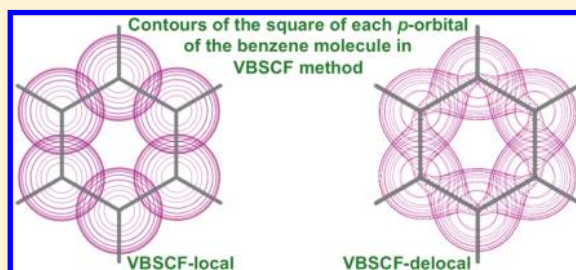


Resonance and Aromaticity: An Ab Initio Valence Bond Approach

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ABSTRACT: Resonance energy is one of the criteria to measure aromaticity. The effect of the use of different orbital models is investigated in the calculated resonance energies of cyclic conjugated hydrocarbons within the framework of the ab initio Valence Bond Self-Consistent Field (VBSCF) method. The VB wave function for each system was constructed using a linear combination of the VB structures (spin functions), which closely resemble the Kekulé valence structures, and two types of orbitals, that is, strictly atomic (local) and delocalized atomic (delocal) p-orbitals, were used to describe the π -system. It is found that the Pauling–Wheland’s resonance energy with nonorthogonal structures decreases, while the same with orthogonalized structures and the total mean resonance energy (the sum of the weighted off-diagonal contributions in the Hamiltonian matrix of orthogonalized structures) increase when delocal orbitals are used as compared to local p-orbitals. Analysis of the interactions between the different structures of a system shows that the resonance in the 6π electrons conjugated circuits have the largest contributions to the resonance energy. The VBSCF calculations also show that the extra stability of phenanthrene, a kinked benzenoid, as compared to its linear counterpart, anthracene, is a consequence of the resonance in the π -system rather than the H–H interaction in the bay region as suggested previously. Finally, the empirical parameters for the resonance interactions between different $4n+2$ or $4n$ π electrons conjugated circuits, used in Randić’s conjugated circuits theory or Herndon’s semi-empirical VB approach, are quantified. These parameters have to be scaled by the structure coefficients (weights) of the contributing structures.



INTRODUCTION

Aromaticity is one of the most important and fundamental concepts in chemistry.^{1–4} It is associated with cyclic electrons delocalization^{5,6} that provides extra stability to the molecular systems. There is, however, still much dispute about what aromaticity really is, and the notion is as elusive as ever.^{1,2,7,8} Because aromaticity is not an observable or directly measurable quantity, it is defined by convention. Several criteria like extra stabilization (delocalization and resonance) energy (energetic criterion^{9–16}), bond length equalization (geometric criterion^{3,17,18}), and π electrons ring currents induced by an external magnetic field (magnetic criterion^{6,19–21}) are frequently used as indicators for aromaticity.

The energetic criterion is widely accepted as an index for aromaticity. Various quantum mechanical and experimental schemes have been proposed to determine this extra stabilization energy due to resonance or delocalization for mono- and polycyclic conjugated compounds. The first theoretical estimate of the delocalization energy came from the work by Hückel^{9–11} (Hückel’s delocalization energy). Subsequently, Pauling and Wheland^{12–14} used Valence Bond Theory to calculate the resonance energies of conjugated systems (Pauling–Wheland’s resonance energy). Later, various other approaches were also put forward to calculate resonance or delocalization energies. These, among others, include Dewar’s method,²² Hess–Schaad’s method,²³ topological or

graph theoretical method,^{24–26} Randić’s conjugated circuits method,^{27–30} Herndon’s semi-empirical VB method,^{31,32} and the block-localized wave function (BLW) method.^{33–38} Some of these methods (Dewar’s method, Hess–Schaad’s method, and BLW method) calculate the extra stabilization energy as the difference between the energy of the real molecule and a separate real or hypothetical “reference” system lacking resonance and/or cyclic delocalization. This leads to a Hückel’s type description of delocalization energy (a detailed discussion about the difference between delocalization energy and the resonance energy can be found elsewhere^{39,40}). The choice of the reference system is crucial in these methods, and the computed delocalization energies depend upon the chosen reference.⁴¹ However, in these approaches, no information regarding the importance of the different contributing (Lewis or Kekulé) valence structures is obtained.

Different isodesmic⁴² and homodesmotic^{43–45} reactions are also frequently used to estimate the extra stabilization due to the π electrons delocalization, the so-called aromatic stabilization energy (ASE).^{3,4,46} In this case too, the ASEs depend upon the formulation of the reactions. An example is the ASE value for the benzene molecule, which ranges from 20.3 to 74.7 kcal/

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mol depending upon the reaction scheme and the level of the theory used in the calculation.^{3,4,46} The same is the case with the experimental estimates, which range from 21 kcal/mol³ to 65 kcal/mol.³³

Pauling and Wheland^{12–14} used the concept of two Kekulé and three Dewar structures (also the two Kekulé valence structures only) for the benzene molecule to study aromaticity. They employed an approximate form of the VB method, which was developed by Heitler and London,⁴⁷ and the concept of quantum mechanical resonance, developed by Heisenberg^{48–50} and later Pauling,¹⁴ was used to measure the aromaticity. In this method, the resonance energy arises as a result of the interaction between the structures that contribute to the ground state of a system, for example, the two VB structures for the benzene molecule, which correspond to its two Kekulé valence structures. Pauling and Wheland^{12–14} defined the resonance energy, which we call the Pauling–Wheland’s resonance energy, as the energy difference between the energy of the multistructure VB wave function and the energy of the most stable contributing structure in the same calculation. Because the resonance energy in this method arises automatically when two or more structures are involved in the VB wave function coupled with the presence of an intrinsic reference (the structure with the lowest energy in the wave function), a separate reference is not required. Thus, the Pauling–Wheland’s approach offers the opportunity to calculate the resonance energy directly as a difference between the total energy of the system and the energy of the most stable contributing structure in the same calculation.

In the *ab initio* form of the VB method, the contributing structures are represented as multiples of singlet-coupled pairs of singly occupied orbitals as in the Valence Bond Self Consistent Field (VBSCF) method^{51–53} and the Spin-Coupled VB (SCVB) method.^{54–57} The latter method uses the Kotani’s branching diagrams method⁵⁸ to construct the spin-coupling patterns, but at the end of the calculation the spin functions can be transformed to Rumer basis⁵⁹ (singlet-coupled pairs of singly occupied orbitals).

