J. Phys. Chem. A **2009,** *113,* 5163–5169 **5163**

The Resonance Energy of Benzene: A Revisit

Yirong Mo*

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008

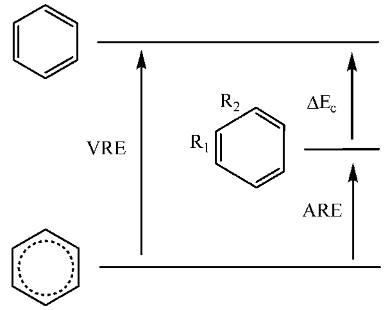
Received: October 9, 2008; Revised Manuscript Received: February 23, 2009

Zielinski and van Lenthe recently extended the block-localized wave function (BLW) method by introducing the resonating BLW (RBLW) method and performed test calculations on hexagonal H_6 and benzene [*J. Phys. Chem. A* **2008**, *112*, 13197]. However, the Pauling's resonance energies from their RBLW and ab initio valence bond (VB) calculations were greatly underestimated largely due to the imperfect use of either one-electron orbitals (method = delocal) or resonance structures (method = local). Whereas it has been well recognized that electronic resonance within a molecular system plays a stabilizing role, there are many indirect experimental evidences available to evaluate the resonance energy and, thus, to justify computational results. Here we used the BLW method, which can be regarded as the simplest variant of modern ab initio VB theory, to re-evaluate the resonance energy of benzene at the B3LYP level, following the original definition by Pauling and Wheland, who obtained the resonance energy "by subtracting the actual energy of the molecule in question from that of the most stable contributing structure". The computed vertical resonance energy (or quantum mechanical resonance energy) in benzene is 88.8, 92.2, or 87.9 kcal/mol with the basis sets of 6-31G(d), 6-311+G(d,p), or cc-pVTZ, respectively, while the adiabatic resonance energy (or theoretical resonance energy) is 61.4, 63.2, or 62.4 kcal/mol, exhibiting insignificant basis set dependency for moderate basis sets. In line with predictions, the geometry optimization of the elusive cyclohexatriene (i.e., the Kekulé structure) with the BLW method also resulted in carbon−carbon bond lengths (e.g., 1.322 and 1.523 Å with the cc-pVTZ basis set) comparable to those in ethylene or ethane.

Introduction

Zielinski and van Lenthe (ZL in short hereafter) recently extended the block-localized wave function (BLW)[1,2] method by introducing the resonating BLW (RBLW) method and performed test calculations on hexagonal H_6 and benzene.[3] The BLW method uses doubly occupied block-localized (or group-localized) molecular orbitals and Slater determinants to construct the wave function for resonance (or in general charge-localized) structures. Thus, the BLW method can be regarded as the simplest variant of the ab initio valence bond (VB) theory with the efficiency of the molecular orbital (MO) theory. ZL confirmed that the removal of spin coupling as the BLW adopts "yields perfectly consistent results" compared with the more general and computationally intensive VB self-consistent field (VBSCF) calculations, but their computed Pauling's resonance energies with both the RBLW and ab initio VBSCF methods seem greatly underestimated. For instance, their ab initio VB benchmark computations of benzene resulted in values of a mere 19.42−27.85 kcal/mol.[4] Before we go into technical details and present more data to elucidate the origin of the discrepancies, we use Scheme 1 to illustrate why ZL's data are fundamentally too low. We note that a more profound and thorough discussion related to Scheme 1 can be found in the excellent review by Shaik and co-workers.[5]

