule taken into account

$$TRE = \sum_{j=1}^{N} g_j(x_j - x_j^{ac}) \quad (21)$$

where N is the number of vertices in a graph (corresponding to the number of atoms in a conjugated system), x_j and x_j^{ac} are the roots of the characteristic polynomial of the aromatic system and the acyclic polynomial of the polyene-like reference structure, respectively, and g_j is the orbital occupation number of the jth MO. In effect, it corresponds to the procedure embodied in the Hückel method for solving the eingenvalues x_j of the Hückel matrix in units of β.[10n] This method was applied to a large number of conjugated hydrocarbons[48,261c] and extended to heterocyclic systems,[264a,b] radicals and ions,[264b,c] excited states,[264d,e] organometallic compounds,[264f] and three-dimensional systems including polyhedral boranes[262c,d] and fullerenes.[264g−j] Good dependencies between the TRE and HSRE values were also found.[264k]

In the conjugated circuit model a conjugated circuit is defined as a cycle within an individual Kekulé valence structure in which there is regular alternation of formal single and double bonds.[265a] The circuits are necessarily of even length. While ($4n + 2$) types of circuits stabilize a system, the ($4n$) conjugated ones lead to its destabilization. Randić has shown that the resonance energy of a polycyclic conjugated molecule may be regarded as the total contribution from all conjugated circuits in the molecule[49]

Table 13. Stabilization Energies (in Kilocalories per Mole) for Benzene at B3LYP/6-311+G (+ZPE)**

No	Reaction Scheme	SE
1	benzene + 6 CH$_4$ ⟶ 3 CH$_3$-CH$_3$ + 3 CH$_2$=CH$_2$	66.9[a]
2	benzene + 3 CH$_3$-CH$_3$ ⟶ cyclohexane + 3 CH$_2$=CH$_2$	55.3[b]
3	benzene + 2 cyclohexane ⟶ 3 cyclohexene	37.5[c]
4	benzene + (butene) ⟶ cyclohexadiene + (butadiene)	36.5[d]
5	toluene (CH$_3$) ⟶ (CH$_2$, H, H) methylenecyclohexadiene	33.2[e]
6	indene (H H) ⟶ isoindene (H, H)	28.3[f]
7	benzene + (butadiene) ⟶ H$_2$C=⟨⟩=CH$_2$ + CH$_2$=CH$_2$	32.2[g]
8	benzene + (quartet heptatriyl) + 2 CH$_3$-CH$_2$· ⟶ (cyclohexyl diradical) + (triene) + CH$_3$-CH$_3$ + (triplet H,H,H,H)	28.9[h]
9	benzene + 3 CH$_2$=CH$_2$ ⟶ 3 (butadiene)	23.2[i]
10	benzene + 3 CH$_2$=CH$_2$ ⟶ 3 (cis-butadiene)	33.6[j]
11	benzene + 3 cyclohexene ⟶ 3 cyclohexadiene + cyclohexane	32.4[k]
12	benzene + (H$_2$C, CH$_2$, H$_2$C, CH$_2$ tetramethylene) + (H$_2$C=⟨⟩=CH$_2$) ⟶ 3 (H$_2$C, CH$_2$ o-xylylene)	28.7
13	benzene + (H$_2$C, CH$_2$, H$_2$C, CH$_2$, H$_2$C, CH$_2$ hexamethylene) + 2 (H$_2$C=⟨⟩=CH$_2$) ⟶ (H$_2$C, CH$_2$, H$_2$C, CH$_2$) + 3 (H$_2$C, CH$_2$)	28.6
14	benzene + 3 (propene) ⟶ 3 (pentadiene)	19.3[l]
15	benzene + 2 CH$_2$=CH$_2$ ⟶ (diene) + (triene)	18.4[m]

[a] Experimental values: 61.1 kcal/mol,[60a] 64.2 kcal/mol,[270] 64.7 kcal/mol,[267] 74.7 kcal/mol at MP2/RHF/SBK(d),[268] 61.4 kcal/mol at RHF/SBK(d),[268] 67.2 kcal/mol at MP2/6-31G//6-31G*,[269] 58.2 kcal/mol at HF/6-31G*,[269] 64.4 kcal/mol at G3 level.[232b] [b] Experimental values: 48.7 kcal/mol,[4] 48.5 kcal/mol,[267] 48.5 kcal/mol at G3 level,[232b] 41.5 kcal/mol at MP2/6-311G**//MP2/6-31G*,[276a] 39.3 kcal/mol BLYP/6-311G**//BLYP/6-31G*.[276a] [c] 36.0 kcal/mol at G3 level.[232b] Experimental values: 35.6 kcal/mol,[50b,66d] 35.9 kcal/mol.[66d,267] [d] Experimental values: 33.4 kcal/mol,[267] 37.0 kcal/mol at B3LYP/6-311+G*,[9j] 39 kcal/mol at MP2/6-311+G*,[10j] 34.0 kcal/mol.[10j,50b] [e] Data corrected for anti−syn diene mismatch (3.6 kcal/mol),[66d] taken from ref 66d. Experimental values: 38 kcal/mol,[301] 23.1 kcal/mol.[301] [f] Data corrected for anti−syn diene mismatch (2 × 3.6 kcal/mol),[66d] 29.0 kcal/mol at B3LYP/6-31G*.[66b] Experimental value: 28.8 kcal/mol.[50b,267] [g] Data corrected for anti−syn diene mismatch (3 × 3.6 kcal/mol),[66d] taken from ref 310. Experimental value (uncorrected for the anti−syn diene mismatch): 16.7 kcal/mol.[267] [h] Taken from ref 289 at B3LYP/6-31G**, 29.1 kcal/mol at MP4(SDQ)/6-31G**.[289] [i] Experimental values: 20.6 kcal/mol,[267] 23.9 kcal/mol at MP4SDTQ/6-31G**/MP2(full)/6-31G**,[231] 24.3 kcal/mol at MP4/6-31G+5D,[273] 23.4 kcal/mol at MP3/6-31G+5D,[273] 28.0 kcal/mol at RMP2/6-311G**,[274] 28.7 kcal/mol at RMP2/6-311G*,[274] 28.9 kcal/mol at RMP2/6-31G*,[274] 24.8 kcal/mol at 6-31G** (SCF),[274] kcal/mol at 6-31G* (SCF),[274] 21.4 kcal/mol,[50b] 22.6 kcal/mol at G3 level[232b]; 42.7 kcal/mol based on 90° twisted butadiene.[257] [j] 34.1 kcal/mol for planar *cis*-butadiene.[180] [k] 31.3 kcal/mol at G3 level;[232b] experimental values: 30.5 kcal/mol,[50b,66d] 28.8 kcal/mol.[66d,267] [l] Experimental values: 22.5 kcal/mol,[267] 20.3 kcal/mol at MP4SDTQ/6-31G**/MP2(full)/6-31G**,[231] 23.4 kcal/mol at 6-31G* (SCF),[256] 24.6 kcal/mol at G3 level.[232b] [m] Experimental values: 21.2 kcal/mol,[267] 27.8 kcal/mol at MP2(fc)/6-31G*,[250] 21.5 kcal/mol at B3LYP/6-31G*.[250]

$$\text{CCRE} = \frac{1}{k}\sum_n (r_n R_n + q_n Q_n) \qquad (22)$$

where k is the number of Kekulé valence structures for a given system, r_n and q_n are the numbers of the conjugated circuits with ring size $(4n + 2)$ and $(4n)$, respectively, in the molecule, and R_n and Q_n are the empirically determined contributions to RE of individual $(4n + 2)$ and $(4n)$ types of circuits. In practice, the set of conjugated circuits is truncated at those of

$n = 4$, because the R_n and Q_n energy contributions diminish with the growing circuit size.[265b] To avoid the size effect the CCRE is normalized by dividing it by the number of π-electrons. The CCM has been extended to cover various types of polycyclic conjugated hydrocarbons,[11,266a−d] their ions and radicals,[266e,f] excited states of benzenoid hydrocarbons,[266g] heterocyclic conjugated analogues,[266h,i] and also three-dimensional systems.[266j−l] Because the graph-topological approaches, especially the CCM, have been recently extensively reviewed by Randić in a lengthy *Chemical Reviews* paper,[11] the interested reader is referred to this excellent review and the references cited therein. It should be pointed out, however, that although the graph-topological indices are undoubtedly useful for large systems, they do not take into account many subtle effects; hence, the values they provide should be treated with a little caution. They are perhaps better suited to estimation and preliminary investigation rather than detailed studies. Any hypotheses they suggest based on qualitative dependencies should be subjected to critical tests against reliable model reaction schemes based on high-level ab initio or thermochemical data[267] wherever possible.

The experimental approach by Kistiakowsky et al.[14] (see Figure 19) leading to the estimation of the stabilization energy of benzene may be easily summarized by a single equation (see reaction 3 in Table 13), where the energy of benzene (derived experimentally or theoretically) is compared with the equivalent energy of three cyclohexenes (three separated CC double bonds) and two cyclohexane units balance the stoichiometry. The nonadditivity of the energies is mostly due to the cyclic π-electron delocalization effect of benzene, although Dewar and Schmeising[224] argued that it is an overestimated value. This reaction exemplifies the idea of isodesmic reactions, due to Hehre et al.,[60] in which the number of bonds of each given formal type, for example, C=C, C−C and C−H is conserved, but the relationship among the bonds is altered. In this way the problem of measuring the extramolecular stability is reduced to the determination of an enthalpy of an appropriate reaction. A great advantage of the isodesmic approach lies in the fact that the reaction may be formulated in a very simple way, and this can be done for practically any molecule for which a unique classical valence structure may be drawn. The simplest isodesmic approach is the bond separation type of reaction, where all formal bonds between nonhydrogen atoms are separated into the simplest two-heavy-parent molecules containing the same kind of linkages, and stoichiometric balance is achieved by the addition of the mono-heavy-atom hydride. Reaction 1[60a] in Table 13, is an illustrative example: the benzene CC and methane CH bonds are formally broken and other CC and CH bonds are formed, producing ethane and ethene. The estimated value of the stabilization energy is 66.9 kcal/mol, which is very different from the stabilization derived from reaction 3, Table 13 (37.5 kcal/mol), and can be attributed to the change in hybridization of the carbon atoms and the alternation in the character of

CH bonding from the point of view of the hybridization of the carbon atom and the number of hydrogens attached to individual carbon atoms.[60c] This is a rather extreme example; but it is important to note that usually many components such as hybridization effects and strain energy, which have no roots in cyclic π-electron delocalization, may play an important role in isodesmic reactions. They therefore serve only as a rough estimate of the total energy of conjugation rather than as an absolute and reliable measure of cyclic π-electron delocalization.