A few years ago some of us calculated the resonance energy of benzene^{60,61} and naphthalene⁶² using the VBSCF approach with fully optimized p-orbitals, and pyrene⁶³ using a VBCI approach with benzene-optimized atomic p-orbitals. In the VBSCF results for the benzene molecule, it was found that the arbitrariness in the choice of the orbitals (restricted atomic p-orbitals, delocalized p-orbitals, and different orbitals for different structures) greatly affects the resonance energy. The purpose of this work is to find whether there is a qualitative trend in the resonance energies of different cyclic conjugated systems, with different VB orbital models, that is, restricted (local) and delocalized atomic p-orbitals. For this purpose, we first treat the well rehearsed system, benzene, the archetypal aromatic compound, and then extend the calculations to different $(4n+2)$ and $4n$ π electrons polycyclic systems. The systems studied include both anthracene and phenanthrene, and our VB results present the opportunity to elucidate the role of the π electrons resonance in their stability difference. At last, we quantify the empirical parameters for the resonance interactions between different $(4n+2)$ and $4n$ conjugated circuits used in Randić’s π electrons conjugated circuits theory^{27–30} and Herdon’s semi-empirical Valence Bond approach.^{31,32} These parameters are scaled by the coefficients (weights) of the structures between which these interactions occur.

METHOD

Valence Bond Method: Theory. In our *ab initio* VBSCF^{51–53} method, a bond is described as a singlet-coupled pair of singly occupied orbitals, ϕ_1 and ϕ_2 centered on atoms 1 and 2, respectively. Thus, a bond is:

$$(\text{bond})_{12} = \mathcal{N}\{|\phi_1\bar{\phi}_2| - |\bar{\phi}_1\phi_2|\} \equiv (1-2) \quad (1)$$

where \mathcal{N} is the normalization constant. A VB structure for a system is defined as a product of all of the bonds:

$$\psi = \hat{\mathcal{A}}\{(\text{core})(1-2)(3-4)(5-6)\dots((n-1)-n)\} \quad (2)$$

where $\hat{\mathcal{A}}$ is an antisymmetrizer, and “core” represents the doubly occupied core orbitals. If the same set of orbitals is used to describe different structures of a system, then these structures differ only in their spin functions, that is, the spin coupling mode of the orbitals. An ionic structure can be defined with orbital ϕ_i occupied twice or alternatively with two singly occupied orbitals on the same atom that share the same space.⁶⁴ The VB wave function for a molecule is then constructed as a linear combination of these VB structures:

$$\Psi_0 = \sum_i c_i \psi_i \quad (3)$$

In the VBSCF method, the orbitals and the structure coefficients are optimized, simultaneously, to get the wave function, which corresponds with the lowest energy expectation value. The relative importance of each structure in the wave function is determined by solving the generalized eigenvalue problem for the structure coefficients:

$$[\mathbf{H} - E\mathbf{S}]c = 0 \quad (4)$$

Here, \mathbf{H} is the Hamiltonian matrix, and \mathbf{S} is the overlap matrix between the structures.

To each structure, a weight can be assigned according to the formula:⁶⁵

$$W_j = N|c_j|^2/(\mathbf{S}^{-1})_{jj}; \quad N^{-1} = \sum_j |c_j|^2/(\mathbf{S}^{-1})_{jj} \quad (5)$$

where c_j represents the coefficient of structure j , \mathbf{S}_{jj}^{-1} is the element of the inverse overlap matrix between the structures, and N is the normalization constant. The sum of the weights of all of the structures in the VB wave function equals 1.

The resonance energy of each system is calculated according to Pauling and Wheland’s^{12–14} definition as:

$$E_{\text{resonance}} = E - E_{\text{struc}} \quad (6)$$

where E is the energy of the VB wave function, and E_{struc} is the energy of the structure that has the lowest energy in the wave function. When the E_{struc} is calculated from the Hamiltonian (\mathbf{H}) matrix of nonorthogonal structures, the calculated resonance energy in eq 6 is called Pauling–Wheland’s resonance energy with nonorthogonal structures, and we designate it as E_{res} . The \mathbf{H} matrix can also be transformed to an orthogonal basis using Löwdin’s symmetric orthogonalization procedure.⁶⁶ In that case, the structures are changed by changing the space of each structure while the total space remains the same. The energies of the contributing structures are, therefore, raised relative to the total energy of the system. After the orthogonalization, there is no overlap between the structures, and these structures can be interpreted as separate from each other as possible while maintaining the closest resemblance to the original nonorthogonal structures. In this

case, the use of eq 6 will give a more negative resonance energy than E_{res} . This resonance energy is called Pauling–Wheland’s resonance energy with orthogonal structures (E_{res}^{\perp}). In the orthogonal \mathbf{H} matrix (\mathbf{H}^{\perp}), the total energy is partitioned into weighted diagonal contribution ($\sum_i c_i^2 \mathbf{H}_{ii}^{\perp}$) of the structures and the weighted off-diagonal or resonance contribution ($c_i c_j \mathbf{H}_{ij}^{\perp}$) between them:⁶³

$$E = \sum_i \sum_j c_i c_j \mathbf{H}_{ij}^{\perp} = \sum_i c_i^2 \mathbf{H}_{ii}^{\perp} + 2 \sum_{i < j} c_i c_j \mathbf{H}_{ij}^{\perp} \quad (7)$$

The sum of the off-diagonal contributions is yet another measure of the resonance energy, called the total mean resonance energy ($E_{\text{res}}^{\perp \text{m}}$) of the system with respect to the weighted mean value of the energy of all structures. The $E_{\text{res}}^{\perp \text{m}}$ of a system can be equal to or even more negative than the E_{res}^{\perp} . If only two symmetrical structures are involved in the VB wave function, for example, the two VB structures for the benzene molecule that correspond with its two Kekulé valence structures, the energies of the two structures and similarly the structure coefficients will be equal to each other, that is, $\mathbf{H}_{11} = \mathbf{H}_{22}$ and $c_1 = c_2$. Equation 7, in that case, becomes $E = \mathbf{H}_{11} + \mathbf{H}_{12}$ (because the structure coefficients are normalized so $2c_1^2 = 2c_2^2 = 1$), which means that the E_{res}^{\perp} and the $E_{\text{res}}^{\perp \text{m}}$ will be the same. In other cases, that is, where two nonsymmetrical or more than two structures are involved, the $E_{\text{res}}^{\perp \text{m}}$ will be more negative than the E_{res}^{\perp} . The orthogonalized \mathbf{H} matrix also enables the analysis of all resonance interactions between different contributing structures of a system. The most important contributions to the resonance energy, in terms of Clar’s sextets^{67,68} or π electrons conjugated circuits,^{27–29} can thus be identified.

