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An Energetic Measure of Aromaticity and Antiaromaticity Based on the Pauling–Wheland Resonance Energies

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Abstract: Various criteria based on geometric, energetic, magnetic, and electronic properties are employed to delineate aromatic and antiaromatic systems. The recently proposed block-localized wave function (BLW) method evaluates the original Pauling–Wheland adiabatic resonance energy (ARE), defined as the energy difference between the real conjugated system and the corresponding virtual most stable resonance structure. The BLW-derived ARE of benzene is 57.5 kcal mol^{-1} with the 6-311+G** basis set. Kistiakowsky's historical experimental evaluation of the stabilization energy of benzene (36 kcal mol^{-1}), based on heats of hydrogenation, seriously underestimates this quantity due to the neglect of the partially counterbalancing hyperconjugative stabilization of cyclohexene, employed as the reference olefin (three times) in Kistiakowsky's evaluation. Based instead on the bond-separation-energy reaction involving ethene, which has no hyperconjugation, as well as methane and ethane, the experimental resonance energy of benzene is found to be 65.0 kcal mol^{-1}. We derived the "extra cyclic resonance energy" (ECRE) to characterize and measure the extra stabilization (aromaticity) of conjugated rings. ECRE is the difference between the AREs of a fully cyclically conjugated compound and an appropriate model with corresponding, but interrupted (acyclic) conjugation. Based on 1,3,5-hexatriene, which also has three double bonds, the ECRE of benzene is 36.7 kcal mol^{-1}, whereas based on 1,3,5,7-octatetraene, which has three diene conjugations, the ECRE of benzene is 25.7 kcal mol^{-1}. Computations on a series of aromatic, nonaromatic, and antiaromatic five-membered rings validate the BLW-computed resonance energies (ARE). ECRE data on the five-membered rings (derived from comparisons with acyclic models) correlate well with nucleus-independent chemical shift (NICS) and other quantitative aromaticity criteria. The ARE of cyclobutadiene is almost the same as butadiene but is 10.5 kcal mol^{-1} less than 1,3,5-hexatriene, which also has two diene conjugations. The instability and high reactivity of cyclobutadiene thus mainly result from the σ-frame strain and the π–π Pauli repulsion.

Keywords: ab initio calculations · aromaticity · block-localized wave function · nucleus-independent chemical shift · resonance energy

Introduction

The special properties of benzene and other aromatic compounds have spawned numerous proposals to characterize aromaticity (and antiaromaticity) based on energetic, geometric, electronic, magnetic, and other spectroscopic (IR and UV) criteria.[1–5] Rather than being "absolute", that is, unique and internal, most of these criteria rely on the selection of reference or comparison systems. These choices are arbitrary, however appropriate they may seem (or have seemed) to be. Although "aromaticity" is a virtual (not directly measurable) quantity, its usefulness as a central chemical concept is undiminished after two centuries. Aromaticity is currently enjoying a renaissance of interest, as its scope of application is far wider than has been appreciated formerly.[6] The nucleus-independent chemical shift (NICS) measure of aromaticity and antiaromaticity is based on chemical shieldings computed in or above ring centers; it does not rely on any other references, and thus provides a benchmark for the evaluation of other criteria.[5]

Abnormal energies govern the chemical behavior of aromatic compounds, which are more stable thermodynamically than "they ought to be". The purpose of the current paper is to present a quantum mechanical method that evaluates the

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"extra" stabilization energies of more conventional aromatic compounds "absolutely" (without recourse to reference molecules). As a consequence, the resonance energy, like NICS value, becomes an internal and unique property of a system. In contrast, the various isodesmic and homodesmotic model reactions,[7,8] employed over the last 70 years to estimate "aromatic energies", have given widely divergent results. The values of some of these evaluations have become entrenched through tradition and familiarity (e.g., in textbooks), even though major flaws in the reasoning are apparent today. Our current understanding of bonding is much more sophisticated than it was decades ago. The intrusion of other effects in the reference systems, such as strain, hyperconjugation, Coulomb repulsion imbalance (especially in charged systems), and uncompensated van der Waals attractions compromises traditional energetic evaluations seriously, if not fatally.[9–11] Examples for benzene are given below and the subject will be discussed in much more detail in a subsequent paper,[11] intended to reconcile the discrepancies in the various evaluations and explain their origin.

As has been pointed out many times, the range of stabilization energy estimates for benzene in the literature is very large,[12–22] due to the variation in the metrics and whether RE, the total resonance energy, or ASE, the extra "aromatic" stabilization energy (greater than the stabilization solely due to conjugation) is being evaluated. The best reference system for aromaticity evaluation would be a virtual, noninteracting (in terms of orbital mixing) version of the molecule itself. According to the original definition of Pauling and Wheland,[12,23–26] the resonance energy is "obtained by subtracting the actual energy of the molecule in question from that of the most stable contributing structure."[25] The Pauling–Wheland resonance energy (RE) therefore is always positive, no matter whether in aromatic or antiaromatic systems. However, the REs of conjugated, nonaromatic reference molecules may be greater than the REs of antiaromatic systems. Hence, the ASEs of the latter may be negative, denoting destabilization relative to the reference models. Similarly, the ASEs of aromatic compounds are considerably less than their REs. To probe the aromaticity and antiaromaticity of conjugated rings, we propose an energy, called the "extra cyclic resonance energy" (ECRE), defined as the difference between the resonance energies of a cyclic conjugated compound and an acyclic polyene either with the same number of double bonds[27] or with the same number of diene conjugations.[14,28] Both these conventions have been employed here. Thus, a positive ECRE measures the magnitude of the aromaticity in a system while a negative ECRE corresponds to an antiaromatic system. The ECREs of nonaromatic systems should be around zero. When based on the same number of double bonds, the ECRE criterion is close in concept to the "isomerization method",[29] which evaluates the energy difference between the energy of a nonaromatic isomer of the aromatic system (e.g., isotoluene) and the aromatic itself (e.g., toluene). Note that open-chain polyenes were similarly employed as reference structures by Dewar and co-workers as well as by Hess and Schaad to deduce the resonance energy of a hypothetical fully conjugated, but not aromatic, comparison model (for example, a virtual conjugated, but nonaromatic cyclohexatriene).[14,28,30] Likewise, we use open-chain polyenes to quantify the extra resonance capability of a fully conjugated ring, whose total resonance energy is computed with reference to its most stable resonance contributor. However, the reference open-chain polyene model for a cyclic ring can either have the same number of π electrons (double bonds)[27] or the same number of conjugated diene moieties.[14,28] As it has been shown that the latter model is an improvement over the former,[28] we compute ECREs with both sets of references (and denote them ECRE1 and ECRE2, respectively).

Unlike previous empirical and semiempirical work, our computation of the Pauling–Wheland resonance energy and ECRE employs a variation of ab initio valence bond (VB) methods, where each resonance structure is represented by a Heitler–London–Slater–Pauling (HLSP) wave function. Ab initio VB theory has been rejuvenated in the past two decades,[17,19,31,32] even though its further broad application will require a significant reduction in its computational demands. Alternatively, the recently proposed block-localized wave function method (BLW) preserves the characteristics and advantages of both the VB and molecular orbital (MO) theories,[33–37] and thus provides a practical means to compute the conventional Pauling–Wheland resonance energy. We now employ the BLW method to examine the energetic and geometric consequences of electron delocalization in aromatic as well as antiaromatic systems. We also demonstrate that the ECRE and NICS of a series of monohetero five-membered ring systems correlate well.

Results and Discussion

Methods

The concept of resonance was introduced to rationalize the behavior of molecules when a single Lewis structure (or resonance contributor) did not account for the geometries, energies, and other properties satisfactorily.[23,26] As a set of resonance structures are required to describe such systems, typically those with delocalized π electrons, the resonance energy was defined as the energy difference between the real molecule and the corresponding major resonance contributor. Pauling and Wheland developed an empirical approach to derive the Hamiltonian matrix elements among resonance structures and used this to solve the secular equation and to derive the resonance energy.[12] Quantitatively, however, each resonance structure K for a system of $2n$ electrons can be expressed by an HLSP function (Φ_K) as shown in Equation (1):

$$\Phi_K = N_K \hat{A}(\varphi_{1,2}\varphi_{3,4}\ldots\varphi_{2n-1,2n}) \tag{1}$$

in which N_K is the normalization constant, $\hat{A}$ is the antisymmetrizer, and $\varphi_{i,j}$ is simply a bond function corresponding to the bond between orbitals χ_i and χ_j, as shown in Equation (2):

$$\varphi_{i,j} = \hat{A}\{\chi_i\chi_j[\alpha(i)\beta(j) - \beta(i)\alpha(j)]\} \qquad (2)$$

in which α and β are electron spin functions. Clearly, each HLSP function can be expanded into 2^n Slater determinants. Classical ab initio VB, in which pure atomic orbitals were used as one-electron orbitals to construct HLSP functions, applied to all of the possible 175 resonance structures of benzene by Norbeck et al.[38] and by Tantardini et al.[15] gave an illogical result: the five covalent Kekulé and Dewar structures contributed less to the ground state of benzene than the remaining 170 ionic structures. In contrast, modern ab initio VB theory allows orbitals to be optimized flexibly.[32,39] Cooper et al. found that five covalent benzene contributors recover almost all the electron correlation energy.[17] However, in order to derive the wave function for a hypothetical localized 1,3,5-cyclohexatriene it is desirable to expand the bond functions in Equation (2) only in the basis space of the two bonded atoms.[40] When this is done, the three localized 1,3,5-cyclohexatriene double bonds do not mix and only interact in terms of electrostatic and Pauli exchange forms and thus should be comparable to the double bond of ethene.[19]