Table 13 presents the stabilization energies of benzene using 15 approaches based on different reference systems at the B3LYP/6-311+G** (+ zero point energy) level of theory. The source of the differences (almost 50 kcal/mol) is due to the choice and definition of reference molecules and the equations used, so the energies may be perturbed by additional effects such as strain, changes of hybridization, unbalanced conjugation, hyperconjugation, and so on. Due to conservation of the number of electron pairs in the products and reactants, the source of the energies (either experimental and theoretical) is expected to play a less significant role, especially if a given reaction scheme is applied to a set of related compounds. However, the span of the estimated stabilization energies for reaction 1, Table 13, is over 13 kcal/mol, depending on the quality of the original data.[60a,268−270]

To reduce the differences between the types of bonds, George et al.[61c] distinguished a subclass of isodesmic reactions (so-called homodesmotic reactions) in which (i) reactants and products contain equal numbers of each type of carbon−carbon bonds ($C^{(sp3)}$—$C^{(sp3)}$, $C^{(sp2)}$—$C^{(sp3)}$, $C^{(sp2)}$—$C^{(sp2)}$, $C^{(sp2)}$=$C^{(sp2)}$, etc.) and (ii) there is matching of the number of CH bonds in terms of the number of hydrogen atoms joined to the individual carbon atoms. This definition can be easily extended to systems containing heteroatoms. Due to closer matching of the hybridization states for a given atom in the reactants and products, the homodesmotic approach is undoubtedly more reliable for estimating the extent of cyclic delocalization and intrinsic strain. An example of the homodesmotic approach is represented by reactions 9−13 in Table 13.

Hess and Schaad[256] proposed in more detail the types of bond to be conserved, which leads to more complicated reactions. Their extension of the idea, called superhomodesmotic,[231,232b,250,256] takes into account additionally the closest neighborhood of given bonds (for examples see reactions 14 and 15 in Table 13). From the formal point of view they bring the types of bonds in products and reactants much closer, so one might expect more accurate estimations of stabilization energy. Unfortunately, superhomodesmotic reactions seem to be less reliable, owing to steric interactions in the complicated, conjugated reference molecules (especially in polyenes).[271] Perversely, some isodesmic approaches that are not truly homodesmotic can exhibit cancellation of errors for the noncyclic π-electron delocalization effects and, as a consequence, work remarkably well for limited series of compounds. The Schleyer and Pühlhofer[66d] isomerization method is a good example.

As previously mentioned, homodesmotic reactions are considered to provide the most sophisticated measure of the "extra" stabilization upon ring closure. However, to match the criteria of homodesmotic reactions, the number and types of reference molecules are usually extended, as compared with isodesmic approaches, especially if the bigger systems (or ones containing heteroatoms) are analyzed. Even for benzene, one may construct quite sophisticated reactions, which diminish the effects other than cyclic π-electron delocalization (for example, see reaction 8, Table 13). Therefore, two points should be made here: (i) a larger number of reference systems may introduce additional (presumably small) "contaminants", which may obscure the estimated effect, and (ii) the reactions may not necessarily be easily extended for more complicated systems, so they often lack generality. It is commonly believed that reliable quantitative aromaticity evaluations will be obtained if data comparisons are made merely by using the same method and similar reference systems.[20,272] This is a naive and in fact erroneous point of view, because the type of reference structure is often most crucial for achieving credible results.[31,32]

3.3.1. Linear Polyenes as Reference Systems

A typical example of a homodesmotic reaction, and probably the most frequently used,[273,274] is reaction 9 in Table 13 (see also reaction 17). In this reaction $6C^{(sp2)}=C^{(sp2)}$, $3C^{(sp2)}-C^{(sp2)}$, and $18C^{(sp2)}-H$ bonds are fully balanced in the products and reactants, so both criteria of homodesmocity are fulfilled. However, one problem is whether the comparison is more reasonable using fragments that most resemble those in the ring (*cis*-butadiene), or if the lowest energy conformers (*trans*-butadiene) should be taken into account. The former has an advantage that no extra rotation of the fragment is needed, but may also show significant repulsive interactions (e.g. close H atoms) not present in the ring.[271] The energy difference between *cis*- and *trans*-butadiene is ~3.4 kcal/mol (at B3LYP/6-311+G** + ZPE), which implies a 10.4 kcal/mol of difference for the estimated stabilization energy of benzene (see reactions 9 and 10 in Table 13). Moreover, the larger the aromatic system, the more conformations of reference units are possible, so the problem generally becomes more acute.

The extent of conjugation in *trans*-butadiene resulting from interactions between the two C=C units can be estimated[60d,275,276a] by the following isodesmic reactions using the lowest energy conformers:

$$\text{(structures)} + \text{(structure)} \xrightarrow{\text{4.2 kcal/mol}} 2 \text{ (structure)} \quad (23)$$

$$\text{(structure)} + \text{(structure)} \xrightarrow{\text{4.1 kcal/mol}} \text{(structure)} + CH_3-CH_3 \quad (24)$$
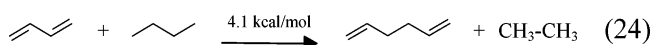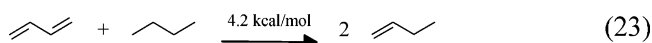
Although the derived energies may be perturbed to some extent by unbalanced hyperconjugation, different steric interactions present in the reference compounds etc., the estimated values of stabilization energy of butadiene are very similar (4.2–4.1 kcal/mol at B3LYP/6-311+G** level + ZPE).[277] This roughly corresponds to the difference in energy between *cis*- and *trans*-butadiene. However, a point

should be made that not only different conjugation but also steric repulsion between the terminal methylene groups determines the energy difference between butadiene conformers. Dewar and Holder[7] argued that the latter effect plays only a minor role because the enthalpies of formation of *trans*-2,3-dimethylbutadiene from propene and *trans*-butadiene from ethene are very similar. The comparison of two conformers of 2-vinylbuta-1,3-diene having similar steric requirements indicates that the syn–anti system is more stable by 2.3 kcal/mol (at B3LYP/6-311+G** + ZPE) than the syn–syn one. In fact, this is an underestimated value of the conjugation difference because steric repulsion is slightly greater in the former case, and the systems are not planar (see Figure 24).
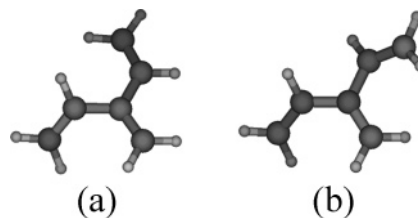
Figure 24. Two conformers of 2-vinylbuta-1,3-diene: (a) syn–anti (mean distance of methylene H···H, $R = 2.477$ Å); (b) syn–syn system (distances of methylene H...H, $R = 2.503$ Å).
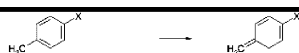
The importance of different syn and anti conjugations was recently pointed by Schleyer and Pühlhofer[66d] on the basis of the difference between methylene cyclohexadiene isomers as shown in reaction 57 (see also ref 66d). Another possible estimate of the difference in cis–trans conjugation is afforded by the following homodesmotic reactions based on planar dimethylene naphthalene derivatives:[278]
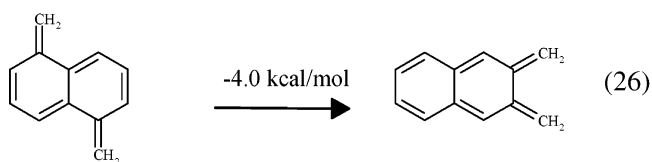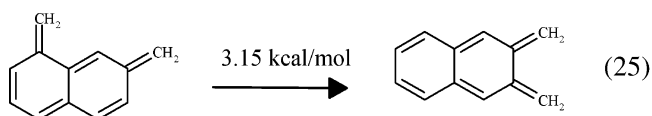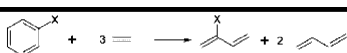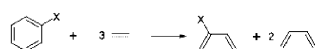
Because the steric repulsion of hydrogens in reaction 25 approximately cancels, the enthalpy of the reaction reflects the imbalance of the topological arrangement of double bonds involving one cis and one trans conformation. The estimated value of 3.15 kcal/mol (at B3LYP/6-311+G** level) attributed to different conjugation corresponds well with the 3.6 kcal/mol of Schleyer and Pühlhofer.[66d] On the other hand, comparison of enthalpies of reactions 25 and 26 leads to an estimation of the steric methylene–methylene repulsion interaction of 0.85 kcal/mol. This is in excellent agreement with the difference in energy between (planar) *cis*- and *trans*-butadiene of 4.0 kcal/mol, resulting from one cis–trans mismatch and one hydrogen–hydrogen repulsive interaction,

Table 14. Aromaticity Indices for Monosubstituted Benzenes: ASE(1−4) (in Kilocalories per Mole); NICS,[84] NICS(1), NICS(1)$_{zz}$,[12b] (in Parts per Million); HOMA,[69−71] and PDI[208] (Adapted from Reference 88)

X	ASE(1)^a	ASE(2)^b	ASE(3)^c	ASE(4)^d	NICS	NICS(1)	NICS(1)$_{zz}$	HOMA	PDI
NN$^+$	35.8	31.0	36.2	28.8	−10.6	−11.2	−28.6	0.96	0.080
NO	31.3	26.9	30.3	33.1	−9.8	−11.2	−29.9	0.98	0.091
NO$_2$	33.4	28.5	31.7	31.3	−10.9	−11.7	−30.5	0.99	0.096
CN	33.5	24.9	31.9	31.6	−10.3	−11.6	−30.9	0.98	0.096
COCl	34.2	28.0	32.2	30.9	−9.9	−11.5	−30.1	0.98	0.095
COCH$_3$	34.1	27.9	31.5	31.3	−9.7	−11.4	−30.4	0.98	0.097
COOCH$_3$	33.5	28.0	32.2	32.0	−9.8	−11.4	−30.4	0.98	0.097
COOH	33.7	27.9	33.1	31.7	−9.7	−11.4	−30.5	0.98	0.097
CHO	32.3	26.4	28.9	33.0	−9.6	−11.4	−30.6	0.97	0.095
CONH$_2$	33.4	26.4	31.1	31.6	−9.9	−11.7	−31.3	0.98	0.098
CCH	33.4	24.8	31.6	32.1	−10.1	−11.4	−30.4	0.97	0.096
Cl	34.6	23.7	30.1	31.9	−10.7	−11.5	−30.5	0.99	0.099
F	33.1	22.6	29.3	32.2	−11.7	−11.8	−31.1	0.99	0.098
H	33.2	24.7	30.7	32.7	−9.7	−11.5	−31.9	0.99	0.103
Ph	33.5	25.8	32.2	32.7	−9.3	−10.9	−30.0	0.98	0.098
CH$_3$	32.6	23.7	30.4	32.1	−9.7	−11.3	−31.0	0.98	0.100
OCH$_3$	35.0	21.8	28.2	31.1	−10.8	−11.3	−30.2	0.98	0.094
NH$_2$	33.2	24.6	29.6	33.3	−9.8	−10.5	−28.3	0.98	0.093
OH	34.1	22.5	29.2	32.1	−10.8	−11.3	−29.9	0.99	0.095
mean	33.6	25.8	31.1	31.8	−10.1	−11.3	−30.3	0.98	0.096
variance	1.0	5.6	3.2	1.1	0.38	0.09	0.67	8.5 10^{-5}	2 10^{-5}