Computational Details. All calculations were performed using the 6-31G basis set.⁶⁹ The geometries of compounds 1–9 in Figure 1 were optimized, within the given point group

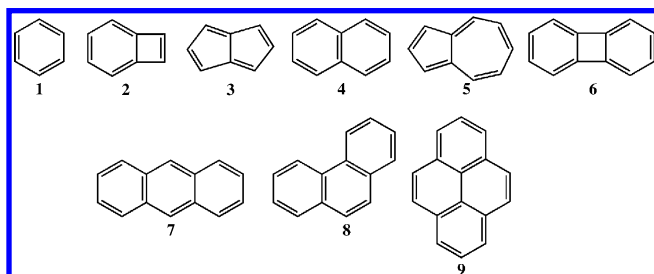


Figure 1. Selected systems for VBSCF study (only a single Kekulé valence structure of each system is shown). 1, benzene (D_{6h}); 2, benzocyclobutadiene (C_{2v}); 3, pentalene (C_{2h}); 4, naphthalene (D_{2h}); 5, azulene (C_{2v}); 6, biphenylene (D_{2h}); 7, anthracene (D_{2h}); 8, phenanthrene (C_{2v}); 9, pyrene (D_{2h}).

symmetry and without any other constraint, at RHF level using GAMESS-UK.⁷⁰ The geometries of compounds 1, 3, 4, 7, 8, and 9 at RHF/6-31G level are in good agreement with B3LYP/6-31G** optimized geometries.^{71,72} Also, it is expected that the geometry optimization at higher levels of the theory would not change the Valence Bond picture of these systems. Hessian calculations confirmed that these geometries are genuine minima.

The ab initio VBSCF calculations were performed with TURTLE.⁷³ For each compound, the VB wave function was constructed by a linear combination of those VB structures that correspond with all of the Kekulé valence structures of the

system. From now on, we will call these VB structures the Kekulé valence structures. The (doubly occupied) σ -orbitals were taken from a preceding RHF calculation, and, as an initial guess, the π system was described by singly occupied atomic p-orbitals. In all of the VB calculations, the σ -orbitals were orthogonal to each other and to the p-orbitals, while the p-orbitals were nonorthogonal to each other. Both the p-orbitals and the structure coefficients were optimized, while the doubly occupied σ -orbitals were frozen.

Two Valence Bond models were used in the orbital optimization procedure. In the first model, each p-orbital is expanded only in the basis functions centered on the same atom, and mixing with the basis functions on different atoms is not allowed. We call this model VB-local. VB-local has an interpretational advantage, and the spin-coupling modes (spin functions) can be directly related to the Lewis or the Kekulé valence structures. In the second model, each p-orbital is allowed to expand arbitrarily; i.e., its tail may lie on the neighboring atoms or beyond, and this model is called VB-delocal. In VB-local, because the atomic orbitals are not allowed to distort freely in a molecule, a large number of (physically untenable) ionic and long-bond (Dewar) structures are required to compensate this effect. However, inclusion of all of the covalent and ionic structures, for example, 170 ionic and 3 longer-bond structures for 1 or 19 362 ionic and 39 longer-bond structures for 4, loses the compactness of the wave function and the real interpretational advantage of VB. We, therefore, considered only Kekulé valence structures in the wave function to compare it with the VB-delocal approach. The VB-delocal level gives an accurate description of cyclic conjugated hydrocarbons in their ground states with only Kekulé valence structures.^{74,75}

It has been shown in the past³⁹ that the VB-delocal resonance energy of benzene (1) is practically insensitive to basis set size: both the 6-31G (66 AOs) and the aug-cc-pVQZ (954 AOs) basis set calculations give a resonance energy of 20 ± 0.5 kcal/mol at the VB-delocal level. This insensitivity of VB-delocal resonance energy with respect to basis set is also expected for other related systems. This means that we can use the modest 6-31G basis set for the VB calculations, which is computationally advantageous.

RESULTS AND DISCUSSION

The Choice of the Orbitals and the Resonance Energy.

The Kekulé valence structures of molecules 1–9 (Figure 1) and their contribution in the VB wave function of each system are shown in Figure 2. The total energies of these systems at RHF, VB-local, and VB-delocal levels and the different resonance energies are presented in Table 1.

Before analyzing the different resonance energies, we discuss the quality of the VB wave function in VB-local and VB-delocal models. In VB-local, each p-orbital, although optimized, is restricted to remain atomic p-orbital. Because of this restriction, the energy of the (multideterminant) VB wave function is higher than the energy of the (single determinant) Hartree–Fock wave function. Also, the bonds (double bonds) described with these restricted p-orbitals are too weak in the contributing Kekulé valence structures, and the energies of the individual structures remain high in the wave function. In VB-delocal, the wave function is much better because the distortion of the orbitals toward the neighboring atoms results in an enhanced overlap between the orbitals (stronger bonds). The individual structures, thus, become more stable in VB-delocal as compared

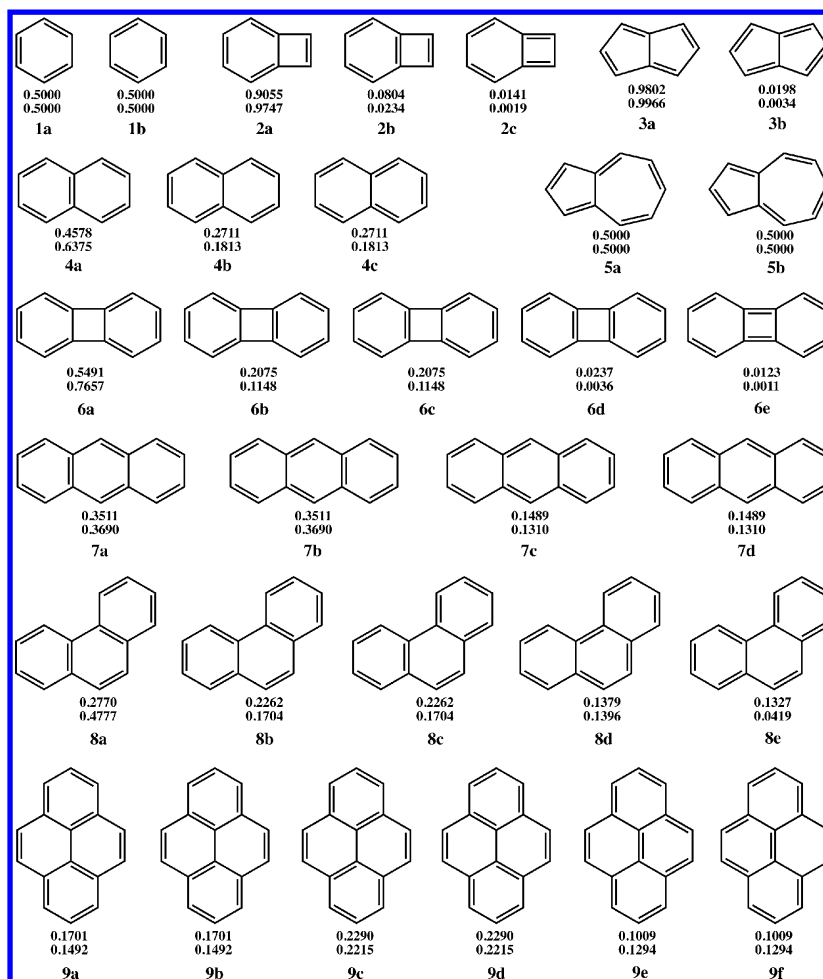


Figure 2. The Kekulé valence structures of molecules 1–9 and their weights in the VB-local (upper value) and VB-delocal (lower value) wave function.