SCHEME 1



ZL's data correspond to the vertical resonance energy (VRE[6,7] or quantum mechanical resonance energy, QMRE[8−10]) as shown in Scheme 1 where the Kekulé structure retains the geometry of benzene with carbon−carbon bond lengths about 1.40 Å. However, with π electrons strictly localized on adjacent carbon−carbon bonds in pairs, the Kekulé structure prefers a bond-alternating geometry, and only the adiabatic resonance energy (ARE[11,12] or equivalently theoretical resonance energy, TRE[4,5,7,9,13]) should be compared with empirical resonance energy (or thermochemical resonance energy, 36 kcal/mol based on the hydrogenation heats[14]) after a few corrections (mostly on the hyperconjugative interaction in the reference molecule cyclohexene).[6,12,15,16] The compression energy ΔE_c[8] is the difference between VRE and ARE. It has been assumed that the single and double carbon−carbon bond lengths in the optimal Kekulé structure are around 1.54 Å (or preferably 1.52 Å, considering the sp^2 hybridization mode on carbon) and 1.34 Å, respectively, corresponding to the bond lengths in ethane and ethylene.[6,8] Thus, ΔE_c can be easily estimated based on the force constants in the prototypes of ethane and ethylene[17] or any modern MO method. For instance, the stretching of the carbon−carbon bond from 1.40 to 1.52 Å for ethane reduces the energy by 6.40 kcal/mol at the B3LYP/cc-pVTZ level, and, similarly, the compressing of the carbon−carbon double bond from 1.40 to 1.34 Å for ethylene stabilizes the system by 3.40 kcal/mol. Summing these energy values together, we can derive ΔE_c, which is three times the sum and equal to 29.4 kcal/mol.

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* Fax: 1-269-387-2909. E-mail: yirong.mo@wmich.edu.

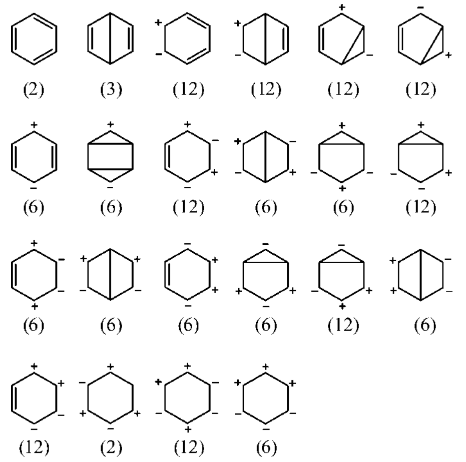
10.1021/jp808941h CCC: $40.75

MP2/cc-pVTZ gives a slightly low but close value, 27.5 kcal/mol. These values are very close to the early prediction, i.e., 30 kcal/mol.[8] Obviously, if ΔE_c were close to or even larger than VRE, then the optimal Kekulé structure with alternating carbon−carbon bonds would be more stable than the delocalized benzene of D_{6h} symmetry, and this is certainly very anti-intuitive and inconsistent with viable experimental evidence. In fact, a simple addition of the compression energy of cyclohexatriene (30 kcal/mol)[8] and the empirical resonance energy (36 kcal/mol)[14] without corrections would result in an empirical VRE value of 66 kcal/mol.[18]

While the resonance theory has become a significant component and a cornerstone in chemical theory,[17,19,20] resonance energy itself is not physically observable and, thus, cannot be experimentally measured in direct ways. However, enormous experimental proofs exist to derive and justify resonance energies. For instance, thermochemical data have been widely cited to derive empirical resonance energies, though care should be taken to include a number of small corrections.[6,12,15,16] The abnormal frequency upshift of the Kekulé-type B_{2u} modes in the 1^1B_{2u} electronically excited state of benzene can also be deciphered by a Kekulé crossing model, which describes the ground and excited states, $^1A_{1g}$ and 1^1B_{2u}, as symmetrical and antisymmetrical combinations of the two Kekulé structures, respectively.[21] As a consequence, the electronic excitation from the ground state of benzene to its 1^1B_{2u} state measures the magnitude of the VRE of benzene.[22] Computationally, various approaches have been devised in an attempt to derive resonance energies and to establish the correlation between experimental proofs and computational results. As such, a wide range of data can be found in the literature regarding the resonance stabilization energy in benzene.[4,7,9,11−13,23−28] In most cases, real reference molecules have been assigned, and various homodesmotic or isodesmic reactions have been proposed to generate the so-called "aromatic stabilization energy". But, here we will focus on the original Pauling−Wheland's definition where the resonance energy is "obtained by subtracting the actual energy of the molecule in question from that of the most stable contributing structure".[20] By this definition, resonance energy becomes an inherent property of a molecule, as it does not depend on any other external reference. As a matter of fact, many researchers have already performed ab initio calculations to directly derive the resonance energy "in its original sense, as the energy difference between the conjugated system and its reference state without resonance".[11] Notably, Kollmar proposed to construct the wave function of the nonresonating structure with isolated double bonds by replacing the delocalized π MOs with localized ethylenic π MOs derived from calculations of ethylene with the same basis set and, subsequently, obtained 95.8 or 96.4 kcal/mol as the VRE of benzene with the minimal or double ζ basis set. Similarly, the ARE of benzene derived by Kollmar is 58.5 or 56.0 kcal/mol.[11] In the latter calculations, the single-bond length was optimized to 1.510−1.527 Å by assuming the double-bond length was 1.34 Å. With the same approach, Shaik et al. got a similar value of 85.2 kcal/mol for the VRE of benzene at the HF/6-31G level.[9,10] With the classical ab initio VB method and the minimal STO-6G basis set, we obtained 74.3 and 44.5 kcal/mol as the VRE and ARE for benzene, respectively.[7] Though there is certain fluctuation among these data due to the calculation levels and basis sets, it is clear that all these data are remarkably larger than those presented by van Lenthe and co-workers.[3,4]