^{a} Following the reaction: ^{b} Following the reaction:

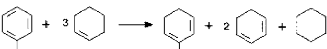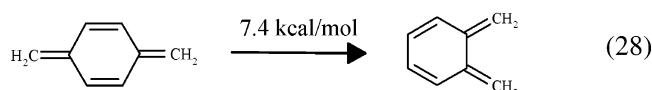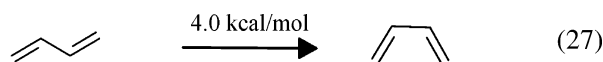^{c} Following the reaction: ^{d} Following the reaction:

and between para and ortho (planar) quinodimethane of 7.4 kcal/mol, resulting from the effect of the cis−trans mismatch and one hydrogen−hydrogen repulsive interaction (see reactions 27 and 28).[279,280]

$$4.0 \text{ kcal/mol} \qquad (27)$$

$$7.4 \text{ kcal/mol} \qquad (28)$$

The problem of the conformational stability of butadiene isomers (as the reference systems) has been recently critically discussed by Krygowski et al.[88] in the context of substituent effects in aromaticity. Both reactions 9 and 10 (but also reactions 5 and 11) in Table 13 lead to significantly different estimates of the extent of stabilization in monosubstituted benzene derivatives. This is mostly due to the fact that the lowest energy substituted reference systems are conformationally unstable and hence the estimated energies are biased by additional effects such as unbalanced syn−syn interactions, unbalanced strain, conjugation, repulsive interactions, etc., which contaminate the estimated ASE values. Table 14 presents the stabilization energy values, together with Krygowski's HOMA,[69−71] Schleyer's NICS,[12b,84] and Solà's PDI[208] indices. Despite substantial variation of the nature of the substituent, no dramatic changes in the π-electron structure of the benzene ring are observed, as quantified by HOMA, NICS, and PDI. However, the aromatic stabilization energies deviate much more, the largest differences (in the range of ∼9−10 kcal/mol) being found for the schemes with substituted butadiene-1,3 as the reference.

This case exemplifies a general problem that the other components may also significantly contribute to the estimated energy values. To disentangle aromatic stabilization energy from other important but complicating effects, a combination of two homodesmotic (or isodesmic) reactions is sometimes used.[15]

Small annulenes attracted a great deal of theoretical interest, because ring strain energy strongly interferes with π-electron delocalization/localization effects.[3,10j,t,220,223b,281] In the case of cyclobutadiene a simple homodesmotic reaction based on a linear reference polyene obviously does not balance the ring strain energy (see also the section on the valence bond approach).
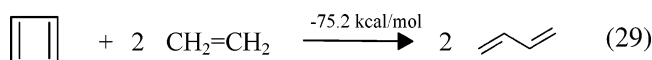
$$-75.2 \text{ kcal/mol} \qquad (29)$$

The estimated SE = −75.2 kcal/mol at MP4SDTQ/6-31G**//MP2/6-31G*[281c] (−87 ± 11 kcal/mol based on experimental ΔH_f^o values)[220] has to be corrected by ∼33.6 kcal/mol (32 ± 2 kcal/mol)[281a] attributed to strain (estimated from the strain energies of cyclobutane and cyclobutene), leading to −41.6 (55 ± 11 kcal/mol).

An unexpected flaw associated with using ring-opening reactions leading to linear polyenes has been found by Cyrański et al.[32] for five-membered heterocycles, especially for charged ones. A generalized approach extended for heteroatoms can be written as follows:
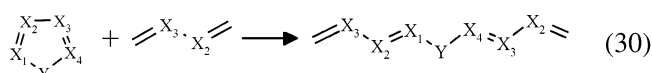

$$(30)$$

Table 15. ASE (in Kilocalories per Mole), NICS (in Parts per Million), and HOMA for Five-Membered Rings (Data Obtained at B3LYP/6-311+G** Level)[32]

system	ASE(l)[a]	ASE(c)[b]	NICS	HOMA
$C_5H_5^-$	−18.1	20.5	−14.3	0.812
$C_4H_4N^-$	−13.2	18.2	−13.6	0.879
$C_4H_4SiH^-$	−11.4	8.7	−5.8	
$C_4H_4B^-$	−40.5	5.0	−12.9	
C_4H_4PH	−0.8	2.7	−4.9	−0.258
C_4H_4O	6.3	12.3	−12.3	0.200
C_4H_4S	10.9	15.6	−13.2	0.745
C_4H_4NH	5.3	18.0	−15.0	0.857
$C_4H_4C{=}O$	−19.0	−16.3	9.2	−1.474
$C_4H_4C{=}S$	−16.5	−16.3	12.4	−0.650
$C_4H_4C{=}Se$	−16.3	−17.6	13.3	−0.455

[a] Based on homodesmotic reaction 30. [b] Based on homodesmotic reaction 31.

Selected values of ASE together with the other estimates, the values of ASE derived from homodesmotic reactions based on cyclic reference systems (see reaction 31),[31] plus NICS and HOMA, are given in Table 15.

$$
\text{(31)}
$$
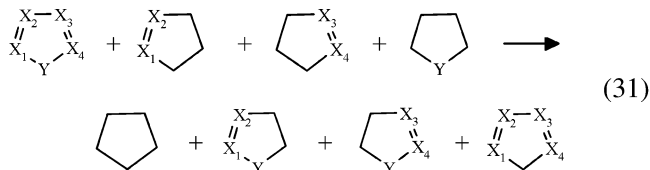
The negative value of stabilization energy for the cyclopentadiene anion (−18.7 kcal/mol) suggests that the system exhibits strong antiaromatic character. Contrary to this finding, the homodesmotic model based on cyclic references (reaction 31) confirms its considerable aromatic character (+20.5 kcal/mol stabilization), as does the strongly negative NICS (−14.0 ppm) and high value of HOMA (0.812). Similar flaws are found for other anionic systems, for example, for $C_4H_4N^-$, $C_4H_4SiH^-$, and $C_4H_4B^-$. This is because the negative charge may be accommodated by delocalization to the ends of polyene chains, where it benefits from better minimization of coulombic charge repulsion; therefore, the acyclic reference systems are more stable than the respective cyclic analogues.[32] As a consequence, the homodesmotic approach (reaction 30) is biased and cannot be expected to give reasonable results, at least for negatively charged systems. For neutral five-membered heterocycles, the reaction gives more consistent results. However, a closer inspection of the data reveals many subtle deviations. Although the values of NICS, HOMA, and SE based on cyclic references in the series of phosphole, furan, thiophene, and pyrrole show in line with chemical expectations[10f,n,15,17,84,272,276,282] that phosphole is the least aromatic and pyrrole the most aromatic in the series, the data based on reaction 30 give inconsistent ordering. A similar inconsistency results also from the semihomodesmotic reaction of Nyulászi et al.,[271] which compares the energy of the ring to that of the conjugated building blocks in the ring. Figure 25 shows considerable scatter between the stabilization energies estimated by reactions 30 and 31 for a set of 102 five-membered systems.[32]
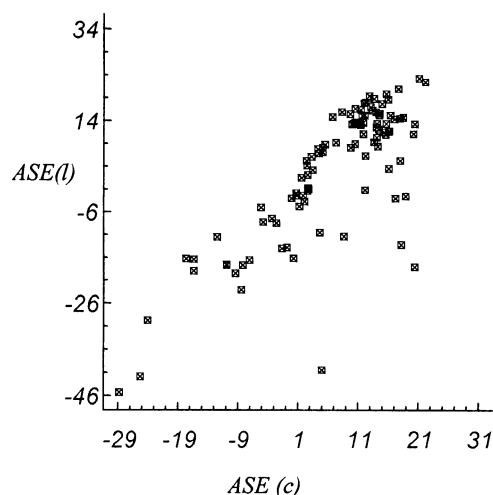

Figure 25. Scatterplot of the stabilization energies based on linear [ASE(l)] and cyclic references [ASE(c)]. Correlation coefficient: 0.796 (102 data). In reactions 30 and 31 the following systems have been considered: (i) X_1, X_2, X_3, and X_4 are C or N or X_1, X_2, X_3, and X_4 are C or P and Y= O, S, NH, PH; (ii) $X_1 = X_2 = X_3 = X_4 = $ C and Y = BeH^-, B^-, BH, BH_2^-, CH^-, CH_2, CF_2, N^-, NH_2^+, Al^-, AlH, AlH_2^-, SiH^-, SiH^+, SiH_2, P^-, PH_2^+, GaH, GaH_2^-, GeH^-, GeH^+, GeH_2, As^-, AsH, AsH_2^+, Se, $C{=}CH_2$, $C{=}O$, $C{=}S$, $C{=}Se$ (based on B3LYP/6-311+G** level of theory). Reprinted with permission from ref 32. Copyright 2003 Elsevier Science.

Apart from the increased stabilization of negatively charged linear acenes, another source of discrepancies may be attributable to strain effects. They cancel to a large extent in the homodesmotic reaction 31, where all of the reference molecules are five-membered rings computed in their most stable conformations. In contrast, the polyene reference systems used in reaction 30 have different conformations and bond angles compared to the rings. Moreover, both homodesmotic approaches can be perturbed by additional effects, such as topological charge stabilization[283] and/or heteroatom−heteroatom interactions. These effects may be minimized but not completely eliminated even by careful formulation of the homodesmotic reactions. It can be concluded that the homodesmotic ring-opening reactions, in the general case, may contain only rough information about the extent of π-electron delocalization, although for some limited series it can serve as a simple and effective diagnostic tool (see, for example, ref 180).