to those in VB-local. The VB wave function also has a lower energy in VB-delocal than in VB-local (or Hartree–Fock) because of the increased interaction between the structures.

In the VB wave function with nonorthogonal structures, each structure also uses the space of other structures both in VB-local and in VB-delocal. Because of the enhanced overlap between the orbitals in VB-delocal, the overlap between the structures is also increased as compared to that in VB-local. This increase in overlap between the structures lowers the energies of the contributing Kekulé structures relative to the total energy. As a consequence, the difference between the energy of the most stable Kekulé valence structure and the total energy of the system (i.e., the E_{res}) becomes smaller in VB-delocal as compared to that in VB-local. The E_{res} of a system calculated with VB-delocal method is, therefore, generally smaller than that calculated with VB-local method. The E_{res} values at VB-delocal level are in excellent agreement with those reported by Cooper et al.^{76–78} (–19.96 to –21.0 kcal/mol for 1 and –18.2 kcal/mol for 4) with their SCVB approach.

When the structures are transformed to an orthogonal basis, the energies of the contributing Kekulé valence structures are raised, and the difference between the total energy and the energy of the most stable Kekulé valence structure increases. The E_{res}^{\perp} is, therefore, much larger than the E_{res} both in VB-local and in VB-delocal. The effect of the orbital delocalization (VB-delocal) on E_{res}^{\perp} is opposite to that on E_{res} . While the E_{res}

generally decreases in VB-delocal as compared to that in VB-local, the E_{res}^{\perp} increases. This is because the overlap between the structures (in the wave function with nonorthogonal structures) is stronger in VB-delocal than in VB-local so orthogonalization raises the energy of the contributing structures more in VB-delocal than in VB-local relative to the total energy at the same level. The E_{res}^{\perp} also shows the same trend, that is, increases when going from VB-local to VB-delocal, because of the increased interactions between the contributing structures.

The E_{res} value of 5 (azulene) shows an opposite trend with delocal orbitals. The reason can be the charge separation in its π -system (calculated dipole moment (μ) at RHF/6-31G = 1.74 D, experimental^{79,80} = 0.80–1.08 D) that cannot be adequately described using the VB-local model with only Kekulé valence structures (shown by the low dipole moment, μ calculated at VB-local with two structures is 0.30 D). So the energy of the wave function does not go as low as it would have been if a few ionic structures had been included. Consequently, the energy difference between the total energy and the energy of the single Kekulé valence structure (the E_{res}) is small. In VB-delocal, the orbitals are allowed to distort freely, and the effects of the ionic structures are automatically included in the space of the Kekulé valence structures. The interaction between the two Kekulé valence structures (the off-diagonal element of the H-matrix) is enhanced (μ at VB-delocal with two structures = 0.85 D),

Table 1. Results of RHF and VBSCF Calculations on Molecules 1–9 and Their Resonance Energies

system	method	E (au)	E_{res} (kcal/mol)	E_{res}^{\perp} (kcal/mol)	$E_{\text{res}}^{\text{Lm}}$ (kcal/mol)
1 (benzene)	RHF	−230.624472			
	VB-local	−230.540385	−27.74	−44.16	−44.16
	VB-delocal	−230.692578	−19.97	−60.79	−60.79
2 (benzocyclobutadiene)	RHF	−306.217848			
	VB-local	−306.131381	−11.80	−26.77	−49.33
	VB-delocal	−306.323242	−4.26	−39.98	−69.46
3 (pentalene)	RHF	−306.229649			
	VB-local	−306.159860	−1.77	−5.05	−9.58
	VB-delocal	−306.344285	−0.41	−6.85	−13.04
4 (naphthalene)	RHF	−383.222722			
	VB-local	−383.070614	−31.90	−61.38	−64.18
	VB-delocal	−383.336654	−13.41	−83.12	−96.36
5 (azulene)	RHF	−383.147289			
	VB-local	−383.000007	−14.44	−16.23	−16.23
	VB-delocal	−383.262309	−19.70	−31.81	−31.81
6 (biphenylene)	RHF	−458.847135			
	VB-local	−458.670739	−32.43	−62.63	−86.16
	VB-delocal	−458.986715	−14.37	−67.81	−103.93
7 (anthracene)	RHF	−535.812437			
	VB-local	−535.595274	−42.26	−71.97	−75.49
	VB-delocal	−535.972929	−26.58	−101.34	−109.82
8 (phenanthrene)	RHF	−535.824583			
	VB-local	−535.600939	−49.72	−92.73	−94.81
	VB-delocal	−535.981031	−21.05	−123.55	−140.21
9 (pyrene)	RHF	−611.555552			
	VB-local	−611.286993	−62.34	−95.38	−100.87
	VB-delocal	−611.731359	−41.15	−134.18	−141.61