As it seems that different applications within the very same VB theory could lead to very different results, we feel the necessity to sort out the origin of the disparity and to elucidate the difference. In this paper, we will briefly discuss the evolution of the computational strategies for resonance energy from the classical to the modern ab initio VB theories including the BLW method, following the initial proposal by Pauling and Wheland, followed by the derivations of the resonance energy of benzene with the BLW method and various basis sets at the DFT level. Finally, discrepancies between the present data and ZL's data will be discussed.

SCHEME 2



Theoretical Methods

Classical and Modern Ab Initio VB Methods. In being consistent with the resonance theory, which describes a molecular system with a number of resonance structures, where each electron is strictly localized either between two bonding atoms or on one atom, the VB theory[29,30] assumes that the overall molecular wave function, Ψ, is a superposition of all independent configurations

$$\Psi = \sum_{K=1}^{M} C_K \Phi_K \tag{1}$$

and each configuration Φ_K corresponds to a resonance structure K whose wave function is expressed by a Heitler−London−Pauling−Slater (HLSP) function

$$\Phi_K = N_K \hat{A}\{(\varphi_1\varphi_2\varphi_3\cdots\varphi_N)\prod_{ij}[\alpha(i)\beta(j) - \beta(i)\alpha(j)]\prod_{k}\alpha(k)\} \tag{2}$$

where N_K is the normalization constant and $\hat{A}$ is an antisymmetrizer. In the above resonance structure K, two electrons on orbitals φ_i and φ_j form a chemical bond, while orbital φ_k is singly occupied. The number of independent resonance structures is determined by the Rumer spin-coupling patterns.[31] In the case of benzene, if only six π electrons are concerned and only one p_π orbital is considered for each carbon atom, there are a total of 175 resonance structures, as shown in Scheme 2 where the numbers in parentheses refer to the equivalent structures.

In the early days of theoretical chemistry, ab initio computations were not available, but it was perceived that an ionic bond is much more unstable than a covalent bond when two bonding atoms are the same. Thus, for the sake of simplicity, benzene was often illuminatingly described as a hybrid of two Kekulé structures or at most five structures after taking three Dewar structures into account.[17,19] Based on the five resonance structure picture, Pauling and Wheland derived the resonance energy (called Pauling's resonance energy, or PRE, by ZL)[3] as the energy difference between benzene and one Kekulé structure at the Hückel theoretical level.[23] But, we should insist that these early calculations are more conceptual than quantitative.

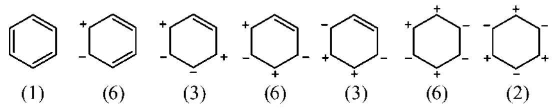
Later, with the advancement of computer technology, ab initio VB methods were developed, and it became viable to re-examine and rethink the resonance theory at the ab initio level. Notably, ab initio VB calculations with all possible 175 resonance structures by Norbeck et al.[32] and Tantardini et al.[26] demonstrated that the five covalent Kekulé and Dewar structures make even a less contribution to the ground state of benzene than the rest of the 170 ionic structures. However, we note that in these calculations one-electron orbitals $\{\varphi\}$ in eq 2 were pure atomic orbitals and no orbital optimization was concerned. As such, VB calculations with pure atomic orbitals $\{\chi\}$ as one-electron orbitals are usually labeled as "classical", and each subsequent HLSP function corresponds to a Heitler−London resonance structure.