As with five-membered rings, Priykumar and Sastry[284] found that the stability of skeletally substituted benzenes is incorrectly estimated when charged compounds are involved in the homodesmotic equation based on polyenes. Other limitations can be found in the case of the reaction proposed recently by Fabian and Lewars[250] for azabenzenes leading to open polyenenes (see reaction 32). In general, the estimated values of stabilization energy depend, at least to some extent, on the position and kind of formally broken CC or CN bond in the cyclic system. Presumably it is not a large effect because, in line with chemical expectations,[249] their estimated stabilization energies and NICS values show a steady decrease in thermodynamic stability with increase

Table 16. Homodesmotic Stabilization Energies for Azines (Given in Kilocalories per Mole) [Calculated at MP2(fc)/6-31G* Level (B3LYP/6-31G* in Parentheses); NICS and NICS Calculated 1 Å above the Molecular Plane Denoted NICS(1) at HF/6-31G* Level Using GIAO on MP2(fc)/6-31G* Geometries (in Parts per Million)][250]

System	ASE	NICS	NICS(1)	System	ASE	NICS	NICS(1)
	25.4 (19.8)	-9.6	-12.4		13.6 (8.3)	-4.1	-12.5
	21.9 (15.5)	-7.7	-12.5		0.6 (-4.0)	-1.7	-12.1
	11.7 (6.1)	-6.1	-12.5		-10.1[a] (-16.9)	-6.8	-14.5

[a] Data for D_2 structure. D_{6h} (hilltop) values: ASE, -12.5 kcal/mol (at MP2(fc)/6-31G*, -19.4 kcal/mol (at B3LYP/6-31G*); NICS $= 0.3$; NICS(1) $= -12.2$.

of the number of nitrogens. An exception is NICS for N_6 (see Table 16).

$$(32)$$
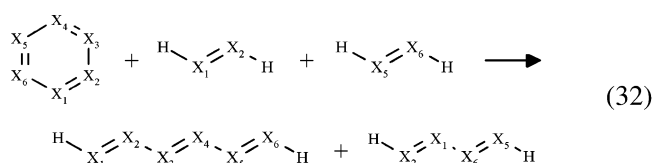
As might be expected, the extension of the ring-opening reactions leading to acyclic polyenes is not an easy task for polycyclic systems.[285] This often lacks generality and involves many additional effects that may obscure the final result, the most important being unbalanced hyperconjugation and strain. Apart from reaction 18, which is not homodesmotic, George et al.[60c] proposed another general approach (see reaction 33), which involves sp^3 type carbon atoms and therefore does not necessarily well balance the $C^{(sp2)}-C^{(sp2)}$ types of bonds between the carbon atoms with no hydrogens joined to them. Consequently, further reference systems have been proposed such as 2-vinylbutadiene[60c] or alternatively 2,3-divinylhexatriene,[61c] although these are nonplanar. It is evident that several schemes are conceivable for one and the same polycyclic system. Even though it is carefully constructed and the criteria of homodesmotic reactions are fulfilled, it is clear that the difference between the stabilization energies of two topological isomers (e.g. anthracene and phenanthrene) is only due to the difference in their total energies (equivalently experimental ΔH_f values).

$$C_{(2p)}H_{(2q)} + p\ CH_2=CH_2 +$$
$$4\ (p-q)\ CH_3-CH=CH_2 =$$
$$2p-q\ CH_2=CH-CH=CH_2 +$$
$$2(p-q)\ CH_2=C(CH_3)_2 \quad (33)$$

Another difficulty in estimating stabilization energies based on acyclic reference compounds is found for nonplanar systems. Fullerenes are rather extreme cases, but serve to illustrate the problem. For C_{60} one may construct the following reactions:[10t]

$$C_{60} + 90\ CH_2=CH_2 \xrightarrow{-90.8\ \text{kcal/mol}} 60 \quad (34)$$

$$C_{60} + 90\ CH_2=CH_2 \xrightarrow{-303.7\ \text{kcal/mol}} 60 \quad (35)$$

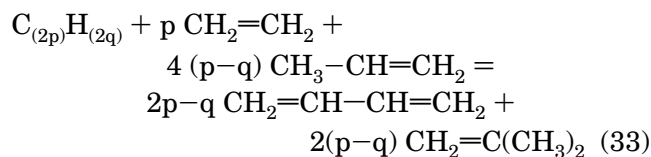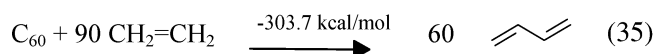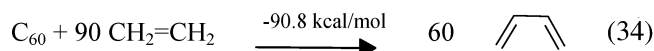The deficiency in this approach is apparent.[10a] The choice of a reference system affects dramatically the findings and, consequently, the two stabilization energies differ by >200 kcal/mol![107] Moreover, both values are strongly biased by strain, which is (so far) impossible to separate out. Even if some clever corrections are devised, the stoichiometry implies an inevitable multiplication of their errors.

3.3.2. Cyclic Reference Systems

First of all, homodesmotic reactions based on cyclic reference systems balance the strain effect much more efficiently than linear polyenes, because the reference compounds are the appropriate rings in their most stable conformations. For benzene, reaction 11 in Table 13 proposed by Schleyer and Jiao,[26] unlike the isodesmic reaction 3, Table 13, takes into account the syn–anti mismatch effect, and the estimated stabilization energy of 32.4 kcal/mol is very close to the result with syn-butadiene as a reference (33.6 kcal/mol, reaction 10 in Table 13). This value is also consistent with two other estimates by Fishtik and Datta[232b] (33.9 kcal/mol, at the G3 ab initio level) and Howard[232a] (33.1 kcal/mol at the MP2/6-311G** level) based on the response reactions formalism[232b,239] and on a unique model for predicting bond energy distributions using the atoms-in-molecules[147] formalism, respectively. For monosubstituted benzenes, Krygowski et al.[88] have shown much smaller variation of stabilization energies compared with the values based on cis(or trans)-butadiene as reference, in line with other geometry- and magnetism-based estimates.

Given that the bond energies in radialenes are perfectly additive (as shown by Dewar and de Llano[45]), other homodesmotic reactions with radialenes as references may be constructed (see reactions 12 and 13 in Table 13). The estimated values (based on the lowest energy conformers) are somewhat smaller than the values obtained with ho-

modesmotic reaction 11 (Table 13) but, nevertheless, are very consistent. Yet another estimate gives 28.6 kcal/mol for benzene (at B3LYP/6-311+G** +ZPE), following reaction 36:

$$ \text{(36)} $$
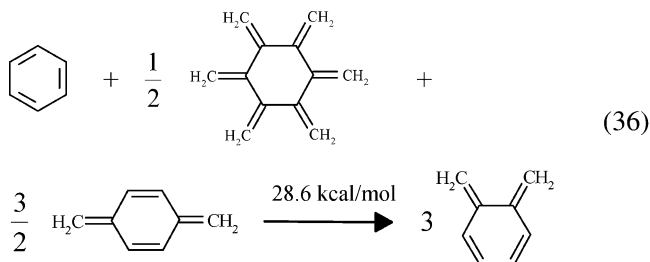
Cyclobutadiene has been the subject of a large number of theoretical calculations including semiempirical,[286] ab initio,[281c,l,287] and G2.[281a] None of the frequently used reactions for cyclobutadiene presented below are homodesmotic. However, because the difference in strain between cyclobutadiene and the reference systems is essentially reduced, they give comparable (exothermic) enthalpy changes. The values given in reactions 37 and 38 are obtained from calorimetric data.[10j,220] Wiberg noted that most probably these experimental estimates are in error, because the values of (de)stabilization energy calculated at different levels of theory[10j] are smaller (e.g. −34.6 and −38.8 kcal/mol, respectively, at the B3LYP/6-311+G** level + ZPE).

$$ \text{(37)} \quad -46\ \text{kcal/mol} $$

$$ \text{(38)} \quad -49\ \text{kcal/mol} $$
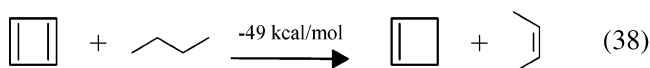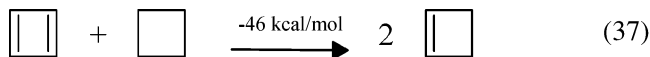
Taking advantage of the bond energy additivity in radialenes,[45] as in the case of benzene, it is possible to construct a homodesmotic reaction where all carbon atoms are sp^2-hybridized. The strain mismatch should be reduced more efficiently in this case, and in addition there should be no unbalanced hyperconjugation. However, still the cis−trans mismatch effect has to be taken into account.[66d] If a value of ∼3.15 kcal/mol is assumed for the latter,[288] the estimated stabilization energy of butadiene is −41.2 kcal/mol (at B3LYP/6-311+G** +ZPE), in perfect agreement with the Suresh and Koga[289] recent estimate based on radical systems (−40.3 kcal/mol at the MP4(SDQ)/6-31G** level).

$$ \text{SE} = -47.5\ \text{kcal/mol} \qquad \text{SE}_{corr} = -41.2\ \text{kcal/mol} \quad \text{(39)} $$

The issue of aromatic stability in five-membered rings has long been discussed (see, for example, refs 10f,n, 15, 17, 84, 271−273, 276, 281d, 282 and 290). Schleyer et al. applied reaction 40 for 11 systems comprising aromatics, nonaromatics, and antiaromatics in a highly cited *Angewandte Chemie* paper[282] pointing out that "classical and magnetic concepts may not be orthogonal".
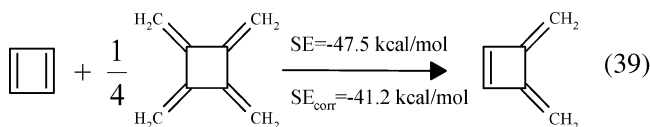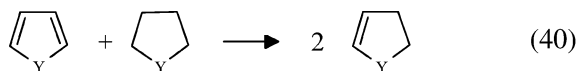
$$ \text{(40)} $$