Table 2. Energies (in atomic units) of the Kekulé Valence Structures of 1–9^a

system/method	VB-local	VB-delocal
1a, 1b	−230.496173 (−230.470018)	−230.660754 (−230.595707)
2a	−306.112587 (−306.088720)	−306.316451 (−306.259536)
2b	−306.036693 (−305.973298)	−306.206720 (−306.088287)
2c	−305.978477 (−305.922757)	−306.124709 (−306.032501)
3a	−306.157042 (−306.151812)	−306.343631 (−306.333363)
3b	−306.020070 (−306.012359)	−306.153677 (−306.132030)
4a	−383.019784 (−382.972802)	−383.315281 (−383.204187)
4b, 4c	−382.991394 (−382.964411)	−383.246728 (−383.161110)
5a, 5b	−382.976987 (−382.974136)	−383.230910 (−383.211612)
6a	−458.619061 (−458.570936)	−458.963775 (−458.878647)
6b, 6c	−458.576114 (−458.524568)	−458.890860 (−458.754201)
6d	−458.517839 (−458.430062)	−458.803825 (−458.597409)
6e	−458.484216 (−458.432553)	−458.724072 (−458.633006)
7a, 7b	−535.527934 (−535.480588)	−535.930574 (−535.811441)
7c, 7d	−535.488766 (−535.461820)	−535.853096 (−535.768051)
8a	−535.521701 (−535.452288)	−535.947492 (−535.819397)
8b, 8c	−535.504245 (−535.452818)	−535.892883 (−535.750870)
8d	−535.479787 (−535.453160)	−535.853078 (−535.747381)
8e	−535.485941 (−535.433868)	−535.844162 (−535.669941)
9a, 9b	−611.187644 (−611.117732)	−611.665779 (−611.496527)
9c, 9d	−611.186540 (−611.135020)	−611.658929 (−611.517535)
9e, 9f	−611.152670 (−611.125702)	−611.587155 (−611.499568)

^aThe values in the parentheses are after the Löwdin orthogonalization.

which lowers the total energy of the system and results in the large energy gap between the energy of the single Kekulé structure and the total energy, that is, the E_{res} value.

The energies of the contributing structures (Table 2) in the VB wave function show that the Kekulé valence structures with

the maximum number of 6π electrons conjugated circuits have the lowest energy in VB-local when the structures are nonorthogonal. This is, however, not the case in VB-delocal or when the structures are transformed to an orthogonal basis

in VB-local (see, for example, the energies of the contributing structures of 8 or 9).

Analysis of the different contributions to the $E_{\text{res}}^{\text{lm}}$ (Tables 3–8) shows that those interactions that lead to the 6π electrons

Table 3. Contribution of Different Interactions to the $E_{\text{res}}^{\text{lm}}$ (in kcal/mol) for 2

structures	VB-local		VB-delocal	
	2a	2b	2a	2b
2b	−30.03		−45.53	
2c	−8.56	−10.73	−14.20	−9.73

Table 4. Contribution of Different Interactions to the $E_{\text{res}}^{\text{lm}}$ (in kcal/mol) for 4

structures	VB-local		VB-delocal	
	4a	4b	4a	4b
4b	−28.69		−42.41	
4c	−28.69	−6.79	−42.41	−11.54

Table 5. Contribution of Different Interactions to the $E_{\text{res}}^{\text{lm}}$ (in kcal/mol) for 6

structures	6a	6b	6c	6d
		VB-local		
6b	−27.09			
6c	−27.09	0.49		
6d	−0.03	−10.61	−10.61	
6e	−0.62	−3.18	−3.18	−4.23
		VB-delocal		
6b	−40.28			
6c	−40.28	0.97		
6d	−0.18	−9.34	−9.34	
6e	−0.67	−1.96	−1.96	−0.88

Table 6. Contribution of Different Interactions to the $E_{\text{res}}^{\text{lm}}$ (in kcal/mol) for 7

structures	7a	7b	7c
	VB-local		
7b	−26.64		
7c	−5.50	−18.28	
7d	−18.28	−5.50	−1.29
	VB-delocal		
7b	−33.63		
7c	−10.13	−26.00	
7d	−26.00	−10.13	−3.92

Table 7. Contribution of Different Interactions to the $E_{\text{res}}^{\text{lm}}$ (in kcal/mol) for 8

structures	8a	8b	8c	8d
		VB-local		
8b	−20.97			
8c	−20.97	0.16		
8d	−13.70	−3.88	−3.88	
8e	0.03	−15.54	−15.54	−0.51
		VB-delocal		
8b	−34.42			
8c	−34.42	0.11		
8d	−22.98	−4.18	−4.18	
8e	−0.25	−14.14	−14.14	−0.30

Table 8. Contribution of Different Interactions to the $E_{\text{res}}^{\text{lm}}$ (in kcal/mol) for 9

structures	9a	9b	9c	9d	9e
VB-local					
9b	−0.09				
9c	−16.97	−16.97			
9d	−16.97	−16.97	0.28		
9e	−9.62	−0.18	−3.15	−3.15	
9f	−0.18	−9.62	−3.15	−3.15	−0.94
VB-delocal					
9b	−0.58				
9c	−22.01	−22.01			
9d	−22.01	−22.01	0.79		
9e	−13.40	−1.06	−5.79	−5.79	
9f	−1.06	−13.40	−5.79	−5.79	−1.69

conjugated circuits or Clar's sextets are the most important contributors to the resonance energy. For 1, there is one 6π electrons conjugated circuit, and this is the only contribution to the $E_{\text{res}}^{\text{lm}}$. Its value increases from −44.16 kcal/mol in VB-local to −60.79 kcal/mol in VB-delocal (Table 1). For 2, 4, 6–9, the values of the contributions of the 6π electrons conjugated circuits range from −9.62 (in 9) to −30.03 kcal/mol (in 2) at VB-local and −9.34 (in 6) to −45.53 kcal/mol (in 2) at the VB-delocal level. The 10π electrons conjugated circuits have a small contribution to the resonance energy in the range of 3–11 kcal/mol. Interestingly, the contributions of the 4π and the 8π electrons circuits in 2 also fall in the range of that of the 10π electrons circuits. Tables 3–8 show that the contributions of the different π electrons conjugated circuits to the $E_{\text{res}}^{\text{lm}}$ are also dependent upon the choice of the orbitals. However, no clear trend is found in the values of these contributions while going from VB-local to VB-delocal.

The large difference in the contribution of the same type of conjugated circuits (especially the 6π electrons conjugated circuits) in different systems can be related to the energy differences of the Kekulé valence structures of a system between which these interactions occur and their weights (the structure coefficients, eq 3) in the VB wave function. For example, 1 has only two structures that contribute equally ($c_{1a} = c_{1b}$) to the wave function. The interaction between these structures involves resonance in the 6π electrons conjugated circuit, and the value obtained for the resonance contribution is equal to $H_{(1a,1b)}^{\dagger}$ (because the wave function is normalized, the $2c_{1a}c_{1b}$ in the second term of eq 7 is equal to 1). In other cases where two nonsymmetrical or more than two structures are involved, the $2c_i c_j$ is smaller than 1, and the resonance contribution (H_{ij}^{\dagger}) is scaled down by $2c_i c_j$.