In contrast to classical ab initio VB methods, modern ab initio VB methods allow one-electron orbitals to expand with either several selected or overall basis functions and, thus, involve the self-consistent field optimizations. Certainly, one-electron orbitals can be expanded with the basis functions centered on only one atom, and the subsequent SCF calculations lead to the optimal hybrid atomic orbitals. For a chemical bond in a diatomic molecule AB, one-electron orbitals can be expressed as the linear combination of two pure unhybridized atomic orbitals χ_A and χ_B (namely $\chi_A + \lambda\chi_B$ and $\chi_B + \lambda\chi_A$, which are polarized and called Coulson−Fisher orbitals).[33] For multiatomic molecules, this kind of Coulson−Fisher orbital has been extended to the whole molecule in the form of overlap-enhanced orbitals (OEOs)[34]

$$\varphi_i = \chi_i + \sum_{j \neq i} \lambda_{ij}\chi_j \tag{3}$$

The significant advantage of this type of MO-like orbital is that most of the correlation energy can be recovered with only a small number of VB structures. For instance, Cooper, Gerratt, and Raimondi performed spin-coupling VB calculations on benzene using five covalent structures and were able to recover as much as 93% of the correlation energy.[27] The OEOs have been adopted by most ab initio VB methods including the GVB method and play a significant role in the construction of compact wave function independent of the growing size of basis sets.[29] However, we must recognize that OEOs are delocalized to the whole system, and, if we expand the wave function of a Kekulé structure with OEOs into classical forms with pure AOs, we will find that all 175 (more if we use a basis set larger than the minimal set) Heitler−London resonance structures shown in Scheme 2 will be involved. It is also incorrect to exclude "the three Dewar structures in VB calculations with localized orbitals based on the findings with OEOs that the three Dewar structures contribute only about 6−7% each in the case of benzene".[3] The poor description of the ground reference state with localized orbitals and only two Kekulé structures would substantially underestimate VREs (e.g., 48.63−47.98 kcal/mol in benzene with RBLW).[3]

SCHEME 3



Bond-Distorted Orbitals. As the only notable difference between classical ab initio VB and modern ab initio VB lies in the one-electron orbitals orbitals $\{\varphi\}$ in eq 2, we first use the classical VB theory to construct a Lewis resonance structure where each bond has its real references (i.e., a CC single bond similar to ethane and a CC double bond similar to ethylene). From the viewpoint of classical VB theory, a bond between two atomic orbitals χ_A and χ_B centered on atoms A and B, respectively, can be well described as a combination of three Heitler−London structures, including one covalent and two ionic structures as

$$\Psi_{AB} = C_1\Phi(A{:}B) + C_2\Phi(A^+B^-) + C_3\Phi(A^-B^+) \tag{4}$$

where

$$\Phi(A{:}B) = N_1\hat{A}[\chi_A\chi_B(\alpha\beta - \beta\alpha)] \tag{5a}$$

$$\Phi(A^+B^-) = N_2\hat{A}(\chi_B\chi_B\alpha\beta) \tag{5b}$$

$$\Phi(A^-B^+) = N_3\hat{A}(\chi_A\chi_A\alpha\beta) \tag{5c}$$

We note that ab initio calculations have confirmed the necessity to include the two ionic structures to accurately describe the A−B bond dissociation energy profile. As a matter of fact, the ionic Heitler−London structures highlight the polarization of atomic orbitals and charge transfer between two atoms due to the bonding interaction. Now we return to the case of benzene. In our understanding, the Kekulé structure should be equivalent to the hypothetical 1,3,5-cyclohexatriene whose double bonds are comparable to ethylene, whereas the single bonds are similar to ethane, albeit that here the carbon atoms adopt an sp^2 hybridization mode instead of sp^3 in ethane. This is in line with the earliest definition of resonance energy by Hückel, which was the energy difference between the π MOs in a conjugated system and ethylene.[35] The Hückel calculations eventually resulted in the famous Hückel $4n+2$ rule for aromatic molecules, which has been well recognized and broadly employed. As a consequence, the wave function for the Kekulé structure should be expanded by $3^3 = 27$ Heitler−London resonance structures as shown in Scheme 3. Apparently, using OEOs to construct the wave function for the Kekulé structure will result in the "contamination" or "intrusion" by the other $175 - 27 = 148$ Heitler−London resonance structures. The effect of intrusion can be observed in the reduced resonance energy, shortened carbon−carbon single bond (compared with around 1.52 Å), and lengthened carbon−carbon double bond lengths (compared with around 1.34 Å) in the optimal Kekulé geometry.[3,4]