Because of the unbalanced contributions of $C^{(cp2)}H-C^{(sp2)}H$, $C^{(cp3)}H_2-C^{(sp3)}H_2$, and $C^{(cp2)}H-C^{(sp3)}H_2$, this reaction is not homodesmotic. However, the variation deals with only one heteroatom (Y), so the imbalance is constant in the whole set of compounds analyzed. The situation becomes much more complicated if the approach is to be extended to include more heteroatoms in the ring.[272] The importance of the proper formulation of the reaction scheme has been recently analyzed by Cyrański et al.[32] By comparing the homodesmotic reaction scheme (reaction 31) with four isodesmic-like reactions 41−44, which can be viewed as truncated versions of reaction 31, they demonstrated that the energies derived from the simplified approaches do not correlate with each other because they have many obvious flaws (see Figure 26). They do not consistently correct or cancel other contributions to the energy, such as changes of hybridization; homoconjugation of heterosubstituted cyclopentadienes; conjugative interactions of C=C or C=X (where X = N or P) with a π- or pseudo-π-orbital at Y; strain; or topological charge stabilization. One of the relationships, presented in Figure 26b, seems to be reasonable, and this is because the truncated reference molecules for monoheteropentatomic systems (cyclopentane, cyclopentene, and cyclopentadiene) are not critical and are the same for all of the systems. In this case (monoheteropentatomic rings) reaction 42 is reduced to reaction 40, which for this set of compounds is equivalent to reaction 31. In fact, closer examination of Figure 26b reveals several subsets of linearly correlated data, indicating local correlations among related molecules. These arise for the same reason as the monohetero rings; that is, the truncated reference molecules are the same in each set.[32] An important point is that approaches less restrictive than the homodesmotic criteria may, under favorable circumstances, accurately reproduce aromatic stabilization energies but only for structurally restricted subgroups of molecules.[102,291,292] The poor correlations clearly demonstrate the deficiency of the isodesmic reactions, which (in the general case) should not be considered as providing reliable information about stabilization due to cyclic π-electron delocalization. The stabilization energies derived from isodesmic reactions are almost always perturbed by additional effects that have no roots in aromaticity.[32]

$$ \text{(41)} \quad + \text{ASE for} $$

$$ \text{(42)} $$

$$ \text{(43)} $$

$$ \text{(44)} $$
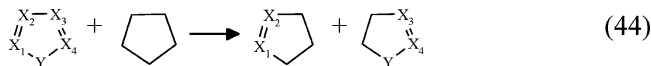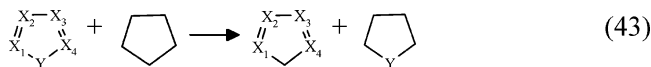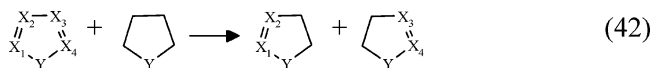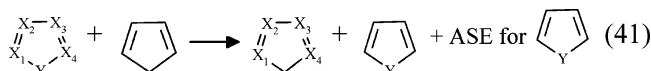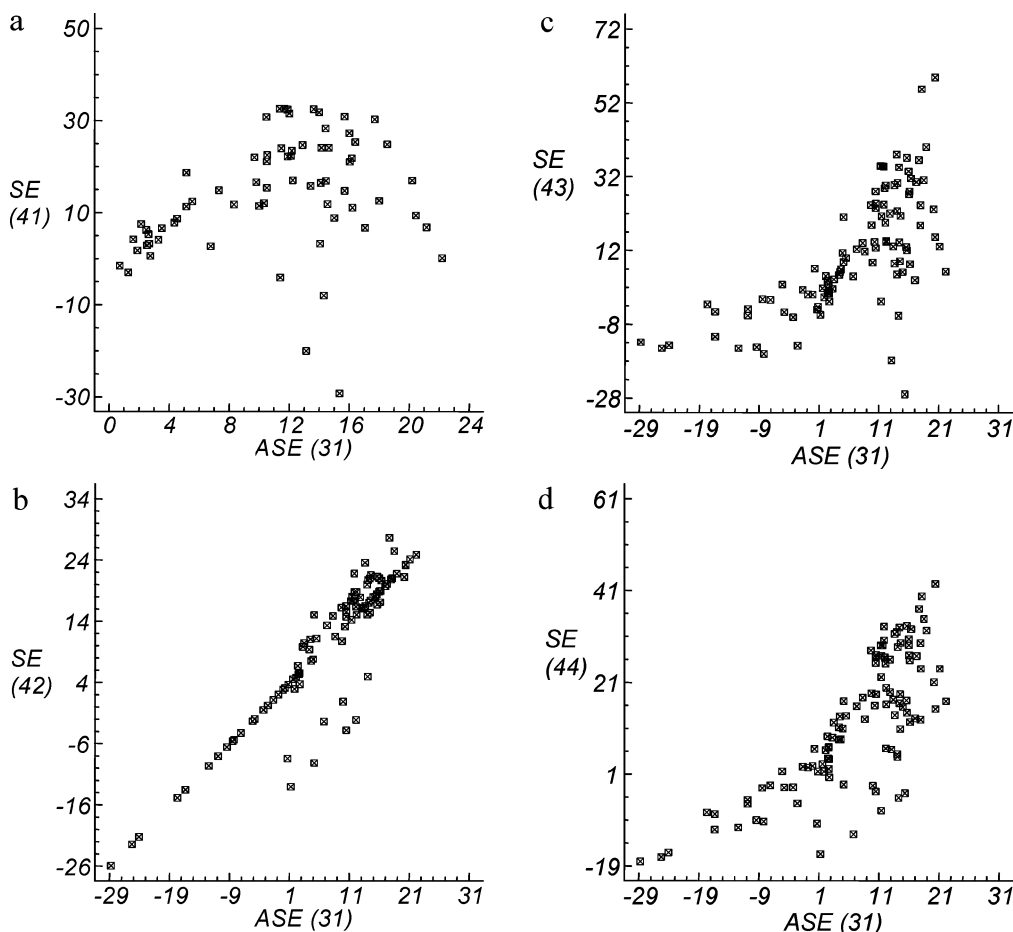
Figure 26. Dependencies between the stabilization energies: (a) ASE (reaction 31) versus SE (reaction 41), correlation coefficient = 0.291, 68 data; (b) ASE (reaction 31) versus SE (reaction 42), correlation coefficient = 0.920, 102 data; (c) ASE (reaction 31) versus SE (reaction 43), correlation coefficient = 0.681, 102 data; (d) ASE (reaction 31) versus SE (reaction 44), correlation coefficient = 0.767, 110 data. In reactions 31 and 41−44 the following systems have been considered: (i) X_1, X_2, X_3, X_4 are C or N or X_1, X_2, X_3, X_4 are C or P and Y = O, S, NH, PH; or (ii) $X_1 = X_2 = X_3 = X_4 = C$ and Y = BeH^-, B^-, BH, BH_2^-, CH^-, CH_2, CF_2, N^-, NH_2^+, Al^-, AlH, AlH_2^-, SiH^-, SiH^+, SiH_2, P^-, PH_2^+, GaH, GaH_2^-, GeH^-, GeH^+, GeH_2, As^-, AsH, AsH_2^+, Se, $C=CH_2$, $C=O$, $C=S$, $C=Se$ (based on B3LYP/6-311+G** level). Reprinted with permission from ref 32. Copyright 2003 Elsevier Science.

The estimated values of ASE based on the homodesmotic reaction 31 together with exaltations of magnetic susceptibility, NICS and HOMA for aza- and phospha derivatives of furane, tiophene, pyrrole, and phosphole (and parent systems) are given in Table 17.[31,32] Table 18 presents the data for mono-endosubstituted five-membered rings.[31,32]

For monohetero five-membered ring systems, the estimated ASEs are on average ∼5 kcal/mol lower than those estimated by Chesnut and Davis.[276a] In line with the values obtained by Nyulàszi et al.[271] using acyclic references, homodesmotic reaction 31 reveals that the aromatic stabilization of the ring is mainly determined by the heteroatom which donates two electrons to the π-system (O, S, PH, or NH). In general, the effect of the next heteroatom is smaller. The ASE of most polyaza derivatives is increased, but for polyphospha derivatives it is usually decreased with respect to their parent systems,[10f,293a,b] consistent with the "rule" that aromaticity (and stability) increases with the decrease in the electronegativity difference between a heteroatom and its neighboring atoms.[15] Hence, replacement of CH by nitrogen in position 2 causes a substantial increase, whereas

replacement in position 3 results in a decrease of ASE. Consequently, 2,5-diaza species have the largest and 3,4-diaza systems the lowest ASEs among the whole set of polyaza derivatives. These generalizations are fully supported by NICS values. The increase of aromaticity in polyphosphole systems is due to the well-known decrease of pyramidality of the tricoordinate phosphorus;[10f,293c] pentaphosphole is known to be planar and aromatic.[293] Systematic comparison with the stabilization energies based on homodesmotic model 31 at two levels of theory, B3LYP/6-311+G** and MP2(fc)/6-311+G**, lead to the conclusion that the level of theory, if adequately high, should not much affect the relative stabilization energy values. The values of ASE are, however, slightly larger (by ∼2.4 kcal/mol) at the MP2/6-311+G** level. Figure 27 shows a relevant dependence.

Many isodesmic approaches for six-membered systems have been proposed (see, for example, refs 249, 276a,b, and 294), Wiberg et al.[249] employed hydrogen transfer reactions (for examples, see reactions 45 and 46) to show that the differences between benzene, pyridine, pyrazine, and pyrimidine are small despite

Table 17. Calculated ASE (in Kilocalories per Mole) (Reaction 31), at MP2(fc)/6-311+G (+ZPE), Exaltations of Magnetic Susceptibility Λ [Using Reaction 31, at CSGT/HF/6-311+G**//MP2(fc)/6-311+G**], NICS, NICS 1 Å above the Ring Centers [Denoted NICS(1); in Parts per Million] (at GIAO/HF/6-311+G**// MP2(fc)/6-311+G**; in Parts per Million), and HOMA for Polyhetero Five-Membered Rings (Including the Parent Systems), Based on MP2(fc)/6-311+G** Optimized Geometries[31]**