The resonance energies per π electron ($E_{\text{res}}^{\text{PE}}$) for these systems (Table 9) show that 1 has the largest values for the $E_{\text{res}}^{\text{PE}}$, $E_{\text{res}}^{\text{PE}}$, and $E_{\text{res}}^{\text{lmPE}}$ at both the VB-local and the VB-delocal levels and, hence, the most aromatic character. For 1, 4, and 7 (linear or straight benzenoids), the aromatic character decreases in the order $1 > 4 > 7$ according to all resonance energies at VB-local level. In VB-delocal, however, only the $E_{\text{res}}^{\text{PE}}$ and the $E_{\text{res}}^{\text{lmPE}}$ show this trend.

The $E_{\text{res}}^{\text{PE}}$ value for 2 is quite small, especially in VB-delocal. However, the $E_{\text{res}}^{\text{PE}}$ and the $E_{\text{res}}^{\text{lmPE}}$ are reasonably high at both the VB-local and the VB-delocal levels. Previous spin-coupled results⁸¹ suggested that 2 is a combination of a distorted benzene ring and an isolated double bond and is a nonaromatic system. The nucleus-independent chemical shift (NICS)^{21,82}

Table 9. Resonance Energy (in kcal/mol) per π Electron for 1–9

system	VB-local			VB-delocal		
	$E_{\text{res}}^{\text{PE}}$	$E_{\text{res}}^{\perp \text{PE}}$	$E_{\text{res}}^{\text{lmPE}}$	$E_{\text{res}}^{\text{PE}}$	$E_{\text{res}}^{\perp \text{PE}}$	$E_{\text{res}}^{\text{lmPE}}$
1	−4.62	−7.36	−7.36	−3.33	−10.13	−10.13
2	−1.48	−3.35	−6.17	−0.53	−5.00	−8.68
3	−0.22	−0.63	−1.20	−0.05	−0.86	−1.63
4	−3.19	−6.14	−6.42	−1.34	−8.31	−9.64
5	−1.44	−1.62	−1.62	−1.97	−3.18	−3.18
6	−2.70	−5.22	−7.18	−1.20	−5.65	−8.66
7	−3.02	−5.14	−5.39	−1.90	−7.24	−7.84
8	−3.55	−6.62	−6.77	−1.50	−8.82	−10.02
9	−3.90	−5.96	−6.30	−2.57	−8.39	−8.85

showed that the six-membered ring is aromatic, while the four-membered ring is antiaromatic, and an overall moderately antiaromatic character was assigned to this system. On the basis of the perpendicular component of magnetic shielding, it was shown⁸³ that **2** is neither an aromatic nor an antiaromatic system. The six-membered ring was classified as a nonaromatic, while the question of the (anti)aromaticity of the four-membered ring was left open. Our VBSCF results show that the resonance in the six-membered ring is of the same magnitude as that in **4**. The $E_{\text{resonance}}^{\text{PE}}$ shows that **2** is stabilized by resonance to some extent. We, therefore, suggest that this system should be considered as nonaromatic if not slightly aromatic. For **3**, a resonance energy of −15.79 kcal/mol was reported⁸⁴ with the VB-local approach in the D_{2h} geometry and including four radical-type structures. Yet the D_{2h} geometry is a transition state between the two symmetry-equivalent C_{2h} minima. In C_{2h} symmetry, the VB wave function of **3** is completely dominated by a single structure (structure **3a** in Figure 2) and results in negligible values for all types of $E_{\text{resonance}}^{\text{PE}}$. The NICS values suggested that **6** is moderately aromatic^{21,82} while **9** is aromatic,^{63,85,86} whereas our VBSCF results show that both **6** and **9** have large $E_{\text{resonance}}^{\text{PE}}$ (nearly of the same magnitude as that of **4**, **7**, or **8**) and are as aromatic in nature as **4**, **7**, or **8**.

In VB-local, the values for all of the $E_{\text{resonance}}^{\text{PE}}$ of **8** are larger than that of **7**, but in VB-delocal the $E_{\text{res}}^{\text{PE}}$ shows the opposite trend. This change is caused by the larger overlap of structure **8a** (the most stable contributing structure of **8**) with the other structures of **8** as compared to the overlap of **7a** or **7b** with the other structures of **7**. As mentioned before, the overlap between the structures (the S matrix in eq 4) lowers the energies of the contributing structures relative to the total energy of the system. We can calculate this overlap as $\sum_i c_i \langle \psi_i | \psi_1 \rangle$ where $\langle \psi_i | \psi_1 \rangle$ are elements of the S matrix and c_i is the coefficient of i th structure. In VB-local, this overlap between **8a** and other structures is 0.7625, while it is 0.7683 in case of **7a** or **7b**. In VB-delocal, it increases to 0.9328 in case of **8a** as compared to 0.8987 in case of **7a** or **7b**. This larger overlap between **8a** and other structures lowers its energy as compared to the energy of **7a** or **7b** and results in smaller E_{res} and $E_{\text{res}}^{\text{PE}}$ for **8** than those for **7**. When the structures are transformed to orthogonal basis (no overlap between the structures), the energy of **8a** again becomes higher than the energy of **7a** or **7b** in VB-delocal, while the total energy of **8** is lower than that of **7**, which results in the larger E_{res}^{\perp} and the $E_{\text{res}}^{\perp \text{PE}}$ for **8** than for **7**.

Because of the use of strictly atomic orbitals, the VB-local approach is generally considered as providing a clear correspondence between the VB structures (spin functions)

and the Lewis or the Kekulé valence structures. In VB-delocal, the orbitals are slightly distorted and have their tails on the neighboring atoms or beyond. To see how much this distortion of the atomic orbitals changes the VB picture of the structures in VB-delocal, we calculated the overlap between the orbitals obtained from VB-local and VB-delocal methods. It has been found that for each system the delocalized atomic orbitals have more than 96% overlap with the strictly atomic orbitals showing that the structures in VB-delocal remain essentially the same as those in VB-local.

Why Is Phenanthrene (8) More Stable than Anthracene (7)? It is well established that the kinked or bent polycyclic benzenoids are more stable than their linear or straight counterparts.^{67,87} The case of **7** and **8** is an archetypal representative. Various experimental^{88–91} and theoretical^{30,92–97} studies have shown that **8** is 4–8 kcal/mol more stable than **7**. The question why kinked benzenoids are more stable than linear ones is still a matter of discussion. Gutman and Stankovic⁹⁸ have found that the greater stability of **8** over **7** is due to the presence of two (symmetry equivalent) disjoint 6π electrons conjugated circuits or Clar's sextets in the former. Bader and co-workers⁹⁹ have reported that the H–H bonding interaction in the bay region in **8** is responsible for its extra stability, as compared to **7**. This proposal of H–H bonding interaction has been challenged both theoretically^{100–103} and experimentally,¹⁰³ and it was shown that, in fact, the H–H interaction in the bay region of **8** is destabilizing rather than bonding.