To simplify the manipulation of HLSP functions, the bond functions are often represented by doubly occupied MO-like localized orbitals.[41] Thereby, VB functions [such as Equation (1)] are reduced to a single Slater determinant, but the bond orbitals are nonorthogonal. This form of wave function was later adopted by Kollmar[42] and Daudey et al.[43] to study the effects of conjugation and hyperconjugation. In their treatment of conjugated systems such as benzene and butadiene, the π MOs in the Hartree–Fock (HF) wave function were replaced by ethylenic π MOs derived from calculations of ethene with the same basis set, neglecting the polarization both of the ethylenic π MOs and of the σ frame. The change in energy due to the orbital switch is used to characterize the resonance strength. Jug and his coworkers also developed a similar strategy at a semiempirical level.[20]

We extended and generalized the idea of localized bond functions recently and proposed the BLW (block-localized wave function) method,[33–37] in which all electrons and primitive basis functions are partitioned into several subgroups and each block-localized orbital is expanded in only one subgroup. The orbitals belonging to the same subgroup are constrained to be mutually orthogonal like conventional MO methods, while those belonging to different subgroups are free to overlap like VB methods. The final block-localized wave function at the HF level is expressed by a Slater determinant. Consequently, the energy difference between the HF wave function, where all electrons are free to delocalize in the whole system, and the block-localized wave function, where electrons are confined to specific zones of the system, can be defined generally as the electron delocalization energy. The BLW method is a generalization of our previously proposed orbital deletion procedure (ODP).[44] The self-consistent optimization of the block-localized orbitals in the BLW can be accomplished by using successive Jacobi rotations, as we adopted initially,[33] or by using the algorithm of Gianinetti et al.[45] Significantly, Gianinetti et al. demonstrated that the self-consistent-field solution of a wave function (as with BLW) can be decomposed to coupled Roothaan-like equations, each of which corresponds to a block.

The consequences are important. The computational cost of the BLW method is reduced and becomes comparable to HF. As the first derivative of the energy with respect to nuclear coordinates can take the form as in regular HF theory directly, the second derivatives can then be computed numerically. We recently implemented the algorithm of Gianinetti et al. into our BLW code on GAMESS,[46] in order to have the capability of geometrical optimizations.[35]

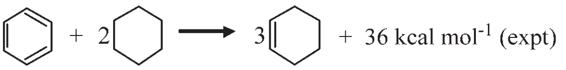
Depending on the geometries employed, two types of resonance energies can be differentiated. The vertical resonance energy (VRE, or quantum mechanical resonance energy)[18,47] is the energy difference between the optimal ground state and its most stable resonance contributor at the same geometry. What we call the adiabatic resonance energy (ARE) is the energy difference between the optimal ground state and the optimal resonance structure, that is, both geometries are relaxed. The difference between VRE and ARE reflects the compression energy for the σ frame.

The current BLW method was implemented at the HF level where electron correlation effects are not considered. Although the extension of the BLW method to the DFT level should be straightforward, electron correlation was not expected to influence the estimation of resonance energy (RE) appreciably. As the RE is a relative quantity, electron correlation contributions to RE in both delocalized and localized states tend to cancel. This can be demonstrated by the allyl ions ($C_3H_5^+$ and $C_3H_5^-$). Both the BLW and the ab initio VB calculations in which electron correlations were taken into account resulted in very similar REs.[33,37,48] The computations reported here were carried out at the HF/6-311+G** level. The experimental heats of formation were taken from the latest NIST compilation.[49]

Resonance in benzene

There are myriad experimental and computational evaluations of the resonance of benzene as well as studies of the consequences.[16,42,50,51] Cyclohexatriene structures (usually attributed incorrectly to Kekulé as an equilibrating pair)[52] are now regarded as the principal resonance contributors,[23,26] but ab initio VB calculations have revealed the additional importance of Dewar (cross ring) and ionic resonance structures.[15,17,19,38] Similarly, analysis with the natural resonance theory (NRT) gave Kekulé and Dewar resonance weights of 58.8 and 7.7%, respectively.[51] The elusiveness of

1,3,5-cyclohexatriene requires energetic evaluations of the benzene resonance to be based on other reference molecules. Kistiakowsky[53] first determined the resonance energy of benzene experimentally to be 36 kcal mol^{-1} by comparing its heat of hydrogenation with that of cyclohexene [shown in Figure 1 and summarized by the isodesmic Equation (3)].



(3)

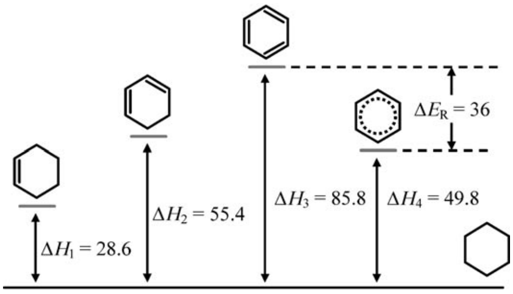


Figure 1. Hydrogenation heats and the experimental resonance energy (ΔE_R) for benzene (all values in kcal mol^{-1}).

Table 1. Optimal structural parameters (bond lengths [Å] and bond angles [°]) of benzene, cyclobutadiene, all-*trans*-1,3,5-hexatriene, and *trans*- and *cis*-1,3-butadiene with the 6-311+G(d,p) basis set. Vertical (E_{VR}) and adiabatic (E_{AR}) resonance energies (see text) are in kcal mol^{-1}.

Molecule	Structural parameters				E_{VR}	E_{AR}	$E_{VR}-E_{AR}$
	$R(C_1C_2)$	$R(C_2C_3)$	$\angle H_1C_1C_2$				
benzene	1.386	1.386	120.0		91.6	57.5	34.8
1,3,5-cyclohexatriene	1.314	1.522	121.6				
cyclobutadiene	1.320	1.565	135.1		10.9	10.3	0.6
localized form of C_4H_4	1.317	1.595	135.4				
	$R(C_1C_2)$	$R(C_2C_3)$	$R(C_3C_4)$				
trans-1,3,5-hexatriene	1.324	1.463	1.329		23.5	20.8	2.7
localized form of C_6H_8	1.316	1.517	1.312				
	$R(C_1C_2)$	$R(C_2C_3)$	$R(C_3C_4)$	$R(C_4C_5)$			
trans-1,3,5,7-octatetraene	1.325	1.463	1.330	1.459	36.2	31.8	4.4
localized form of C_8H_{10}	1.315	1.517	1.312	1.518			
	$R(C_1C_2)$	$R(C_2C_3)$					
trans-butadiene	1.323	1.468			11.0	9.9	1.1
localized form of *trans*-C_4H_6	1.316	1.517					
cis-butadiene	1.323	1.480			10.0	9.1	0.9
localized form of *cis*-C_4H_6	1.315	1.529					

Although this historically important result and method of evaluation are still widely quoted and employed, both suffer from the major flaw of having considerable hyperconjugation imbalance.[54] (Kistiakowsky could not have appreciated this at the time, as Mulliken's seminal paper on hyperconjugation was published in 1941.[54b] Mulliken's estimate of the benzene resonance energy was 74.4 kcal mol^{-1}, based both on his computations and his treatment of experimental data based on bond energies.) Each cyclohexene is stabilized hyperconjugatively by the two methylene groups attached to the double bond, but this large effect is not compensated on the left side of Equation (3). This effect is shown directly by Equation (4), which is based on the hyperconjugation-free ethene rather than on cyclohexene:

$$\begin{aligned}&\text{benzene} + 3\,\text{ethane} \rightarrow \text{cyclohexane}\\&+3\,\text{ethene} + 49.5\ \text{kcal mol}^{-1}\ \text{(expt)}\end{aligned} \tag{4}$$

Consequently, the "historical" resonance stabilization energy of benzene is underestimated by 13.5 kcal mol^{-1} based on the energy difference between Equations (3) and (4), or by 29 kcal mol^{-1} based on Equation (5) (see below). In Equation (3), the aromatic stabilization of benzene is partly counterbalanced by the hyperconjugative stabilization[29] due to the six interactions present in the three cyclohexene reference molecules. However, Equation (4) is not ideal either, as attractive van der Waals 1,3-interactions stabilize cyclohexane substantially,[11] and these have no counterpart on the left side of the equation. Pople's "bond separation energy (BSE)"[8] evaluation [Eq. (5)] overcomes this problem, but is imbalanced with regard to the bond types on the left and right sides.

$$\begin{aligned}&\text{benzene} + 6\,\text{methane} \rightarrow 3\,\text{ethane} + 3\,\text{ethene}\\&+65.0\ \text{kcal mol}^{-1}\ \text{(expt, 298 K)}\end{aligned} \tag{5}$$

While this further "homodesmotic" complication is not serious, it is quite clear from Equations (3), (4), and (5) that the unambiguous estimation of the experimental resonance energy of benzene is fraught with difficulties.