compound	ASE	a	Λ	NICS	NICS(1)	HOMA	compound	ASE	a	Λ	NICS	NICS(1)	HOMA
furan	14.8	(12.3)	−2.9	−12.3	−9.4	0.298	2-phosphafuran	13.2	(11.9)	−1.6	−11.4	−9.3	
thiophene	18.6	(15.6)	−7.0	−13.8	−10.8	0.891	2-phosphathiophene	17.5	(14.7)	−7.2	−13.5	−11.4	
pyrrole	20.6	(18.0)	−6.5	−14.9	−10.6	0.876	2-phosphapyrrole	20.3	(18.6)	−6.1	−13.6	−10.8	
phosphole	3.2	(2.7)	−1.7	−5.4	−6.0	0.236	2-phosphaphosphole	5.0	(3.5)	−4.9	−7.4	−7.7	
2-azafuran	17.3	(14.3)	−2.7	−12.4	−10.6	0.527	3-phosphafuran	13.5	(10.3)	−3.0	−11.9	−10.3	0.326
2-azathiophene	20.2	(16.2)	−7.1	−14.0	−11.7		3-phosphathiophene	17.0	(13.4)	−8.4	−13.0	−11.6	0.854
2-azapyrrole	23.7	(20.5)	−7.1	−14.8	−11.9	0.926	3-phosphapyrrole	19.9	(16.1)	−6.9	−14.3	−11.3	0.829
2-azaphosphole	3.3	(2.6)	−1.5	−5.7	−6.8		3-phosphaphosphole	3.0	(2.5)	−2.7	−5.3	−6.9	0.378
3-azafuran	12.4	(9.8)	−1.8	−11.3	−9.5	0.332	2,3-diphosphafuran	12.2	(10.5)	−2.0	−11.9	−10.4	
3-azathiophene	17.4	(14.5)	−6.2	−13.1	−11.4	0.905	2,3-diphosphathiophene	15.1	(12.1)	−8.8	−13.9	−12.2	
3-azapyrrole	18.8	(16.2)	−5.2	−13.9	−10.8	0.908	2,3-diphosphapyrrole	19.2	(16.4)	−6.7	−14.0	−11.6	
3-azaphosphole	3.0	(2.8)	−1.2	−3.8	−6.3	0.276	2,3-diphosphaphosphole	4.3	(2.5)	−5.5	−8.9	−9.2	
2,3-diazafuran	17.2	(14.1)	−1.6	−13.0	−12.0	0.443	2,4-diphosphafuran	12.1	(10.6)	−1.7	−11.1	−10.1	
2,3-diazathiophene	20.5	(15.7)	−7.8	−14.4	−13.7		2,4-diphosphathiophene	16.1	(12.9)	−8.4	−12.9	−12.2	
2,3-diazapyrrole	24.4	(20.2)	−6.7	−14.9	−13.5	0.931	2,4-diphosphapyrrole	18.9	(16.0)	−6.2	−12.9	−11.4	
2,3-diazaphosphole	2.6	(1.9)	−1.0	−4.1	−8.6		2,4-diphosphaphosphole	6.2	(4.4)	−7.1	−8.5	−9.3	
2,4-diazafuran	14.2	(11.4)	−1.3	−11.5	−10.4	0.553	2,5-diphosphafuran	12.7	(11.9)	−1.1	−10.3	−9.3	
2,4-diazathiophene	18.3	(14.6)	−6.3	−13.5	−12.0		2,5-diphosphathiophene	16.0	(13.7)	−7.9	−13.1	−12.0	
2,4-diazapyrrole	21.3	(18.0)	−5.3	−13.7	−11.8	0.940	2,5-diphosphapyrrole	19.2	(17.7)	−6.4	−11.8	−10.9	
2,4-diazaphosphole	3.0	(2.7)	−1.1	−4.6	−7.2		2,5-diphosphaphosphole	8.0	(5.2)	−9.8	−10.0	−10.3	
2,5-diazafuran	20.2	(15.4)	−1.6	−12.7	−12.5	0.677	3,4-diphosphafuran	12.2	(8.3)	−3.3	−12.4	−11.1	
2,5-diazathiophene	22.7	(17.1)	−7.6	−14.5	−13.0		3,4-diphosphathiophene	16.8	(12.3)	−9.6	−13.1	−12.4	
2,5-diazapyrrole	26.7	(22.2)	−7.9	−14.8	−13.6	0.960	3,4-diphosphapyrrole	19.5	(14.2)	−7.0	−14.5	−12.0	
2,5-diazaphosphole	3.1	(2.2)	−1.3	−5.5	−7.6		3,4-diphosphaphosphole	4.1	(3.3)	−4.9	−6.9	−8.5	
3,4-diazafuran	7.8	(5.2)	−0.6	−10.7	−10.0	0.243	2,3,4-triphosphafuran	11.8	(9.7)	−2.9	−12.7	−11.4	
3,4-diazathiophene	13.7	(10.5)	−5.3	−13.0	−12.3	0.849	2,3,4-triphosphathiophene	15.2	(11.5)	−10.3	−14.1	−13.2	
3,4-diazapyrrole	15.0	(12.2)	−3.5	−13.1	−11.5	0.823	2,3,4-triphosphapyrrole	18.4	(14.4)	−6.8	−14.4	−12.4	
3,4-diazaphosphole	1.8	(1.3)	−0.9	−2.9	−7.0	0.025	2,3,4-triphosphaphosphole	7.2	(4.6)	−11.5	−12.4	−11.8	
2,3,4-triazafuran	9.7	(6.8)	0.4	−12.9	−12.3	0.413	2,3,5-triphosphafuran	12.7	(11.7)	−1.2	−11.0	−10.3	
2,3,4-triazathiophene	14.7	(10.0)	−6.6	−15.2	−14.7		2,3,5-triphosphathiophene	14.5	(12.0)	−8.8	−13.6	−12.9	
2,3,4-triazapyrrole	18.3	(14.1)	−3.5	−14.8	−14.1	0.897	2,3,5-triphosphapyrrole	18.0	(15.7)	−6.1	−12.4	−11.6	
2,3,4-triazaphosphole	1.5	(0.7)	−1.3	−4.2	−8.7		2,3,5-triphosphaphosphole	8.9	(5.6)	−12.4	−12.3	−11.9	
2,3,5-triazafuran	18.7	(13.1)	−0.1	−13.8	−13.8	0.586	2,3,4,5-tetraphosphafuran	12.3	(11.4)	−2.5	−13.4	−12.0	
2,3,5-triazathiophene	21.6	(15.0)	−7.9	−15.5	−15.0		2,3,4,5-tetraphosphathiophene	12.8	(10.5)	−10.6	−15.0	−14.4	
2,3,5-triazapyrrole	26.5	(21.2)	−7.0	−15.0	−14.6	0.960	2,3,4,5-tetraphosphapyrrole	17.1	(14.0)	−6.0	−14.6	−13.0	
2,3,5-triazaphosphole	2.2	(1.6)	−0.5	−4.9	−9.2		2,3,4,5-tetraphosphaphosphole	11.2	(7.3)	−20.8	−17.2	−14.9	

[a] Data in parentheses estimated at B3LYP/6-311+G** (+ZPE) level.[32]

Table 18. Calculated ASE (in Kilocalories per Mole) (Reaction 31), at MP2(fc)/6-311+G (+ZPE), Exaltations of Magnetic Susceptibility Λ (Using Reaction 31, at CSGT/HF/6-311+G**//MP2(fc)/6-311+G**), NICS and NICS 1 Å above the Ring Centers [Denoted NICS(1), in Parts per Million] (at GIAO/HF/6-311+G**//MP2(fc)/6-311+G**), and HOMA (Estimated on the Basis of Three CC Bond Lengths) for Mono-endosubstituted Rings (C4H4X) Based on MP2(fc)/6-311+G** Optimized Geometries[31]**

X	ASE	a	Λ	NICS	NICS(1)	HOMA	X	ASE	a	Λ	NICS	NICS(1)	HOMA
BeH⁻	−7.8	(−8.4)	10.2	9.1	4.0	−0.166	P⁻	23.1	(19.0)	−9.8	−13.4	−11.0	0.859
B⁻	9.1	(5.0)	−13.5	−12.7	−6.9	0.420	PH2⁺	−8.3	(−9.4)	4.2	−0.7	−2.6	0.016
BH	−22.5	(−24.0)	16.1	17.2	9.2	−0.595	GaH	−10.0	(−10.8)	13.4	6.7	3.2	−0.300
BH2⁻	−0.2	(0.3)	−0.2	0.1	−2.8	0.281	GaH2⁻	−1.0	(−0.8)	3.5	1.8	−0.5	−0.059
CH⁻	22.1	(20.5)	−10.2	−14.0	−10.3	0.736	GeH⁻	4.9	(4.7)	−2.7	−4.3	−4.9	0.626
CH2	0.0	(0.0)	0.0	−3.2	−4.8	0.306	GeH⁺	−23.9	(−25.2)	18.5	11.3	6.9	−0.628
CF2	−11.9	(−12.4)	6.7	3.4	0.5	−0.287	GeH2	−3.0	(−3.3)	3.7	0.4	−1.5	0.037
N⁻	19.6	(18.2)	−9.4	−13.3	−11.0	0.818	As⁻	22.2	(17.3)	−10.8	−12.9	−10.6	0.877
NH2⁺	−2.1	(−2.5)	1.6	−5.2	−5.3	0.135	AsH	1.7	(0.9)	−0.1	−3.9	−4.6	0.447
Al⁻	−6.9	(−7.0)	8.9	5.6	1.2	0.058	AsH2⁺	−6.6	(−8.2)	4.1	−1.1	−2.3	0.010
AlH	−10.0	(−10.8)	13.1	6.4	3.1	−0.261	Se	16.7	(13.7)	−7.4	−12.8	−10.0	0.878
AlH2⁻	−2.1	(−1.7)	3.8	2.8	0.0	0.007	C=CH2	−3.1	(−5.1)	1.0	−0.7	−3.4	0.280
SiH⁻	9.3	(8.7)	−8.9	−9.1	−7.9	0.792	C=O	−14.7	(−16.3)	9.1	9.6	2.8	−0.326
SiH⁺	−26.6	(−28.7)	18.6	12.4	7.7	−0.664	C=S	−12.0	(−16.3)	10.5	12.6	3.5	0.031
SiH2	−4.6	(−4.8)	4.1	1.1	−1.4	−0.035	C=Se	−11.4	(−17.6)	12.4	13.5	3.8	0.092

[a] Data in parentheses estimated at B3LYP/6-311+G** (+ZPE) level.[32]

significant changes in bond angles and lengths on going from benzene to these azines. They argued that the thermochemical stabilization associated with a six π-electron system is not strongly dependent on the structure. In particular, it does not require a regular hexagon and tolerates considerable variations

in geometry.[249] A comparison of stability for pyridazine and benzene (reaction 46) fulfills the homodesmotic reaction criteria. Due to the presence of a NN bond, a significant lowering of stability is observed (by 9.9 kcal/mol at B3LYP/6-311+G** level +ZPE), which is somewhat larger than the value
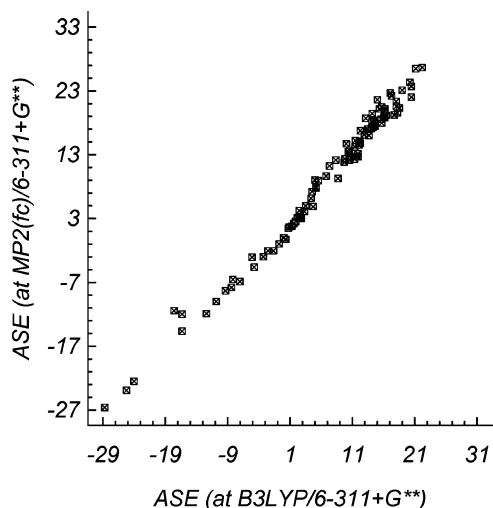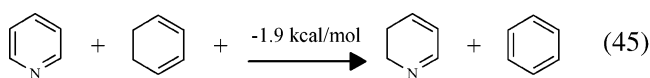
Figure 27. Dependence between ASE estimated by reaction 31 at MP2(fc)/6-311+G** (+ZPE) and B3LYP/6-311+G** (+ZPE) levels. Correlation coefficient $R = 0.992$ for 102 data.

obtained by Fabian and Lewars using linear reference compounds.[250]

 (45)

 (46)

Recently Sauers et al.[248] proposed a homodesmotic reaction (see reaction 47) for pyridine and other azines. This is in fact an extension of the homodesmotic approach for benzene (see reaction 11 in Table 13). The estimated stabilization energy of pyridine (31.0 kcal/mol at B3LYP/6-311+G** +ZPE) is in perfect agreement with that obtained from reaction 45 (30.5 kcal/mol at B3LYP/6-311+G** +ZPE), taking the ASE value of benzene from homodesmotic reaction 11, Table 13.