We present further evidence based on our VBSCF study on **7** and **8** that the extra stability of **8** is not due to the H–H interaction in the bay region; instead, it is a consequence of resonance. The VBSCF calculations on the single most stable structure of **7** (**7a** or **7b**, Figure 2) and **8** (**8a**, Figure 2) were performed, and the results are presented in Table 10. If there

Table 10. VBSCF Energy (atomic units) for the Single Kekulé Valence Structure of **7** and **8**

method	system	
	7a/7b	8a
VB-local	−535.527965	−535.521742
VB-delocal	−535.950550	−535.957943

would be a H–H stabilizing effect, it should be present in the single structure of **8** at both VB-local and VB-delocal levels. In our VBSCF method, the σ orbitals for both systems were taken from a preceding RHF and were frozen. So the H–H interaction if present is included in the core. The π system in both **7** and **8** is equally crude in VB-local (atomic p-orbitals). If it is assumed that the stability of **8** is due to the H–H bonding interaction, its single structure is expected to be more stable than that of **7**. Yet this is not the case (see Table 10). On the other hand, **8** is 3.55 kcal/mol more stable than **7** at the VB-local level (see Table 1), which shows that it is resonance that makes **8** more stable than **7**.

When the local restriction is removed from both systems, the single structure of **8** becomes more stable as compared to that of **7** (Table 10) only by changes in its π electrons system. Note that the energy of the single structure of both systems is lower than the energy of the corresponding structures in the multistructure wave function. This is because in the single structure wave function the orbitals need to minimize the energy of one structure only instead of being a compromise to

minimize the total energy at the expense of the energy of individual structures, and the structure also uses the space of the other (missing) structures both in VB-local and in VB-delocal. This latter effect (which is unavoidable in a single structure calculation) is less prominent in VB-local because the orbitals are not allowed to distort freely. However, in VB-delocal, it is quite obvious where it is in favor of **8a** than **7a** or **7b** because of the symmetry of the former. Structure **8a** transforms as the totally symmetric representation of **8**, while for **7** only the combination **7a** + **7b** transforms as the totally symmetric representation. Therefore, **8a** can adapt the orbitals better than can **7a** or **7b** to recover the effect of the missing structures, although it cannot recover the whole effect of the resonance in the absence of other structures. So the energy of **8a** becomes more negative than that of **7a** or **7b** in VB-delocal. The same effect is also present in the multistructure VB wave function in the form of overlap between the structures (the **S** matrix in eq 4) when the structures are nonorthogonal. As mentioned in the previous section, this overlap is larger between **8a** and the other structures of **8** than **7a** or **7b** and other structures of **7**. It lowers the energy of **8a** as compared to the energy of **7a** or **7b**, and, therefore, a smaller E_{res} for **8** than for **7**. However, in the multistructure wave function, we can transform the VB structures to orthogonal basis to avoid the overlap between them. After this transformation, the energy of **8a** again becomes higher than the energy of **7a** or **7b** in VB-delocal (see Tables 1 and 2), while the total energy of **8** is still lower than that of **7**, which again shows that the resonance is the factor that makes **8** more stable than **7**.

A comparison of the different contributions to the resonance in both systems (Tables 6 and 7) shows that all interactions favor **7**, except those that result from the resonance in the outer six-membered rings of **8** and lead to the 6π electrons conjugated circuits. The collective contribution of these 6π electrons conjugated circuits in **8** dominates all other contributions that favor **7** and makes **8** more stable than **7**. These results are in line with Gutman and Stanković's⁹⁸ findings. We conclude from these results that the extra stability of **8** over **7** is a consequence of resonance and/or delocalization in the π -system and not because of the H–H bonding interaction in the bay region.

Resonance Interactions between Different π Electrons Conjugated Circuits. The π electrons conjugated circuits theory^{27–29} has proven to be very useful in getting insight into aromaticity especially for the big systems that are far beyond the reach of ab initio VB methods. The same can be said about Herdon's semi-empirical VB method.^{31,32} The Kekulé valence structures are central in both of these approaches, and the interactions between these structures are determined empirically to agree with the delocalization energies derived from the Molecular Orbital Theory-based calculations in the former case and the spectroscopic data in the latter case. The resonance energy and the resonance energy per π electrons, calculated by Jiang and Li¹⁰⁴ with their VB approach, have also been used²⁹ to determine these parameters. However, the parameters derived from these VB results show that the interaction between 14π electrons conjugated circuits is more important than that of 10π electrons conjugated circuits, which is counterintuitive.

In our ab initio VBSCF method, the resonance (off-diagonal) interactions between the structures, that is, $\langle \psi_i | \mathbf{H} | \psi_j \rangle$ (short $\psi_a \leftrightarrow \psi_b$), in the orthogonalized **H** matrix give a direct measure of these resonance parameters. The values obtained for these

interactions in **1–9** and the mean values for each type of interaction (conjugated circuit) are collected, respectively, in Tables 11 and 12. The mean values show that the interactions

Table 11. Values for the Resonance Interactions (kcal/mol) between Different π Electrons Conjugated Circuits for **1–9^a**