We now find that the energy required to completely localize the three double bonds in benzene by inactivating their π conjugation not only is remarkably large (57.5 kcal mol^{-1}, see Table 1) but approaches the Pople BSE value, based on experimental data [65.0 kcal mol^{-1}, Eq. (5)]. Our direct evaluation of the total π conjugation effect in benzene began by optimizing the geometry of the hypothetical noninteracting (localized) 1,3,5-cyclohexatriene with the BLW method (Figure 2). Table 1 compares the optimal geometries of delocalized benzene and localized 1,3,5-cyclohexatriene as well as the VRE and ARE (resonance energies). Note that the VRE is very close to the value obtained by Shaik et al. (85.2 kcal mol^{-1} with the 6-31G basis set[55a]) based on Kollmar's approach;[42] Shaik et al. reported an ARE of about 65 kcal mol^{-1}. (An identical "quasiexperimental" value had been deduced much earlier by Hornig in 1952.[55b]) Shaik's

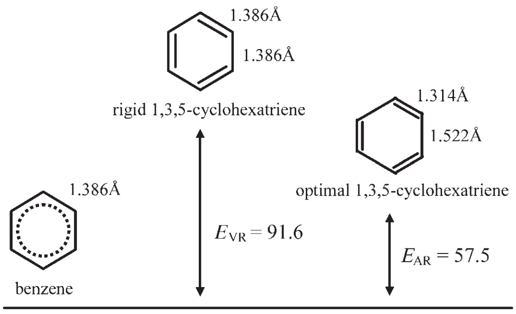


Figure 2. Vertical resonance energy (E_{VR}) and adiabatic resonance energy (E_{AR}) in the case of benzene (computed with the 6-311+G(d,p) basis set; values in kcal mol^{-1}).

value is actually based on an approximation of the current BLW method since the relaxation (or polarization) of the ethylenic π MOs and of the σ frame in Kollmar's method was not considered. The usual HF optimizations of fully delocalized benzene result in CC bond lengths (1.386 Å) only slightly shorter than experiment (1.399 Å). In contrast, the CC double-bond lengths in the optimal BLW localized 1,3,5-cyclohexatriene structure are essentially the same as in ethene [1.319 Å at the HF/6-311+G(d,p) level], whereas the single Csp^2–Csp^2 bond lengths (1.522 Å) are only slightly shorter than the Csp^3–Csp^3 bond lengths in ethane (1.526 Å). The similarity between the Csp^2–Csp^2 and Csp^3–Csp^3 single-bond lengths implies that the carbon hybridization only influences bond lengths modestly, as evidenced by the small variation (within 3.2 %) of the experimental C–H bond lengths in ethane (1.096 Å), ethene (1.085 Å), and ethyne (1.061 Å).[56] In other words, large variations of the C–C single-bond lengths in organic molecules are due mostly to other factors such as electron delocalization, steric repulsion, and so forth, rather than to carbon hybridization.[40]

The strong stabilization of benzene by π delocalization (57.5 kcal mol^{-1}, Figure 2) lengthens the double bonds by 0.07 Å and shortens the single bonds by 0.14 Å. The difference between VRE and ARE ($E_d = 34.8$ kcal mol^{-1}), the σ-compression energy, reflects the energy required to distort the optimal geometry of the benzene ring with a localized wave function and alternating bond lengths to the geometry with equal bond lengths (while maintaining the π-electron localization). Our results for this σ-compression energy (Table 1) are in accord with earlier estimates (30 kcal mol^{-1}).[26,47] Recently, van Lenthe and co-workers[21] employed an ab initio valence-bond method and the 6-31G basis set to deduce the geometry and energy of localized 1,3,5-cyclohexatriene. Their 1.433 and 1.369 Å bond lengths, however, do not agree with our BLW results (Table 1). The discrepancy results from the definition of bonding orbitals χ_i and χ_j in Equation (2). Van Lenthe et al. adopted atomic orbitals for χ_i and χ_j, a treatment similar to the classical VB method. Our BLW bond functions are built with bond-distorted orbitals (BDOs),[40] as such bond functions correspond more closely to real bonds. As BDOs, both χ_i and χ_j are expanded with atomic orbitals centered on the two bonding atoms instead of only on one atom, as in Van Lenthe's treatment.

Annulated benzenes with alternating bond lengths, in which conjugation is alleged to be inhibited by the strain or the electronic interactions of the pendant rings, have been proposed to simulate 1,3,5-cyclohexatriene.[57–59] Beckhaus et al. reported that the strain-corrected heat of hydrogenation of a benzannulated species ([4]phenylene) with a cyclohexatriene-like geometry was nearly the same as that of three cyclohexenes.[60] As discussed below, this was evidently due to the absence of antiaromatic cyclobutadiene character in the substituents. In contrast, computational studies of deformed benzenes, for example, with substantial alternation of the bond lengths, have not revealed any such appreciable decrease in the cyclic electron delocalization.[19,59,61,62] It is apparent that virtual (but interacting with orbital mixing) 1,3,5-cyclohexatriene (with bond-length alternation) would be nearly as aromatic as the real benzene. Instead of being the aromatic paradigm, benzene is the exception among all other benzenoid hydrocarbons, none of which have equal CC bond lengths. Shaik and Hiberty have stressed repeatedly that the σ framework is responsible for the equal CC bond lengths of benzene, and overcomes the π-system preference for bond alternation.[18,50,61] This is illustrated by naphthalene,[63] which has rather substantial CC bond-length differences (ca. 0.07 Å), despite the same σ preference for (very nearly) equal bond lengths, as are found in decalin. If naphthalene is computed by imposing all equal CC bond lengths and CCC angles set to the benzene values, its energy clearly must be higher than that of fully relaxed naphthalene (by 3.1 kcal mol^{-1} at B3LYP/6-31G*). Unlike benzene, the distortive tendency of the π electrons (apart from their delocalization stability) in naphthalene dominates the geometry.

Our data indicate that the energy required to completely localize the three double bonds in benzene by inactivating their π conjugation is remarkably large (57.5 kcal mol^{-1}). Whereas the optimal geometry is achieved by the electron localization alone, there is considerable residual resonance interaction in annulated benzenes with CC bond-length alternation. The residual conjugation energy (VRE) at the optimal geometry of localized 1,3,5-cyclohexatriene with 1.314 and 1.522 Å alternating CC bond lengths is 40.2 kcal mol^{-1}, 44 % of the VRE at the bond-equivalent geometry! The behavior of tris(benzocyclobutadieno)benzene[60] as well as tris(bicyclo[2.1.1]hexeno)benzene[58] evidently originates from the inhibition of conjugation in order to avoid benzocyclobutadiene-like antiaromaticity or to reduce the strain of the benzannulated groups.

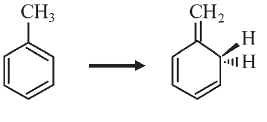
The extra aromatic stabilization due to the cyclic electron delocalization of benzene is based on comparisons of its conjugation energy with the stabilization of comparably conjugated, but nonaromatic models. The acyclic triene, 1,3,5-hexatriene, is the simplest possibility. As with benzene, we optimized both the delocalized (fully relaxed) and strictly localized structures (also listed in Table 1). The double-bond lengths in the optimal localized structure are close to the localized benzene value as well as to the ethene CC distance. As in localized benzene, the single-bond lengths of the localized triene are approximately 1.52 Å. Full optimization of the acyclic triene lengthens the double bonds by only 0.01 Å and shortens the single bonds by 0.05 Å. These changes are much smaller than those in benzene and reflect the much lower (36.7 kcal mol^{-1}) resonance energy in 1,3,5-hexatriene ($E_{AR}=20.8$ kcal mol^{-1}) than in benzene ($E_{AR}=57.5$ kcal mol^{-1}). Our computed E_{AR} for *trans*-1,3,5-hexatriene is comparable to the hydrogenation heat difference (17.7 kcal mol^{-1}) between *trans*-1,3,5-hexatriene and ethene (three times), but somewhat smaller than the experimental resonance energy (28.5 kcal mol^{-1}) based on the BSE Equation (6a), which is subject to downward homodesmotic corrections of 5 ± 2 kcal mol^{-1}.

$$\begin{array}{l}\textit{trans}\text{-1,3,5-hexatriene} + 4\,\text{methane} \rightarrow \\ 2\,\text{ethane} + 3\,\text{ethene} + 28.5\,\text{kcal mol}^{-1}\ \text{(expt)}\end{array} \quad (6a)$$

$$\begin{array}{l}1,\textit{cis}\text{-},3,5\text{-hexatriene} + 4\,\text{methane} \rightarrow \\ 2\,\text{ethane} + 3\,\text{ethene} + 27.5\,\text{kcal mol}^{-1}\ \text{(expt)}\end{array} \quad (6b)$$

Our computed 36.7 kcal mol^{-1} difference between the ARE of benzene and that of 1,3,5-hexatriene quantifies the enhanced resonance stabilization (ECRE1) of benzene attributable to the cyclic π-electron delocalization. This ECRE1 is larger than the experimental ASE (27.6 kcal mol^{-1}) based on the difference between the experimental RE of benzene [65.0 kcal mol^{-1}, Eq. (5)] and the RE of 1,*cis*-3-5-hexatriene [27.5 kcal mol^{-1}, Eq. (6b)]. But the latter triene has two *anti*-diene conformations, which are each 3.5 kcal mol^{-1} more stable than the *syn* conformations,[29] as are present in benzene. When corrected by 7 kcal mol^{-1}, the Equation (6b) result agrees with our ECRE1 value quite well.