 (47)
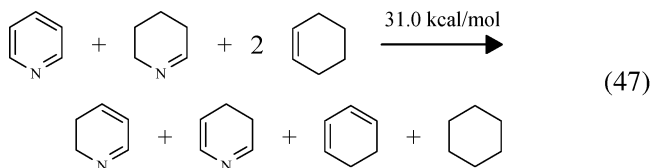
The approach of Wiberg et al.[249] to azine stabilization energy exemplifies another type of isodesmic reaction (some of them fulfill homodesmotic requirements) where the comparison involves two or more aromatic systems. Obviously, this kind of approach may be extremely useful both for aromatic and antiaromatic annulenes and for polycyclic systems (see, for example, refs 236, 295, and 296). However, in the latter case the danger exists that the reactions may again lack generality. The reaction schemes 48[297]−50 illustrate this point.[295] The differences in stabilization energy (estimated at the B3LYP/6-311+G** + ZPE level) result only from the energies of a single polycyclic component (e.g. chrysene, benz-[e]phenanthrene and triphenylene). It should be recognized that the difference in energy of topological

isomers is not only due to different π-electron delocalization effects but also that other factors such as steric repulsions between hydrogens[298] play an important role.

 (48)

 (49)

 (50)
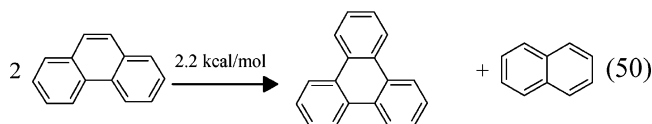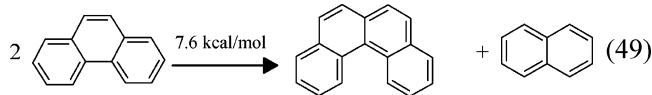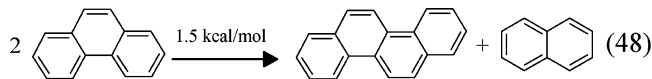
It is also generally true that many possible ASE reactions for a given polycyclic system may be formulated; for example, for triphenylene (reaction 50) a reaction similar to that of phenanthrene and anthracene[295] would also be valid. Moreover, these formally homodesmotic reactions may be still significantly improved. For example, to prevent the same number of "bay-regions"[298] in products and reactants (which diminishes the effect of hydrogens repulsions), the following approach for triphenylene might be more appropriate:

 (51)
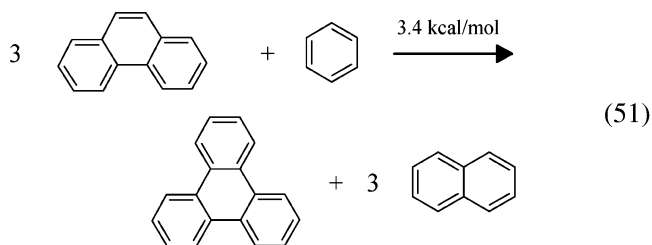
It should be fairly clear that any relative stabilities predicted in this way are necessarily limited by the accuracy with which ASEs are known for the reference system(s).

Despite this criticism, it is fair to observe that cyclic reference systems are far more appropriate standards for estimating stabilization energies of benzenoid and nonbenzenoid hydrocarbons than the linear (or branched) polyenes. They are certainly more efficient for the nonplanar aromatics, because the reference compounds ought to have very have similar strains due to distortion from planarity. It is believed that this factor is effectively canceled out or at least significantly reduced.

Two general approaches for estimating the extent of π-electron delocalization in fullerenes involve (i) comparisons between the energies of structural isomers of heterofullerenes, where the heteroatoms impose favored or unfavored bond localization patterns (but also introduce potentially unfavorable repulsive interactions between heteroatoms),[178,299] and (ii) the hydrogenation of fullerenes and its fragments.[12k,107,242] In both cases, the cyclic reference systems are significantly bent. The literature on fullerene stability is already vast (see, for example,

refs 10c, 170c, 208b, 211, and 300). For example, the magnitude of the three-dimensional delocalization (stabilization) effect of C_{60} can be estimated by reactions 52 and 53, where both reference compounds are the fragments of the fullerene with one six- or five-membered ring omitted, and the last shell is terminated with six (or five) CH_2 groups imposing electron delocalization on half of the sphere.[107]

$$ \text{(52)} \qquad -9.8 \text{ kcal/mol} $$

$$ \text{(53)} \qquad -9.0 \text{ kcal/mol} $$
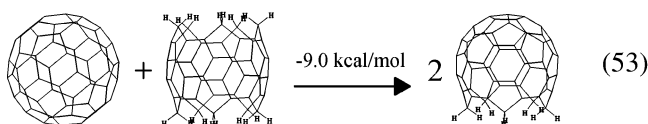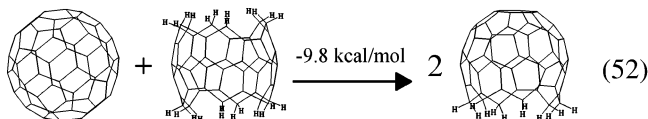
Despite the fact that the reactions utilize subtly different reference compounds with presumably different electron (de)localization effects, both approaches predict far lower destabilization of C_{60} (by ~0.15 kcal/mol per π-electron) compared to the reference systems. The extension of this approach to fullerenes other than C_{60} would be difficult because the number of topologically different reference systems significantly increases. This sheds light on an important problem: it is not an easy task to design a unique and general reaction scheme, which effectively cancels out contributions other than cyclic π-electron delocalization to the stabilization energy.[66a]

This challenge may perhaps be met by the further development of the isomerization method based on tautomeric equilibria proposed by Schleyer and Pühlhofer.[66d] This idea originates from the experimental work of Beak et al.[54] and Katritzky et al.,[55] who first suggested the use of the tautomeric equilibria as potentially generally applicable quantitative criteria for aromaticity. However, as dictated by the availability of experimental data, there have been only a few applications.[10n,54−57] The isomerization stabilization energy method (ISE) involves comparison of the total energies of only two species: a methyl derivative of the cyclic conjugated system and its nonaromatic exocyclic methylene isomer. The value for benzene can be derived from the value for toluene (having practically the same stabilization energy as benzene, see Table 14)[88] and two nonaromatic methylenecyclohexadiene isomers as shown in reactions 54 and 55[301] (compare also reaction 5, Table 13).

$$ \text{(54)} \qquad ISE=33.2 \text{ kcal/mol} \qquad ISE_{corr}=33.2 \text{ kcal/mol} $$

$$ \text{(55)} \qquad ISE=29.6 \text{ kcal/mol} \qquad ISE_{corr}=33.2 \text{ kcal/mol} $$
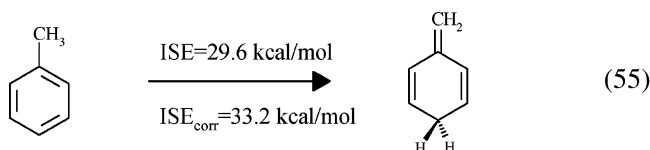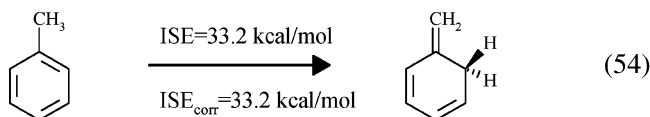
Because the equations have a syn−anti mismatch, Schleyer and Pühlhofer[66d] corrected the former reaction (54) by the addition of eq 56 and the latter (55) by the addition of eq 57. This gives a value comparable to the other stabilization energies based on cyclic reference systems.

$$ \text{(56)} \qquad 0.0 \text{ kcal/mol} $$

$$ \text{(57)} \qquad 3.6 \text{ kcal/mol} $$
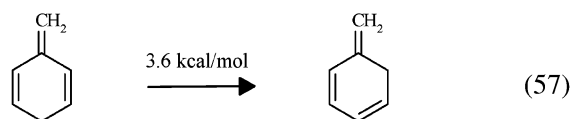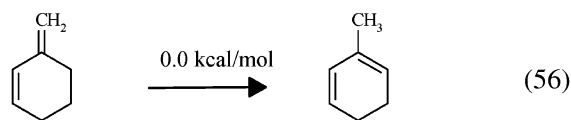
The isomerization reaction can be easily extended to systems containing heteroatoms,[199] charged species (e.g. the cyclopropenium cation),[281d] and radical systems (e.g. benzynes)[302] and polycyclic compounds.[206b,303] Figure 28 presents the isomerization
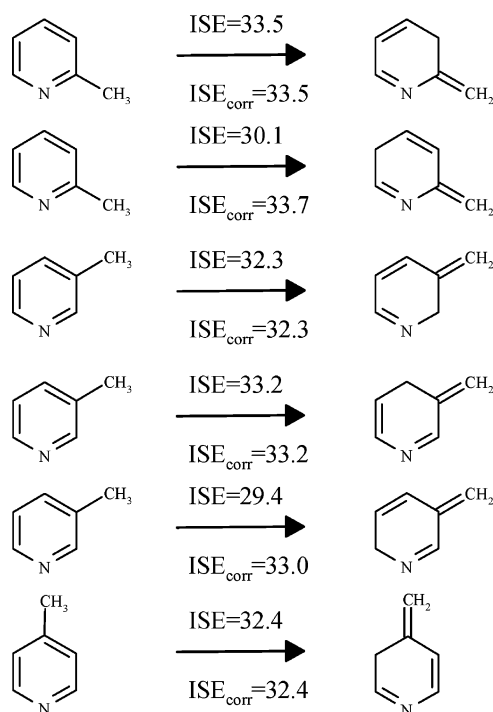
Figure 28. Application of the ISE method for pyridine.[66d]

method applied to pyridine as an example. All of the corrected values lie within 1.4 kcal/mol range and are not far from the pyridine ASE.[66d] In the case of benzenoid hydrocarbons the corrections become more critical and the estimated corrected value for naphthalene lies within 51.3−54.3 kcal/mol.[66d]