To construct a compact wave function form for the Kekulé structure (and others), we have extended the Coulson−Fisher orbital in an alternative way and proposed bond-distorted orbitals (BDOs) as[36]

$$\varphi_i = \chi_i + \lambda_{ij}\chi_j \tag{6}$$

where $\lambda_{ij} = 0$ if there is no bond between χ_i and χ_j. Thus, BDOs are still strictly localized orbitals which are expanded with the basis functions centered on two bonding atoms. By adopting BDOs as one-electron orbitals and with only one VB structure (here we call it Lewis resonance structure), we were able to achieve almost the identical energy derived from a VB-CI calculation with all 27 Heitler−London VB structures shown in Scheme 3.[36]

Thus, whereas delocalized OEOs allow us to derive a compact expression for the ground state of benzene with a majority of electron correlation taken into account, localized BDOs are essential to derive the electron-localized reference state, which refers to a Lewis structure. Pure atomic orbitals (unless for lone pairs) are inferior to both OEOs and BDOs in practical applications but provide benchmarks for the computation of resonance energies when all configurations (e.g., 175 and 27 Heitler−London structures for benzene and 1,3,5-cyclohexatriene, respectively) are taken into account. It should be pointed out that similar self-consistent localized orbitals have been adopted by Hiberty and co-workers in the study of the resonance effect in carboxylic acids and enols and the validity of the resonance model in formamide and thioformamide using the ab initio VB method.[37]

BLW Method. The BLW method, which is a generalization of the Kollmar's approach, can uniquely and self-consistently define a charge-localized state by assuming that all basis functions and electrons can be partitioned into a few subgroups, and all one-electron orbitals are expanded in terms of the basis functions in only one subgroup.[1] The MOs in the same subgroups are constrained to be orthogonal, but the MOs belonging to different subgroups are nonorthogonal. In fact, the BLW method effectively combines the advantages of the VB and the MO methods and can be regarded as the simplest variant of ab initio VB theory.[12,38−40] The wave function for the hypothetical 1,3,5-cyclohexatriene, where the double bonds are expected to resemble to the ethylene molecule, is

$$\Psi^{\mathrm{BLW}} = N_1\hat{A}[\sigma\phi^2_{\mathrm{C_1C_2}}\phi^2_{\mathrm{C_3C_4}}\phi^2_{\mathrm{C_5C_6}}] \tag{7}$$

where $\varphi_{\mathrm{C}_i\mathrm{C}_j}$ denotes the doubly occupied $\mathrm{C_iC_j}$ π bond and σ represents all σ MOs. In comparison, the wave function for benzene is

$$\Psi = N_0\hat{A}[\sigma\pi_1^2\pi_2^2\pi_3^2] \tag{8}$$

where the π orbitals are delocalized over all six carbon atoms. Note that both Ψ^{BLW} and Ψ are self-consistently optimized. Since the delocalized wave function Ψ corresponds to the real state that is a superposition of all possible resonance states, the energy difference between Ψ^{BLW} and Ψ is generally defined as the electron delocalization energy (ΔE_{DE})

$$\Delta E_{\mathrm{DE}} = E(\Psi^{\mathrm{BLW}}) - E(\Psi) \tag{9}$$

The agreement between the BLW results and the ab initio VB data has legitimated the BLW approach and indicated that the electron correlation, which is largely self-canceled in eq 9, is insignificant in the estimation of electron delocalization energy.[1,40,41] This is in accord with ZL's finding that the removal of spin coupling, which is a major part of the electron correlation effect, yields perfectly consistent results.[3]

The BLW method recently has been extended to the DFT level with the geometrical optimization capability[2,38] and ported to the GAMESS software in house,[42] which enables us to examine the electron delocalization effect in terms of not only molecular energetics, but also geometries.

We would like to note that the BLW method can also be applied to the analysis of intermolecular interactions by decomposing the interaction energy into a few physically meaningful components such as electrostatic, repulsion, polarization, and charge transfer energy terms.[43] The energy decomposition scheme recently introduced by Khaliullin et al. under the name of "absolutely localized molecular orbitals"[44] is essentially identical to our BLW energy decomposition (BLW-ED) approach.