A recently proposed "isomerization energy" evaluation method was based on the energy differences between cyclically delocalized and merely conjugated isomers, and does take the *anti*/*syn* diene difference into account.[29] Thus, the isomerization reaction [Eq. (7)] estimates a 33.2 kcal mol^{-1} aromatic stabilization energy of benzene (when adjusted by small corrections, see ref. [29]); this ASE is very close to the ECRE1 value for six π-electron comparisons.

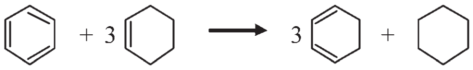


+ 33.2 kcal mol^{-1} (7)

However, 1,3,5-hexatriene has only two diene conjugations (each involving a central single bond) compared with three in the virtual cyclohexatriene motif. Thus, a better BLW reference for benzene is 1,3,5,7-octatetraene having three conjugated diene moieties. Geometrical parameters for the delocalized and strictly localized C_8H_{10} are listed in Table 1. Based on 1,3,5,7-octatetraene, ECRE2 of benzene (the ASE value) is 25.7 kcal mol^{-1}.

The aromatic stabilization energy (ASE) of benzene measures its "extra stabilization" in excess of the RE of analogous conjugated systems. The latter, as well as other reference compounds, must be chosen well to balance perturbing energy influences to the greatest possible extent. Numerous isodesmic and homodesmotic reactions have been proposed to compute the ASE of benzene.[29] Equation (8) gives 28.8 kcal mol^{-1} (expt), which is close to the ECRE2 estimate above (25.7 kcal mol^{-1}).

We have argued that Equation (8) is superior to many other alternatives for several reasons.[29] There are three conjugated diene moieties each with a single bond on both sides of the equation. Strain and hyperconjugation are balanced. Cyclohexene and 1,3-cyclohexadiene have two hyperconjugation interactions each. Furthermore, the cyclic reference molecules, 1,3-cyclohexadiene, cyclohexene, and cyclohexane in Equation (8), are clearly much more closely related to benzene structurally than acyclic models. *Syn*-diene conformations are present in the rings, while conjugated acyclic polyene favors *anti* conformations.[29] Of course, Equation (8), like all equations devised to evaluate the virtual "resonance energies" from experimental (or comparable computational) data, is not free from other flaws.



+ 28.8 kcal mol^{-1} (expt) (8)

Nevertheless, the RE of benzene can be derived from the ASE of Equation (8) by taking the conjugation energy of 1,3-cyclohexadiene into account. We computed its E_{AR} to be 9.6 kcal mol^{-1} by using the BLW method. By using this value to adjust Equation (8), the resonance energy of benzene is 57.6 kcal mol^{-1}, which is in remarkable agreement with the 57.5 kcal mol^{-1} E_{AR} value. BLW computations on *syn*-butadiene (C_{2v}) result in $E_{AR}=9.1$ kcal mol^{-1}, slightly smaller than the 9.9 kcal mol^{-1} *anti*-butadiene (C_{2h}) E_{AR} value (Table 1).

Resonance in cyclobutadiene

Singlet cyclobutadiene, whose ground state has rectangular (D_{2h}) symmetry, has long been regarded as the antiaromatic paradigm,[3,4,16,19,22,64,65] but its extraordinary instability [as indicated by Eq. (9)] is not representative of 4*n* π-electron systems generally.[66]

$$\begin{array}{l}2\,\text{cyclobutene} \rightarrow \text{cyclobutadiene} + \text{cyclobutane} \\ +35\,\text{kcal mol}^{-1}\end{array} \quad (9)$$

Note that the low-lying cyclobutadiene triplet has square (D_{4h}) symmetry and is aromatic.[67] Cyclobutadiene also brings out the rivalry between MO and VB theories.[68] Structural parameters from both HF and BLW geometry optimizations are listed in Table 1. The VRE of rectangular cyclobutadiene is quite small compared with benzene. For the square (D_{4h}) singlet structure, Voter and Goddard derived a resonance energy of about 21 kcal mol^{-1} based on the resonating GVB approach. While the resonance energy in benzene decreases slowly upon the change of geometry from D_{6h} to D_{3h} symmetry, it decays quickly in cyclobutadiene from D_{4h} to D_{2h}.[19,61,69] Further BLW optimizations with π-bond localization change neither the geometry nor the energy of the D_{2h} ground state of cyclobutadiene remarkably. According to these BLW calculations, deactivation of the resonance effect destabilizes cyclobutadiene by only about 10 kcal mol^{-1}; this value is very close to that of its acyclic reference 1,3-butadiene (Table 1). Hence, the ECRE1 of D_{2h} cyclobutadiene is close to zero, indicating that cyclobutadiene is nonaromatic based on this four π-electron comparison. However, based on *trans*-1,3,5-hexatriene, which also has two diene conjugations (two single bonds between the double bonds), the ECRE2 of cyclobutadiene is −10.5 kcal mol^{-1}, suggesting significant π antiaromatic character. Note that this decreased stabilization relative to a conjugated system is much less than the conventional evaluations. As a consequence, the thermochemical instability and high reactivity of cyclobutadiene comes mainly from the σ-frame strain[70] as well as from the π–π Pauli repulsion.[61,71] According to the Hückel theory, the π electronic energy of cyclobutadiene is two times that of ethene; thus, the resonance energy is zero and cyclobutadiene is a nonaromatic system. Note that the computed ARE of *trans*-butadiene (9.9 kcal mol^{-1}; 9.1 kcal mol^{-1} for *cis*-butadiene, see Table 1) is comparable to the experimental conjugation energy of 8.5 kcal mol^{-1}, which is the difference between the hydrogenation heats of two moles of ethene and one mole of *trans*-butadiene.[54] Instead of the conventional interpretation of cyclobutadiene as the antiaromatic paradigm, it should be regarded as a unique molecule. Compared with the bond equivalent D_{4h} geometry, the D_{2h} singlet-state geometry does not result from π distortivity alone or lack of resonance stabilization.[61,69,72]

Deniz et al. determined the enthalpy of formation of cyclobutadiene as 114 ± 11 kcal mol^{-1} and estimated that the cyclobutadiene is destabilized by 87 ± 11 kcal mol^{-1} compared with a virtual reference structure based on four strain-free and unconjugated CH units.[65] After subtracting the estimated strain energy, 32 ± 2 kcal mol^{-1},[16] Deniz et al. concluded that the remaining 55 kcal mol^{-1} is due to the antiaromaticity. Our evaluation is very different quantitatively; ECRE2 indicates that cyclobutadiene has only a modestly antiaromatic π system: the resonance stabilization of cyclobutadiene is only 10 kcal mol^{-1} less than 1,3,5-hexatriene. Thus, most of Deniz's 55 kcal mol^{-1} destabilization energy most probably arises from the Pauli repulsion between the two double bonds[71] and the σ antiaromaticity of the four CC ring single bonds.[70] The large interactions between two parallel hydrogen molecules (optimal bond length 0.7435 Å) support this argument. If these are placed 1.5 Å apart to form rectangular $(H_2)_2$, the destabilization energy is 32.9 kcal mol^{-1} at the CCSD(T)/6-311++G(d,p) level. If the intermolecular distance is reduced to 1.33 Å, the repulsion becomes 54.9 kcal mol^{-1}. Wu et al. used a VBDFT approximation to evaluate the π–π Pauli repulsion in cyclobutadiene as 25 kcal mol^{-1}.[73] Note that the two single CC bonds in D_{2h} cyclobutadiene are parallel and are separated by only 1.33 Å; much less than the 1.577 Å separation of the two double bonds. This should result in substantial σ–σ and π–π Pauli repulsion, as in our $(H_2)_2$ example. None of the reference molecules (like cyclobutene) commonly used to model the ring strain of cyclobutadiene have parallel CC bonds separated by only 1.33 Å. They thus drastically undercompensate for the ring strain of cyclobutadiene [e.g., Equation (9)].

The NICS(0) value in the center of cyclobutadiene is +20.8 ppm.[74] This large positive value at first glance suggests cyclobutadiene is very antiaromatic. However, dissected NICS analyses, based on the contribution of individual localized MOs, showed that the π contribution to NICS is close to zero and the large paratropic NICS(0) value comes from the σ antiaromaticity of the four-membered ring.[70] More refined NICS analyses, based on tensor contributions, reveal a more complex picture. Details will be presented in a subsequent paper, which will also analyze the factors (mentioned above) contributing to the high energy of cyclobutadiene.