The annulenes are cyclic, fully conjugated polyenes that attract a great deal of theoretical interest concerning bond equalization/alternation (see, for example, ref 304), stability (see, for example, refs 66b−d, 273, and 305), and magnetic properties (see, for example, refs 12f, 66b−d, 136, 181, and 305d). The application of the ISE method is straightforward for both $4N$ and $4N + 2$ systems. Figure 29 presents the estimated ISE values per π-electron versus the ring size for annulenes.
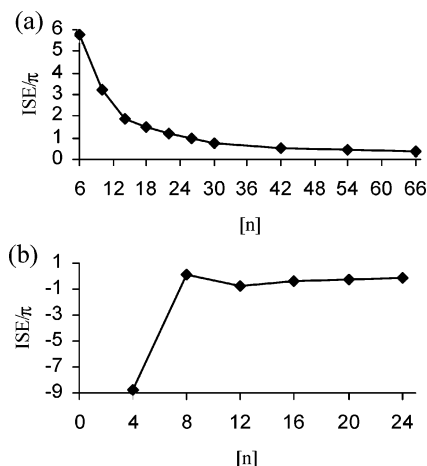
Figure 29. ISE values per π-electron versus the ring size for (a) $4N + 2$ annulenes[66c] and (b) $4N$ annulenes.[66b]

As noted by Wannere and Schleyer[66c] the estimated values agree well with those obtained by Choi and Kertesz[305a,b] based on linear polyenes. They also confirm that Dewar's π-approximation[45] largely underestimates the stabilization energies. For $4N + 2$ annulenes, the values of ISE/π exhibit progressive decrease with increasing ring size, whereas for $4N$ annulenes the trend is toward more positive values of stabilization energy. In fact, apart from cyclobutadiene, the $4N$ annulenes are not destabilized appreciably, whereas cyclooctatetraene can be considered to be essentially nonaromatic.[91,140]

The ISE method is particularly useful for evaluating the ASE of the most difficult cases: highly strained systems. For cyclophanes, Van Eis et al.[306] suggested evaluating the loss of resonance energy in highly strained cyclophanes by comparing the energy of a bent benzene ring with that of a correspondingly bent but localized cyclohexa-1,3,5-triene having imposed single and double bonds as in butadiene. However, as discussed before, such artificial localization of bonds has practically no effect on the pattern of π-electron delocalization.[142,143] In the case of the ISE method, both aromatic and reference systems have similar strain, so the estimated values are much more realistic. An old controversy dealing with the aromaticity of [5]paracyclophane[307] and 1,6-methano-[10]annulene,[308] a bridged annulene with 10 π-electrons, was effectively solved using the ISE. In the former case, the benzene fragment is stabilized by 19.5 kcal/mol, so the distortion reduces its stabilization by $\sim$12 kcal/mol. Also 1,6-methano[10]annulene is appreciably aromatic, with an ISE of approximately half the stabilization energy of naphthalene. The ISE values are listed in Figure 30.

Although the ISE method is an important step forward (in principle, the energies of just two systems are compared!), it should be pointed out that the stabilization energies of methylated derivatives are estimated in this way, and, moreover, the reaction scheme is isodesmic rather than homodesmotic. Some corrections should be made if strongly electron-accepting substituents are present.[88] Furthermore, including an sp^3-hybridized carbon atom in a ring may lead to some unbalanced strain and, in the case of smaller or ionic systems, lead to additional stabi-
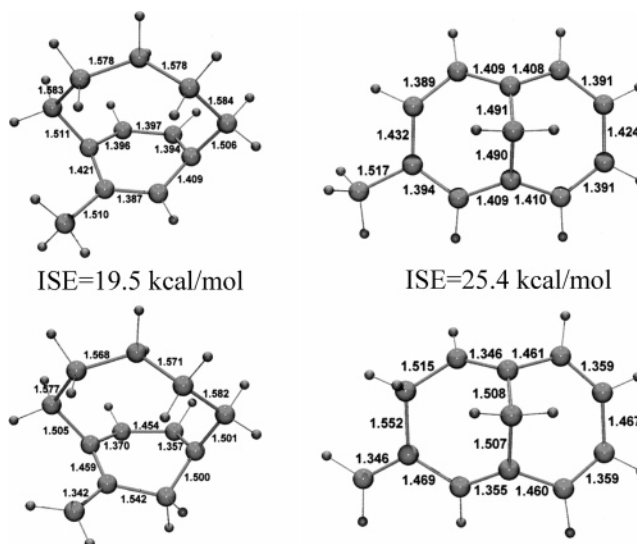
Figure 30. Aromaticity of [5]paracyclophane[66d,307] and 1,6-methano[10]annulene[66d,308] Reprinted with permission from ref 66d. Copyright 2002 American Chemical Society.

lization of a nonaromatic reference compound due to hyperconjugation effects and/or homoaromaticity.[175,309] Recently, Wannere et al.[66b] proposed a homodesmotic reaction scheme involving the addition of cyclopentadiene (see, for example, reaction 6[66b] in Table 13 — the so-called "indene—isoindene" evaluation method). Obviously the cis—trans mismatch has to be taken into account. A great advantage of this approach (as with reaction 7,[310] Table 13) is that only sp^2 carbon atoms are present in the ring in question, and its stability is assessed rather than that of the methylated derivative. Despite the fact that condensation with cyclopentadiene leads to increased strain (which, however, seems to be efficiently canceled out), good consistency with the methyl/methylene ISE method has been found for $4N$ annulenes. Figure 31 shows an appropriate dependence.
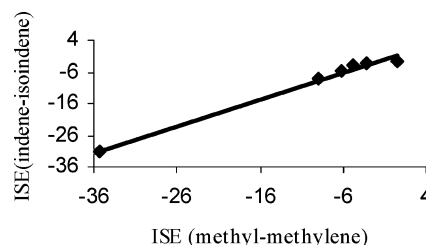
Figure 31. Dependence between ISE values derived from two models: "indene—isoindene"[66b] and "methyl—methylene"[66d] for $4N$ annulenes. Correlation coefficient $cc = 0.993$, 6 points.

4. Mono- or Multidimensional Perspective of π-Electron Delocalization Description?

To what extent are the energetic, magnetic, and geometric criteria of cyclic π-electron delocalization quantitatively related? The extent to which all of these criteria agree is a question fundamental to a proper understanding of the concept of aromaticity.[31] By the late 1980s, it was generally assumed that the various indices of aromaticity are roughly equivalent. In 1989 Katritzky et al.[290a] published an important paper concluding that, from a statistical perspective,

aromaticity is a multidimensional concept. Their analysis was followed by several reports,[79,311] using multidimensional statistics (e.g. principal component analysis and/or factor analysis),[10n,312] that two or three orthogonal factors were necessary to describe the variation in a range of aromaticity indices for many aromatic, nonaromatic, and antiaromatic systems. It is, however, fair to point out that, due to the limitations of the current methodology, these conclusions could be due to shortcomings in the currently available indices.

An assessment of cyclic π-electron delocalization usually requires comparisons with nonaromatic model compounds or is derived from the nonadditivity of some property based on data for nonaromatic reference species judged to be appropriate. However well-chosen for the purpose, such selections are arbitrary. The discussion of the methods for determining aromatic stabilization energies presented in this review clearly show the great importance of choosing an appropriate reaction scheme (and reference compounds therein) to achieve reliable results.

Schleyer et al.[282] were the first to use well-defined criteria and demonstrated for a limited set of closely structurally related monoheteropentaatomic systems that linear dependencies between the energetic, geometric, and magnetic indices exist. The extension of this analysis to polyhetero five-membered systems (over 100 systems)[31] applying well-defined criteria of aromaticity (carefully devised homodesmotic reaction for stability estimation, exaltation of magnetic susceptibility, NICS for magnetic behavior, and HOMA as a measure of bond length equalization, see Tables 17 and 18) led to the important conclusion that various manifestations of aromaticity are related to some extent and allow a rough division of conjugated cyclic compounds into three major groups: aromatic, nonaromatic, and antiaromatic. However, within any one of these three main groups the various descriptors were not strongly correlated. A similar conclusion based on carefully chosen reliable descriptors of cyclic π-electron delocalization has recently been reached for antiaromatic $4N$ annulenes[66b] and for fullerenes.[107] These three examples indicate that the phenomenon of aromaticity can be regarded as multidimensional. Obviously this is a problem for any supposedly unique description of cyclic π-electron delocalization, especially if one wants to compare very different types of systems.

In this context it seems reasonable, and careful, to consider that each quantitative definition of aromaticity represents a slightly different manifestation of π-electron delocalization. Despite personal preferences, none of these realities should be either preferred or abandoned. There are many ways to argue that some criteria are more sound than the other ones; and in particular cases, some approaches may indeed be demonstrably more efficient than others.

It is true that many relationships have been found between the various descriptors (see, for example, refs 102 and 282), which in turn has helped to clarify some chemical problems. The cases in which the descriptors do not "speak with the same voice" are still challenging! They stimulate new ideas, new experimental work, and new compounds[19] and should enforce further development of the concept. When working with the fascinating phenomenon of π-electron delocalization we should always follow this multidimensional perspective; otherwise, our knowledge may be somewhat limited.

5. Acronyms

AIM	atoms in molecules (theory)
A_J	Julg's index of aromaticity
AM1	Austin model 1 (a semiempirical method)
ASE	aromatic stabilization energy
B3LYP	Becke's three-parameter hybrid functional using the LYP (Lee−Yang−Parr) correlation functional (used in DFT method)
BE	bond energy (method)
CC	correlation coefficient
CCM	conjugated circuits model
COT	cyclooctatetraene
DFT	density functional theory
DI	delocalization index
DRE	Dewar resonance energy
ED	(gas-phase) electron diffraction
ELF	electron localization function
FLU	aromatic fluctuation index
G2	Gaussian-2 (method for computing very accurate energies)
GIAO	gauge-independent atomic orbital (method)
HF	Hartree−Fock (level of theory)
HMO	Hückel molecular orbital (theory)
HOMA	harmonic oscillator model of aromaticity
HOSE	harmonic oscillator stabilization energy
HOMO	highest occupied molecular orbital
HRE	Hückel resonance energy
HSRE	Hess−Schaad resonance energy
HSREPE	Hess−Schaad resonance energy per π-electron
I_6	Bird's index of aromaticity
ISE	isomerization stabilization energy (method)
IUPAC	International Union of Pure and Applied Chemistry
LUMO	lowest unoccupied molecular orbital
MO	molecular orbital (theory)
MP2 (3...)	Møller−Plesset perturbation theory of second (third...) order
MW	microwave spectroscopy (measurement of molecular geometry)
NICS	nucleus independent chemical shift
NMR	nuclear magnetic resonance
PDI	para-delocalization index
PM3	parametric model 3 (semiempirical method)
QMRE	quantum mechanical resonance energy
RE	resonance energy
REPE	resonance per π-electron
SI	stability index (by Ciosłowski)
θ	Matta and Hernàndez-Trujillo index aromaticity
TRE	topological resonance energy
VB	valence bond (theory)
VRE	vertical resonance energy
ZPE	zero point vibrational energy correction

6. Acknowledgments

7. References

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(279) Note that two corrections for cis−trans mismatch have to be taken into account.

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