BLW Calculation Results

Most of the definitions of resonance energies are based on reference molecules.[45] But other effects, such as strain, hyperconjugation, Coulomb repulsion imbalance, etc., are often implicated in reference systems and, thus, compromise traditional energetic measures seriously[16,46] and ultimately lead to a wide range of resonance energy estimates in the literature.[4,7,9,12,13,23,24,26,27] The most general and robust definition of resonance energy, however, was originally presented by Pauling and Wheland,[17,19,20,23,47] who stated that the resonance energy can be "obtained by subtracting the actual energy of the molecule in question from that of the most stable contributing structure."[20] For benzene, the most stable resonance structure is the Kekulé structure or 1,3,5-cyclohexatriene, and the original Pauling−Wheland resonance energy can be computed using eq 9.

Table 1 compiles the optimal carbon−carbon bond lengths and resonance energies in benzene at the B3LYP level with the basis sets of 6-31G(d), 6-311+G(d,p), and cc-pVTZ. In a previous paper, we have reported data at the Hartree−Fock (HF) level.[12] ZL pointed out that "Mo's definition of resonance energy, based on block localized wave functions, is heavily basis set dependent".[3] Nevertheless, both geometries and resonance energies listed in Table 1 show insignificant basis set dependency for the basis sets used here. The computed VRE and ARE in Table 1 are also close to the data derived from the Kollmar's method,[5,10,11] suggesting that the relaxation (polarization) of both the σ frame and π orbitals stabilizes the Kekulé structure to a very moderate degree. In addition, the compression energy varies

TABLE 1: Optimal Structural Parameters[a]

basis set	structure	R_1	R_2	VRE	ARE	ΔE_c
6-31G(d)	benzene	1.397	1.397	88.8	61.4	27.4
	1,3,5-cyclohexatriene	1.329	1.528			
6-311+G(d,p)	benzene	1.395	1.395	92.2	63.2	29.0
	1,3,5-cyclohexatriene	1.325	1.532			
cc-pVTZ	benzene	1.391	1.391	87.9	62.4	25.5
	1,3,5-cyclohexatriene	1.322	1.523			

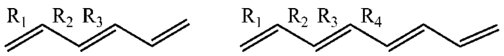
[a] Bond lengths are in Å and bond angles are in degrees for benzene and 1,3,5-cyclohexatriene. Resonance energies are in kcal/mol.

TABLE 2: Optimal Structural Parameters of Real Delocalized and Fictitious Localized All-*Trans* 1,3,5-Hexatriene and Octa-1,3,5,7-tetraene and Their Resonance Energies[a]

basis set	structure	R_1	R_2	R_3	R_4	VRE	ARE
6-31G(d)	delocalized C_6H_8	1.343	1.450	1.351	–	30.2	25.7
	localized C_6H_8	1.329	1.521	1.327	–		
6-311+G(d,p)	delocalized C_6H_8	1.340	1.449	1.349	–	31.7	26.7
	localized C_6H_8	1.326	1.526	1.322	–		
cc-pVTZ	delocalized C_6H_8	1.336	1.446	1.345	–	30.2	25.9
	localized C_6H_8	1.321	1.516	1.319	–		
6-31G(d)	delocalized C_8H_{10}	1.345	1.448	1.357	1.441	47.7	39.8
	localized C_8H_{10}	1.330	1.523	1.329	1.521		
6-311+G(d,p)	delocalized C_8H_{10}	1.343	1.447	1.354	1.440	50.0	41.3
	localized C_8H_{10}	1.327	1.527	1.324	1.526		
cc-pVTZ	delocalized C_8H_{10}	1.339	1.443	1.351	1.436	47.7	40.1
	localized C_8H_{10}	1.323	1.518	1.321	1.516		

[a] Bond lengths are in Å, and relative engeries are in kcal/mol.

SCHEME 4



from 25.5 to 29 kcal/mol and endorses the estimations in the previous text (27.5−29.4 kcal/mol) using model molecules of ethane and ethylene.