Resonance in five-membered rings

The systematic exploration of the characteristics and driving force for aromaticity and antiaromaticity is best carried out systematically on sets of closely related molecules with similar structures, but with properties ranging widely from highly aromatic to highly antiaromatic.[2,10,75–78] Five-membered-ring diene derivatives, whose ring strain should be nearly the same, were first employed in 1995 for this purpose by Schleyer, Freeman, Jiao, and Goldfuss.[75] Their comparisons of various aromaticity measures (the Julg geometric indexes, ASEs, and magnetic susceptibility exaltations) showed excellent correlation values (cc = 0.99).[75] Since then, this benchmark approach has been used frequently to evaluate other aromaticity criteria, including NICS,[79] proton chemical shifts,[77] and delocalization indexes.[78] In this work, we studied the resonance effect in twelve representative monohetero five-membered ring systems, C_4H_4X (X = AlH, BH, CH^+, CH^-, CH_2, NH, O, PH, S, SiH^+, SiH^-, SiH_2). This set of rings comprises very aromatic, aromatic, nonaromatic, and antiaromatic, neutral, positively, and negatively charged systems. The ECRE definitions of the rings as well as their linear counterparts are illustrated in Figure 3.

Criteria based on CC bond lengths afforded early aromaticity measures, as cyclic electron delocalization increases the degree of bond-length equalization.[4,75] The BLW-optimized geometries provide a direct measure of the structural

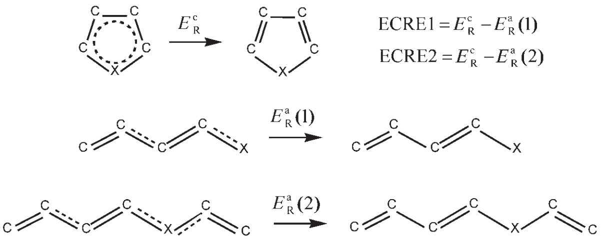


Figure 3. Definition of the resonance energies of five-membered rings and their acyclic counterparts, for which the difference between the two is defined as the extra cyclic resonance energy (ECRE). X = AlH, BH, CH^+, CH^-, CH_2, NH, O, PH, S, SiH^+, SiH^-, SiH_2.

Table 2. Optimal bond lengths [Å] for the delocalized (HF) and localized (BLW) five-membered rings C_4XH_4 with the 6-311+G(d,p) basis set.

X	HF			BLW		
	R(X−C)	R(C=C)	R(C−C)	R(X−C)	R(C=C)	R(C−C)
AlH	1.955	1.336	1.508	1.965	1.327	1.553
BH	1.587	1.329	1.514	1.603	1.322	1.549
CH^+	1.448	1.331	1.549	1.510	1.317	1.544
CH^-	1.405	1.406	1.405	1.533	1.325	1.547
CH_2	1.505	1.329	1.477	1.547	1.314	1.539
NH	1.363	1.359	1.428	1.453	1.311	1.539
O	1.342	1.340	1.442	1.420	1.305	1.537
PH	1.717	1.374	1.422	1.849	1.314	1.537
S	1.724	1.346	1.437	1.828	1.309	1.528
SiH^+	1.815	1.334	1.523	1.850	1.324	1.550
SiH^-	1.784	1.406	1.407	1.940	1.320	1.539
SiH_2	1.876	1.332	1.494	1.899	1.321	1.544

Table 3. Vertical and adiabatic resonance energies [kcal mol^{-1}] of five-membered rings C_4XH_4 and their acyclic systems, $CH_2{=}CH{-}CH{=}CH{-}XH$ and $CH_2{=}CH{-}CH{=}CH{-}X{-}CH{=}CH_2$, with the 6-311+G(d,p) basis set.

X	C_4XH_4			$CH_2{=}CH{-}CH{=}CH{-}XH$			$CH_2{=}CH{-}CH{=}CH{-}X{-}CH{=}CH_2$		
	E_{VR}	E_{AR}	$E_{VR}-E_{AR}$	E_{VR}	E_{AR}	$E_{VR}-E_{AR}$	E_{VR}	E_{AR}	$E_{VR}-E_{AR}$
AlH	12.8	11.9	0.9	14.4	13.0	1.4	16.7	15.4	1.3
BH	15.6	14.9	0.7	19.5	17.6	1.9	25.1	23.1	2.0
CH^+	39.8	36.3	3.5	82.4	64.5	17.9	84.3	71.7	12.5
CH^-	134.2	104.2	30.0	83.1	61.4	21.7	102.6	85.1	17.5
CH_2	26.5	23.4	3.1	17.4	15.7	1.7	21.9	20.0	1.9
NH	79.9	63.5	16.4	34.2	29.3	4.9	51.6	45.6	6.0
O	61.5	50.2	11.3	28.0	24.4	3.6	42.0	37.4	4.6
PH	72.8	52.1	20.7	24.6	21.3	3.3	39.6	34.2	5.4
S	51.4	39.6	11.8	20.4	17.9	2.5	30.7	26.9	3.8
SiH^+	23.3	22.1	1.2	36.4	31.0	5.4	42.1	37.6	4.5
SiH^-	95.8	67.0	28.8	42.1	32.7	9.4	61.5	49.8	11.7
SiH_2	16.6	15.3	1.3	15.2	13.9	1.3	17.5	16.1	1.4

Table 4. Extra cyclic resonance energies [kcal mol^{-1}] and NICS values [ppm] of five-membered rings C_4XH_4.

X	ECRE1	ECRE2	NICS
AlH	−1.1	−3.5	5.4
BH	−2.7	−8.2	15.8
CH^+	−28.2	−35.4	46.9
CH^-	42.8	19.1	−13.7
CH_2	7.7	3.4	−4.1
NH	34.2	17.9	−14.4
O	25.8	12.8	−14.8
PH	30.8	17.9	−17.2
S	21.7	12.7	−15.9
SiH^+	−8.9	−15.5	11.2
SiH^-	34.3	17.2	−14.1
SiH_2	1.4	−0.8	0.3

changes as well as the extent of electron delocalization in molecules. Table 2 compares the bond lengths in the delocalized and the localized forms of twelve monohetero cyclopentadienes. Electron delocalization shortens both the C−X and the single C−C bonds significantly but lengthens the C=C double bonds modestly. These changes in bond lengths correlate with the resonance energies also listed in Table 2 very well, and thus provide a measure of the electron delocalization. The single C−C bond-length range is 1.467 ± 0.050 Å whereas the C=C double-bond range is 1.352 ± 0.029 Å. The BLW localization of the π electrons shortens the double C=C bonds to 1.317 ± 0.007 Å, very near the C=C length in localized benzene, cyclobutadiene, and the polyenes, and lengthens the C−C single bonds to 1.542 ± 0.007 Å. The localization significantly reduces the range of carbon–carbon bond lengths. The geometries of the most stable resonance contributors in all systems, whether they are aromatic or antiaromatic, neutral or charged, tend to converge. Perhaps because of the modest ring strain, the localized five-membered-ring single C−C bonds are slightly longer than those in the optimal 1,3,5-cyclohexatriene and linear polyenes (Table 1).

Because the adiabatic resonance energy (ARE) is always positive, it is not a conventional aromaticity indicator. Consequently, we employed the extra cyclic resonance energies (ECRE) for this purpose. Table 3 lists both the VREs and the AREs of the C_4H_4X rings and two sets of their corresponding linear counterparts: the $CH_2(CH)_3XH$ set has the same number of π electrons and the $CH_2(CH)_3XCHCH_2$ the same number of single bonds involved in the conjugated system. ECRE1 is the difference between the AREs of C_4H_4X rings and the linear $CH_2(CH)_3XH$ set, whereas ECRE2 compares the C_4H_4X rings with the linear $CH_2(CH)_3XCHCH_2$ set. Table 4 compiles the ECREs and the NICS values of the rings. Although the ECRE1 data correlate satisfactorily with NICS (cc = 0.84, the gray line in Figure 4), the ECRE2 plot not only has a much higher correlation coefficient (cc = 0.95, the black line in Figure 4), but also crosses very near to the origin. Thus, acyclic references with the same kinds and number of single bonds between the π units measure the aromaticity of conjugated rings better than references having only the same number of π electrons.[14,28] NICS is negative and ECRE is positive for aromatic systems, whereas NICS is positive and ECRE is negative for their antiaromatic counterparts.

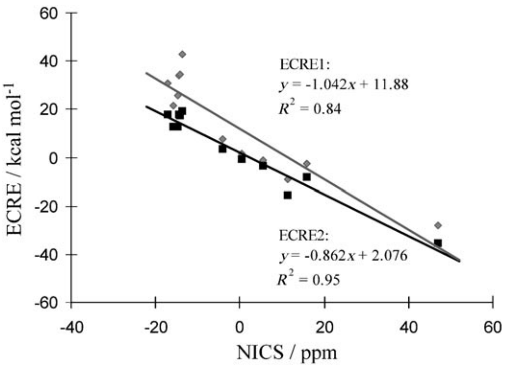


Figure 4. Correlation of the ECREs with the NICS values in five-membered rings.