system	method	
	VB-local	VB-delocal
6π		
1a \leftrightarrow 1b	−44.12 (3.93)	−60.74 (4.07)
2a \leftrightarrow 2b	−39.02 (1.17)	−60.84 (4.17)
4a \leftrightarrow 4b/4c	−40.67 (0.48)	−59.99 (3.32)
6a \leftrightarrow 6b/6c	−43.63 (3.44)	−62.36 (5.69)
6b/6c \leftrightarrow 6d	−38.93 (1.26)	−55.73 (0.94)
7a \leftrightarrow 7b	−38.03 (2.16)	−48.85 (7.82)
7a \leftrightarrow 7d , 7b \leftrightarrow 7c	−39.91 (0.28)	−56.15 (0.52)
8a \leftrightarrow 8b/8c	−41.28 (1.09)	−59.79 (3.12)
8a \leftrightarrow 8d	−36.45 (3.74)	−51.88 (4.79)
8b/8c \leftrightarrow 8e	−43.05 (2.86)	−60.91 (4.24)
9a/9b \leftrightarrow 9c/9d	−40.78 (0.59)	−56.07 (0.60)
9a \leftrightarrow 9e , 9b \leftrightarrow 9f	−36.46 (3.73)	−46.76 (9.91)
10π		
4b \leftrightarrow 4c	−12.76 (0.24)	−23.56 (1.59)
5a \leftrightarrow 5b	−16.23 (3.23)	−31.81 (9.84)
7a \leftrightarrow 7c , 7b \leftrightarrow 7d	−12.02 (0.98)	−21.87 (0.10)
8b/8c \leftrightarrow 8d	−12.12 (0.88)	−14.90 (7.07)
9c/9d \leftrightarrow 9e/9f	−11.86 (1.14)	−17.73 (4.24)
14π		
7c \leftrightarrow 7d	−4.29 (1.18)	−12.58 (6.52)
8d \leftrightarrow 8e	−1.90 (1.21)	−1.67 (4.39)
9a \leftrightarrow 9f , 9b \leftrightarrow 9e	−0.67 (2.44)	−2.66 (3.40)
9e \leftrightarrow 9f	−5.57 (2.46)	−7.34 (1.28)
4π		
2b \leftrightarrow 2c	43.60 (2.98)	43.89 (12.11)
6d \leftrightarrow 6e	37.63 (2.98)	19.67 (12.11)
8π		
2a \leftrightarrow 2c	18.58 (0.65)	32.07 (4.24)
3a \leftrightarrow 3b	21.62 (2.39)	30.21 (2.38)
6b , 6c \leftrightarrow 6e	17.48 (1.75)	21.21 (6.62)
12π		
6a \leftrightarrow 6d	−0.08 (0.70)	−0.58 (1.25)
6a \leftrightarrow 6e	2.42 (1.80)	3.90 (3.23)
6b \leftrightarrow 6c	1.12 (0.50)	2.79 (2.12)
8a \leftrightarrow 8e	0.06 (0.56)	−0.67 (1.34)
8b \leftrightarrow 8c	0.38 (0.24)	0.30 (0.37)
9a \leftrightarrow 9b	−0.21 (0.83)	−2.31 (2.98)
9c \leftrightarrow 9d	0.68 (0.06)	1.28 (0.61)

^aValues in parentheses are the absolute deviations from the corresponding mean values.

Table 12. Mean Values for the Resonance Interactions (kcal/mol) between Different π Electrons Conjugated Circuits

circuit	method	
	VB-local	VB-delocal
6π	−40.19	−56.67
10π	−13.00	−21.97
14π	−3.11	−6.06
4π	40.62	31.78
8π	19.23	27.83
12π	0.62	0.67

in the $(4n+2)$ π electrons conjugated circuits have a negative (stabilizing) contribution, while those in $4n$ π electrons conjugated circuits have a positive (destabilizing) contribution. These negative and positive contributions of, respectively, $(4n+2)$ and $4n$ π electrons conjugated circuits decrease with increasing value of n . Table 12 also shows that these values for all interactions are dependent upon the choice of the orbitals and, except for the 4π electrons conjugated circuit, increase in VB-delocal as compared to those in VB-local. Also, these values are substantially higher than those chosen in refs 27–29,31,32.

CONCLUSION

The resonance energy is a nonobservable property, and its calculated value for any system depends upon the underlying method and its definition. We used two types of p-orbital models (VB-local and VB-delocal) within the framework of VBSCF method to see their effect on the calculated Pauling–Wheland’s resonance energies and the total mean resonance energies of cyclic conjugated systems. In the VB-local method, the variational space of the p-orbitals is restricted, which has an interpretational advantage, but the quality of the VB wave function is not so good. In VB-delocal, the wave function is much better due to the distortion of the atomic p-orbitals, which results in enhanced overlap between the orbitals. It has been found that the choice of these two types of orbitals has a profound effect on the calculated resonance energies and their qualitative trend.

When the contributing structures are nonorthogonal to each other (as in the original Pauling–Wheland’s definition of the resonance energy), each structure also uses the space of the other structures that are present in the wave function. This overlap between the structures (which lowers their energies relative to the total energy of the system) increases in VB-delocal as compared to that in VB-local. The E_{res} calculated with the VB-delocal method is, therefore, generally smaller than that obtained from VB-local for each system studied here, except for compound 5 (azulene).

On transforming the VB wave function to orthogonal basis, the contributing structures are changed and gain some positive energy. In this case, the use of Pauling–Wheland’s definition results in large E_{res}^{\perp} as compared to the E_{res} at the corresponding VB-local or VB-delocal level. As the overlap between the contributing structures is larger in VB-delocal than in VB-local, orthogonalization raises the energy of the structures more in VB-delocal than in VB-local relative to the total energy at the same level. This results in larger E_{res}^{\perp} in VB-delocal than in VB-local. The same trend is found also for the $E_{\text{res}}^{\perp\text{m}}$ with the two choices of the p-orbitals.

For structural isomers, in general, none of the three different resonance energies are in accordance with the order in their total energies in any of the VB-local or VB-delocal methods. For structural isomers in benzenoids only, however, the E_{res}^{\perp} and the $E_{\text{res}}^{\perp\text{m}}$ values are in the same order as their total energies.

The resonance energy in cyclic conjugated systems is a ground-state property, and the VB-delocal method is much better for calculating the ground states of these systems as compared to the VB-local method. We, therefore, conclude that the resonance energies calculated using the VB-delocal method are more reliable than those calculated with the VB-local method. Although the wave function in VB-delocal includes the effect of the ionic and the long-bond (Dewar) structures, the orbitals still remain predominantly atomic orbitals as they have more than 96% overlap with the strictly atomic orbitals in VB-

local in all cases studied here, thus retaining essentially the same correspondence between the VB spin functions and the intuitive Lewis or Kekulé valence structures as in VB-local. Among the three definitions of the resonance energy, the E_{res}^{\perp} and the $E_{\text{res}}^{\perp\text{m}}$ (which are close to each other and show similar trends) are more reliable than the E_{res} because the use of nonorthogonal structures in the latter case can create ambiguities in the estimates of the resonance.

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Notes

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LIST OF ABBREVIATIONS

E , total energy of the system

E_{res} , Pauling–Wheland’s resonance energy with nonorthogonal structures

E_{res}^{\perp} , Pauling–Wheland’s resonance energy with Löwdin-orthogonalized structures

$E_{\text{res}}^{\perp\text{m}}$, total mean resonance energy with Löwdin-orthogonalized structures

$E_{\text{res}}^{\text{PE}}$, resonance energy per π electron

$E_{\text{res}}^{\text{PE}}$, Pauling–Wheland’s resonance energy per π electron with nonorthogonal structures

$E_{\text{res}}^{\perp\text{PE}}$, Pauling–Wheland’s resonance energy per π electron with Löwdin-orthogonalized structures

$E_{\text{res}}^{\perp\text{mPE}}$, total mean resonance energy per π electron with Löwdin-orthogonalized structures

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