The resonance energy of cyclopentadiene[79] as well as the cyclopentadienyl cation and anion, which represent the extremes of aromaticity and antiaromaticity, is of particular interest. The behavior of their acyclic counterparts affords instructive comparisons. There are large variations in the structures of cyclopentadiene and its ions (shown in Figure 5): C_5H_6 and $C_5H_5^+$ exhibit bond alternation, whereas $C_5H_5^-$ favors D_{5h} symmetry. In contrast, all their localized forms have similar single C–C and double C=C bond lengths. Necessarily, the C–C bonds differ in length: the neutral C–C(H$_2$) bond is longer than both C–C(H)$^-$ and C–C(H)$^+$, but the C–C(H)$^+$ bond is even shorter than the C–C(H)$^-$ length, suggesting electrostatic attraction in the cation and repulsion in the anion. These features are also found in the linear systems shown in Figure 6. The delocalization of the charge (no matter whether it is positive or negative) governs the stabilization of the acyclic systems. Thus, like the allyl ions,[33,37,48] the resonance energies of $C_5H_7^+$ and $C_5H_7^-$ are essentially identical. In contrast, the resonance energies of $C_5H_5^+$ and $C_5H_5^-$ differ considerably; the resonance stabilization of the cyclopentadienyl anion is almost three times greater than the cyclopentadienyl cation. Consequently, the cyclopentadienyl cation shows a large negative ECRE whereas the ECRE for the cyclopentadienyl anion is positive. Similar behavior is also observed in silicon systems (Table 4).

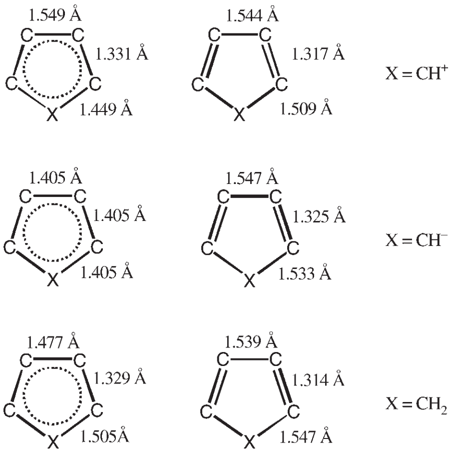


Figure 5. Optimal delocalized and localized geometries for five-membered $C_5H_5^+$, $C_5H_5^-$, and C_5H_6 with the 6-311+G(d,p) basis set.

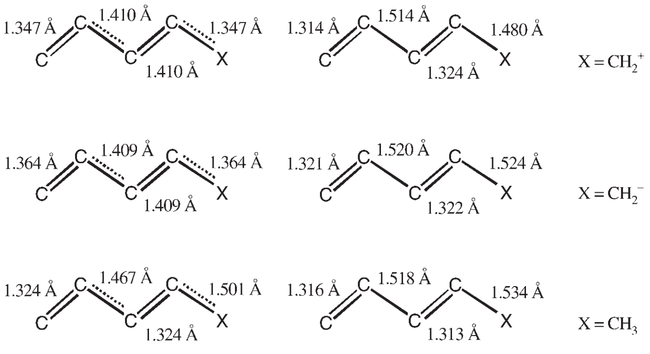
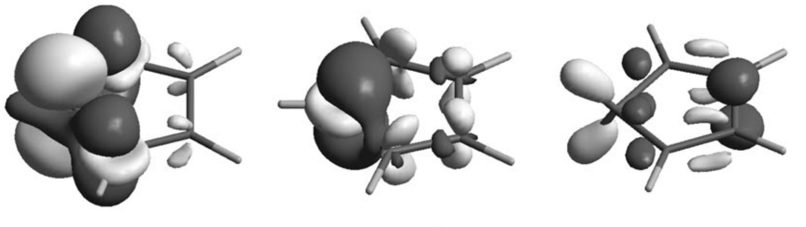


Figure 6. Optimal delocalized and localized geometries for linear $C_5H_7^+$, $C_5H_7^-$, and C_5H_8 with the 6-311+G(d,p) basis set.

What role does the methylene group play in cyclopentadiene? Does this CH$_2$ group disrupt the cyclic π-electron delocalization or, conversely, does it provide the extra two π-symmetric Hückel electrons needed to render cyclopentadiene aromatic? The relatively low methylene π-electron orbital energy reduces the delocalization propensity, compared with other $4n+2$ aromatic systems such as pyrrole and thiophene. Nevertheless, the electron delocalization in the neutral cyclopentadiene has now been firmly established.[79] Our computations confirm that the methylene group can participate weakly but significantly in the cyclic delocalization. The CH$_2$ group interacts with the adjacent double bonds (akin to the hyperconjugation in alkyl-substituted alkenes and polyenes[80]). Based on its linear 1,3-pentadiene model, cyclopentadiene has a modest positive ECRE (Table 4) and thus is weakly aromatic, which is nicely confirmed by the NICS criterion.[79]

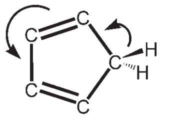
The electron-density differences (EDDs) between the BLW and HF wave functions intuitively reveal details of the charge migration from the most stable resonance structure to the delocalized minimum energy state. The EDD maps



a) $C_5H_5^-$ b) $C_5H_5^+$ c) C_5H_6

Figure 7. Electron-density difference (EDD) maps showing the electron delocalization effect in which black denotes the gain of electron density and gray means the loss of electron density (the contour isocharges are a),b) 0.005, and c) 0.003 au).

for cyclopentadiene and its ions are plotted in Figure 7. Interestingly, the electron-rich carbon in the BLW-localized form of $C_5H_5^-$ only donates its negative charges to the two vicinal carbon atoms, whereas in $C_5H_5^+$ the electron-deficient carbon collects electron density almost equally from the other four carbons. The electron delocalization in the neutral cyclopentadiene is in exact accord with the traditional "arrow" depiction (see left).



Conclusions

The BLW (block-localized wave function) method, which combines the advantages of both VB and MO theories, offers a quantitative ab initio electron-localization probe of the resonance effect. A BLW corresponds to a single resonance contributor. Following the conventional Pauling–Wheland resonance energy (RE) definition, the most stable resonance structure, appropriately selected,[23,26] is employed to evaluate the RE. This is equal to the energy difference between the BLW and the HF wave function. As electron correlation is of comparable magnitude in both the delocalized and localized states, its inclusion is not critical in the computation of Pauling–Wheland resonance energies. Cancellation occurs when the energy differences between the delocalized and localized states are taken. Comparisons of BLW and ab initio VB results demonstrate that electron correlation has a negligible effect on the resonance energies.[33,36,37,81] The BLW REs are also verified by thermochemical evaluations using experimental energies provided that adjustments for perturbations, such as conjugation, hyperconjugation, and so forth, are considered. A prime example is benzene; its ARE is about 20 kcal mol^{-1} higher than the traditional experimental estimate based on cyclohexene as a reference system. Although various evaluation methods give very different resonance energy values for benzene, REs [e.g., 65.0 kcal mol^{-1} with Eq. (5)] in agreement with our computations (57.5 kcal mol^{-1}) are found when the appropriate adjustments are made. The ARE of cyclobutadiene is essentially the same as butadiene (which also has four π electrons), and merely 10 kcal mol^{-1} less than 1,3,5-hexatriene (which also has two diene conjugations). Hence, we conclude that cyclobutadiene has only a modestly antiaromatic π system. Other factors contribute more to the instability of cyclobutadiene.

Based on the Pauling–Wheland definition of resonance energy, we measured aromaticity or antiaromaticity by the "extra cyclic resonance energy" (ECRE). This is defined as the RE difference between a cyclic fully conjugated system and an acyclic polyene with similar but disrupted conjugation. As illustrated by the cyclobutadiene example discussed above, the reference acyclic polyene can either be chosen to have the same number of π electrons (ECRE1) or the same number of diene conjugations (single bonds between double bonds; ECRE2). Our results (see Figure 4) support the literature conclusions that the latter choice is better than the former.[14,28] Computations on a series of conjugated five-membered rings demonstrated the utility of the BLW method and quantified the generally good agreement between ECRE and NICS criteria (Figure 4). Note also that the ECRE2 values for cyclopentadiene and the cyclopentadienyl cation and anion are 3.4, −35.4, and 19.1 kcal mol^{-1}, compared with the −4.1, 46.9, and −13.7 ppm NICS values, respectively.

Acknowledgements

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[1] a) P. von R. Schleyer, *Chem. Rev.* **2001**, *101*, 1115–1117; b) K. Jug, A. M. Koster, *J. Phys. Org. Chem.* **1991**, *4*, 163–169; c) C. W. Bird, *Tetrahedron* **1997**, *53*, 3319–3324; d) D. B. Chesnut, *Chem. Phys.* **2000**, *231*, 1–11; e) R. J. Abraham, M. Canton, M. Reid, L. J. Griffiths, *J. Chem. Soc. Perkin Trans. 2* **2000**, 803–812; f) T. M. Krygowski, M. K. Cyranski, Z. Czarnocki, G. Hafelinger, A. R. Katritzky, *Tetrahedron* **2000**, *56*, 1783–1796; g) C. A. Tsipis, E. E. Karagiannis, P. F. Kladou, A. C. Tsipis, *J. Am. Chem. Soc.* **2004**, *126*, 12916–12929; h) N. S. Mills, A. Levy, B. F. Plummer, *J. Org. Chem.* **2004**, *69*, 6623–6633; i) J. Poater, I. Garcia-Cruz, F. Illas, M. Solà, *Phys. Chem. Chem. Phys.* **2004**, *6*, 314–318; j) P. Lazzeretti, *Phys. Chem. Chem. Phys.* **2004**, *6*, 217–223; k) E. Matito, M. Duran, M. Solà, *J. Chem. Phys.* **2005**, *122*, 014109.

[2] a) C. W. Bird, *Tetrahedron* **1985**, *41*, 1409–1414; b) M. K. Cyranski, T. M. Krygowski, A. R. Katritzky, P. von R. Schleyer, *J. Org. Chem.* **2002**, *67*, 1333–1338.

[3] P. J. Garratt, *Aromaticity*, 3rd ed., Wiley, New York, **1986**.

[4] V. I. Minkin, M. N. Glukhovtsev, B. Y. Simkin, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley, New York, **1994**.

[5] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

[6] a) X. Li, A. E. Kuznetsov, H.-F. Zhang, A. I. Boldyrev, L.-S. Wang, *Science* **2001**, *291*, 859–861; b) A. E. Kuznetsov, K. A. Birch, A. I. Boldyrev, X. Li, H.-J. Zhai, L.-S. Wang, *Science* **2003**, *300*, 622–625; c) P. W. Fowler, R. W. A. Havenith, E. Steiner, *Chem. Phys. Lett.* **2002**, *342*, 85–90; d) H. Tanaka, S. Neukermans, E. Janssens, R. E. Silverans, P. Lievens, *J. Am. Chem. Soc.* **2003**, *125*, 2862–2863; e) Z. Chen, C. Corminboeuf, T. Heine, J. Bohmann, P. von R. Schleyer, *J. Am. Chem. Soc.* **2003**, *125*, 13930–13931.

[7] a) P. George, M. Trachtman, C. W. Bock, A. M. Brett, *Theor. Chim. Acta* **1975**, *38*, 121–129; b) P. George, M. Trachtman, C. W. Bock, A. M. Brett, *Tetrahedron* **1976**, *32*, 317–323.

[8] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.

[9] S. W. Slayden, J. F. Liebman, *Chem. Rev.* **2001**, *101*, 1541–1566.

[10] M. K. Cyranski, P. von R. Schleyer, T. M. Krygowski, H. Jiao, G. Hohlneicher, *Tetrahedron* **2003**, *59*, 1657–1665.

[11] M. D. Wodrich, C. S. Wannere, Y. Mo, P. D. Jarowski, K. N. Houk, P. von R. Schleyer, **2005**, unpublished results.

[12] L. C. Pauling, G. W. Wheland, *J. Chem. Phys.* **1933**, *1*, 362–374.

[13] a) J. van Dranen, J. A. A. Ketelaar, *J. Chem. Phys.* **1950**, *18*, 151–152; b) D. F. Hornig, *J. Am. Chem. Soc.* **1950**, *72*, 5772–5774; c) G.

Glockler, *J. Chem. Phys.* **1953**, *21*, 1249–1254; d) P. George, C. W. Bock, M. Trachtman, *Tetrahedron Lett.* **1985**, *26*, 5667–5670; e) R. Janoschek, *THEOCHEM* **1991**, *229*, 197–203; f) J. R. Collins, G. A. Gallup, *THEOCHEM* **1991**, *229*, 91–102; g) N. Matsunaga, T. R. Cundari, M. W. Schmidt, M. S. Gordon, *Theor. Chim. Acta* **1992**, *83*, 57–68; h) F. M. Tao, Y. K. Pan, *Theor. Chim. Acta* **1992**, *83*, 377–388; i) O. Exner, S. Bohm, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1994–1999.

[14] M. J. S. Dewar, C. De Llano, *J. Am. Chem. Soc.* **1969**, *91*, 789–795.

[15] G. F. Tantardini, M. Raimondi, M. Simonetta, *J. Am. Chem. Soc.* **1977**, *99*, 2913–2918.

[16] B. A. Hess, Jr., L. J. Schaad, *J. Am. Chem. Soc.* **1983**, *105*, 7500–7505.

[17] D. L. Cooper, J. Gerratt, M. Raimondi, *Nature* **1986**, *323*, 699–701.

[18] S. S. Shaik, P. C. Hiberty, J. M. Lefour, G. Ohanessian, *J. Am. Chem. Soc.* **1987**, *109*, 363–374.

[19] Y. Mo, W. Wu, Q. Zhang, *J. Phys. Chem.* **1994**, *98*, 10048–10053.

[20] S. Behrens, A. M. Koster, K. Jug, A. M. Koster, *J. Org. Chem.* **1994**, *59*, 2546–2551.

[21] J. H. van Lenthe, R. W. A. Havenith, F. Dijkstra, L. W. Jenneskens, *Chem. Phys. Lett.* **2002**, *361*, 203–208.

[22] C. H. Suresh, N. Koga, *J. Org. Chem.* **2002**, *67*, 1965–1968.

[23] L. C. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.

[24] G. W. Wheland, *J. Am. Chem. Soc.* **1941**, *63*, 2025–2027.

[25] G. W. Wheland, *The Theory of Resonance*, Wiley, New York, **1944**.

[26] G. W. Wheland, *Resonance in Organic Chemistry*, Wiley, New York, **1955**.

[27] R. Breslow, E. Mohacis, *J. Am. Chem. Soc.* **1963**, *85*, 431–434.

[28] L. J. Schaad, B. A. Hess, *Chem. Rev.* **2001**, *101*, 1465–1476.

[29] P. von R. Schleyer, F. Puhlhofer, *Org. Lett.* **2002**, *4*, 2873–2876.

[30] a) M. J. S. Dewar, G. J. Gleicher, *J. Am. Chem. Soc.* **1965**, *87*, 685; b) B. A. Hess, L. J. Schaad, *J. Am. Chem. Soc.* **1971**, *93*, 305–310.

[31] a) G. A. Gallup, R. L. Vance, J. R. Collins, J. M. Norbeck, *Adv. Quantum Chem.* **1982**, *16*, 229–272; b) Q. Zhang, X. Li, *J. Mol. Struct.* **1989**, *198*, 413–425; c) P. C. Hiberty, *THEOCHEM* **1997**, *398–399*, 35–43; d) T. Thorsteinsson, D. L. Cooper, *J. Math. Chem.* **1998**, *23*, 105–126; e) W. Wu, A. Wu, Y. Mo, M. Lin, Q. Zhang, *Int. J. Quantum Chem.* **1998**, *67*, 287–297; f) R. Mcweeny, *Int. J. Quantum Chem.* **1999**, *74*, 87–96; g) S. Shaik, A. Shurki, *Angew. Chem.* **1999**, *111*, 616–657; *Angew. Chem. Int. Ed.* **1999**, *38*, 586–625.

[32] a) D. L. Cooper, J. Gerratt, M. Raimondi, *Chem. Rev.* **1991**, *91*, 929; b) M. Raimondi, D. L. Cooper, *Top. Curr. Chem.* **1999**, *203*, 105–120; c) F. Dijkstra, J. H. van Lenthe, *J. Chem. Phys.* **2000**, *113*, 2100–2108; d) W. Wu, L. Song, Y. Mo, Q. Zhang, XIAMEN - An ab initio spin-free valence bond (VB) program, Xiamen University, Xiamen, **2000**; e) D. L. Cooper, *Valence Bond Theory*, Elsevier, Amsterdam, **2002**; f) L. Song, Y. Mo, Q. Zhang, W. Wu, *J. Comput. Chem.* **2005**, *26*, 514–521.

[33] Y. Mo, S. D. Peyerimhoff, *J. Chem. Phys.* **1998**, *109*, 1687–1697.

[34] a) Y. Mo, Y. Zhang, J. Gao, *J. Am. Chem. Soc.* **1999**, *121*, 5737–5742; b) Y. Mo, G. Subramanian, D. M. Ferguson, J. Gao, *J. Am. Chem. Soc.* **2002**, *124*, 4832; c) Y. Mo, W. Wu, L. Song, M. Lin, Q. Zhang, J. Gao, *Angew. Chem.* **2004**, *116*, 2020–2024; *Angew. Chem. Int. Ed.* **2004**, *43*, 1986–1990.

[35] Y. Mo, *J. Chem. Phys.* **2003**, *119*, 1300–1306.

[36] Y. Mo, L. Song, W. Wu, Q. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 3974–3982.

[37] Y. Mo, *J. Org. Chem.* **2004**, *69*, 5563–5567.

[38] J. M. Norbeck, G. A. Gallup, *J. Am. Chem. Soc.* **1974**, *96*, 3386–3393.

[39] P. C. Hiberty, S. Humbel, C. P. Byrman, J. H. van Lenthe, *J. Chem. Phys.* **1994**, *101*, 5969–5976.

[40] Y. Mo, Z. Lin, W. Wu, Q. Zhang, *J. Phys. Chem.* **1996**, *100*, 11569–11572.

[41] O. J. Sovers, C. W. Kern, R. M. Pitzer, M. Karplus, *J. Chem. Phys.* **1968**, *49*, 2592–2599.

[42] H. Kollmar, *J. Am. Chem. Soc.* **1979**, *101*, 4832–4840.

[43] J. P. Daudey, G. Trinquier, J. C. Barthelat, J. P. Malrieu, *Tetrahedron* **1980**, *36*, 3399–3401.

[44] a) Y. Mo, Z. Lin, *J. Chem. Phys.* **1996**, *105*, 1046–1051; b) Y. Mo, P. von R. Schleyer, H. Jiao, Z. Lin, *Chem. Phys. Lett.* **1997**, *280*, 439–443; c) Y. Mo, H. Jiao, Z. Lin, P. von R. Schleyer, *Chem. Phys. Lett.* **1998**, *289*, 383–390; d) Y. Mo, W. Wu, Q. Zhang, *J. Chem. Phys.* **2003**, *119*, 6448–6456; e) Y. Mo, H. Jiao, P. von R. Schleyer, *J. Org. Chem.* **2004**, *69*, 3493–3499.

[45] a) E. Gianinetti, Raimondi, E. Tornaghi, *Int. J. Quantum Chem.* **1996**, *60*, 157–166; b) A. Famulari, E. Gianinetti, M. Raimondi, M. Sironi, *Int. J. Quantum Chem.* **1998**, *69*, 151–158.

[46] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. J. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347–1363.

[47] C. A. Coulson, S. L. Altmann, *Trans. Faraday Soc.* **1952**, *48*, 293–302.

[48] Y. Mo, Z. Lin, W. Wu, Q. Zhang, *J. Phys. Chem.* **1996**, *100*, 6469–6474.

[49] NIST Standard Reference Database, http://webbook.nist.gov/chemistry/form-ser.html.

[50] a) S. S. Shaik, P. C. Hiberty, *J. Am. Chem. Soc.* **1985**, *107*, 3089–3095; b) A. Shurki, S. Shaik, *Angew. Chem.* **1997**, *109*, 2322–2324; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2205–2208; c) E. D. Glendening, R. Faust, A. Streitwieser, K. P. C. Vollhardt, F. Weinhold, *J. Am. Chem. Soc.* **1993**, *115*, 10952–10957; d) T. M. Krygowski, M. K. Cyranski, *Chem. Rev.* **2001**, *101*, 1385–1419.

[51] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **2000**, *21*, 411–413.

[52] Kekulé's concept of the structure of benzene usually is misinterpreted; he postulated that the static average of two equivalent virtual 1,3,5-cyclohexatriene structures results in the equivalence of the six CC bonds. See: J. P. Snyder in *Nonbenzenoid Aromatics, Vol. 1*, (Ed.: J. P. Snyder), Academic Press, New York, **1969**, pp. 16–18.

[53] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, W. E. Vaughan, *J. Am. Chem. Soc.* **1936**, *58*, 146–153.

[54] a) P. D. Jarowski, M. D. Wodrich, C. S. Wannere, P. von R. Schleyer, K. N. Houk, *J. Am. Chem. Soc.* **2004**, *126*, 15036–15037; b) R. S. Mulliken, C. A. Riecke, W. G. Brown, *J. Am. Chem. Soc.* **1941**, *63*, 41–56.

[55] a) S. S. Shaik, P. C. Hiberty, G. Ohanessian, J. M. Lefour, *J. Phys. Chem.* **1988**, *92*, 5086–5094; b) D. F. Hornig, *J. Am Chem. Soc.* **1950**, *72*, 5772–5774.

[56] B. Delley, *J. Chem. Phys.* **1991**, *94*, 7245–7250.

[57] a) R. Diercks, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1986**, *108*, 3150–3152; b) K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1992**, *114*, 9583–9587; c) R. Boese, D. Blaser, W. E. Billups, M. M. Haley, A. H. Maulita, K. P. C. Vollhardt, *Angew. Chem.* **1994**, *106*, 321–325; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 313–317; d) E. D. Jemmis, B. Kiran, *J. Org. Chem.* **1996**, *61*, 9006–9008; e) A. Matsuura, K. Komatsu, *J. Am. Chem. Soc.* **2001**, *123*, 1768–1769; f) R. Rathore, S. V. Lindeman, A. S. Kumar, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 6012–6018; g) A. Stanger, E. Tkachenko, *J. Comput. Chem.* **2001**, *22*, 1377–1386.

[58] H.-B. Bügi, K. K. Baldridge, K. Hardcastle, N. L. Frank, P. Gantzel, J. S. Siegel, J. Ziller, *Angew. Chem.* **1995**, *107*, 1575–1577; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1454–1456.

[59] N. L. Frank, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1995**, *117*, 2102–2103.

[60] H. D. Beckhaus, R. Faust, A. J. Matzger, D. L. Mohler, D. W. Rogers, C. Ruchardt, A. K. Sawhney, S. P. Verevkin, K. P. C. Vollhardt, S. Wolff, *J. Am. Chem. Soc.* **2000**, *122*, 7819–7820.

[61] S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *C hem. Rev.* **2001**, *101*, 1501–1539.

[62] U. Fleischer, W. Kutzelnigg, P. Lazzeretti, V. Muehlenkamp, *J. Am. Chem. Soc.* **1994**, *116*, 5298–5306.

[63] P. C. Hiberty, D. Danovich, A. Shurki, S. Shaik, *J. Am. Chem. Soc.* **1995**, *117*, 7760–7768.

[64] a) R. Breslow, D. R. Murayama, S. Murahashi, R. Grubbs, *J. Am. Chem. Soc.* **1973**, *95*, 6688–6699; b) M. J. S. Dewar, K. M. Merz, Jr., J. J. P. Stewart, *J. Am. Chem. Soc.* **1984**, *106*, 4040–4041; c) S. Zilberg, Y. Haas, J . *Phys. Chem. A* 1**998**, 102, 10843–10850; d) K. B. Wiberg, *Chem. Rev.* **2001**, *101*, 1317–1332.

[65] A. A. Deniz, K. S. Peters, G. J. Snyder, *Science* **1999**, *286*, 1119–1122.

[66] C. S. Wannere, D. Moran, N. L. Allinger, B. A. Hess, Jr., L. J. Schaad, P. von R. Schleyer, *Org. Lett.* **2003**, *5*, 2983–2986.

[67] V. Gogonea, P. von R. Schleyer, P. R. Schreiner, *Angew. Chem.* **1998**, *110*, 2045–2049; *Angew. Chem. Int. Ed.* **1998**, *37*, 1945–1948.

[68] R. Hoffman, S. Shaik, P. C. Hiberty, *Acc. Chem. Res.* **2003**, *36*, 750–756.

[69] A. F. Voter, W. A. Goddard, III, *J. Am. Chem. Soc.* **1986**, *108*, 2830–2837.

[70] D. Moran, M. Manoharan, T. Heine, P. von R. Schleyer, *Org. Lett.* **2003**, *5*, 23–26.

[71] J. S. Murray, J. M. Seminario, P. Politzer, *Int. J. Quantum Chem.* **1994**, *49*, 575–579.

[72] T. Bally, S. Masamune, *Tetrahedron* 1**980**, 36, 343–370.

[73] W. Wu, D. Danovich, A. Shurki, S. Shaik, *J. Phys. Chem. A* **2000**, *104*, 8744–8758.

[74] P. von R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta, N. J. R. van Eikema Hommes, *Org. Lett.* **2001**, *3*, 2465–2468.

[75] P. von R. Schleyer, P. K. Freeman, H. Jiao, B. Goldfuss, *Angew. Chem.* **1995**, *107*, 332–335; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 337–340.

[76] a) P. von R. Schleyer, H. Jiao, *Pure Appl. Chem.* **1996**, *68*, 209–218; b) B. S. Jursic, *J. Heterocycl. Chem.* **1997**, *34*, 1387–1389; c) R. Balawender, L. Komorowski, F. De Proft, P. Geerlings, *J. Phys. Chem. A* **1998**, *102*, 9912–9917; d) G. P. Bean, *J. Org. Chem.* **1998**, *63*, 2497–2506; e) S. I. Kotelevskii, O. V. Prezhdo, *Tetrahedron* **2001**, *57*, 5715–5729; f) V. I. Minkin, R. M. Minyaev, *Chem. Rev.* **2001**, *101*, 1247–1265.

[77] D. B. Chesnut, L. J. Bartolotti, *Chem. Phys.* **2000**, *253*, 1–11.

[78] J. Poater, X. Fradera, M. Duran, M. Sola, *Euro. J. Chem.* **2003**, *9*, 400–406.

[79] L. Nyulaszi, P. von R. Schleyer, *J. Am. Chem. Soc.* **1999**, *121*, 6872–6875.

[80] C. J. Cramer in *Encyclopedia of Computational Chemistry* (Ed.: P. von R. Schelyer), Wiley, Berlin, **1998**, pp. 1294–1298.

[81] Y. Mo, P. von R. Schleyer, W. Wu, M. Lin, Q. Zhang, J. Gao, *J. Phys. Chem. A* **2003**, *107*, 10011–10018.

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