As expected, the double-bond length in the optimal Kekulé structure, using the BLW method, is essentially the same as the ethylene bond length (1.32−1.33 Å with various basis sets at the B3LYP level), while the single carbon−carbon bond is very close to that in ethane. The latter suggests that the hybridization of atomic orbitals influences bond lengths insignificantly, as evidenced by the small fluctuation of C−H bond lengths in very different molecules determined experimentally.[48] All these results are consistent with our previous studies.[7,12] For comparison, van Lenthe and co-workers derived the bond lengths 1.369 and 1.433 Å for 1,3,5-cyclohexatriene with the ab initio VB method and the 6-31G basis set.[4] As we have described, both pure atomic and molecular orbitals cannot define the strictly localized double bond well. Only those expanded in the subspace of two bonding carbon atoms can correctly result in a double bond comparable to the ethylene case, as demonstrated by our BLW computations.

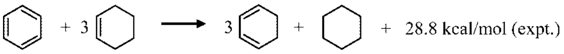
π electron delocalization also stabilizes benzene more than many people initially thought. At the optimal geometry of benzene, the VRE converges to 88 kcal/mol. After costing 26 kcal/mol to distort the σ-frame to a bond-alternating geometry, benzene exhibits an ARE of 62 kcal/mol, compared with 57.5 kcal/mol derived at the HF level.[12] The present ARE is much higher than the experimental estimate 36 kcal/mol, where notably the hyperconjugation effect in the reference molecule cyclohexene is not considered. We have extensively examined literature values and justified the BLW results in a recent full article,[12] where we also adopted the extra cyclic resonance energy (ECRE)[13,28,49] to characterize and measure the extra stabilization (aromaticity) of conjugated rings. ECRE is the difference between the AREs of a full cyclically conjugated compound and an appropriate model having corresponding, but interrupted (acyclic) conjugation. For the present case of benzene, the reference system can be either 1,3,5-hexatriene (ECRE1) or preferably 1,3,5,7-octatetraene (ECRE2), as we have demonstrated[12] that ECRE2[13,28] has a better correlation than ECRE1 with the NICS values.[50] Table 2 lists the geometrical and energetic results, and Scheme 4 shows the labels of bond distances.

Similar to the Kekulé geometry, BLW optimizations consistently result in double-bond lengths of about 1.32 Å and single-bond lengths of about 1.52 Å. Conjugation among the π bonds lengthens the double bonds by 0.015−0.030 Å and shortens the single bonds by 0.070−0.080 Å. These variations are much smaller than those in benzene and echo the much lower resonance energies in these linear polyenes compared with benzene. The difference between the AREs in benzene and 1,3,5-hexatriene or 1,3,5,7-octatetraene, however, measures the extra cyclic resonance stabilization in benzene, which is about 36.5 or 22.3 kcal/mol at the B3LYP/cc-pVTZ level. These data are very similar to our previously reported data (36.7 and 25.7 kcal/mol at the HF/6-311+G(d,p) level) and consistent with a number of reaction energy changes.[12] For instance, ECRE1 (36.7 kcal/mol) is close to the experimental aromatic stabilization energy (ASE, 32.8 kcal/mol) based on the difference between the experimental resonance energy of benzene (49.5 kcal/mol, eq 10) and the resonance energy of 1,3-*cis*-5-hexatriene (16.7 kcal/mol, eq 11).

$$\text{benzene} + 3\ \text{ethane} \rightarrow \text{cyclohexane} + 3\text{ethene} + 49.5\ \text{kcal/mol (expt.)} \quad (10)$$

$$1,3\text{-}cis\text{-}5\text{-hexatriene} + 3\text{ethane} \rightarrow \text{n-hexane} + 3\text{ethene} + 16.7\text{kcal/mol(expt.)} \quad (11)$$

However, the best measure of the aromaticity in benzene is eq 12,[51] which gives an experimental value of 28.8 kcal/mol. This value is very close to ECRE2 (22.3 kcal/mol).



(12)

More discussions related to the aromatic energy can be found in ref 12.

Discussion and Conclusion

Based on the brief historical review of the VB approaches, we understand that the most stable resonance structure in the original Pauling−Wheland's definition of resonance energy is a hypothetical molecule whose double and single carbon−carbon bonds are comparable to those in ethylene and ethane, respectively. This understanding is also in accord with the Hückel's derivation of resonance energy. As such, we propose that benchmark values of Pauling−Wheland resonance energy can be derived with the classical ab initio VB theory in the spirit of full CI method. Within the modern ab initio VB theory where one-electron orbitals are self-consistently optimized in order to get the final wave function compact, however, we proposed the BDOs construct the wave function for the most stable resonance structure. The recently developed BLW method follows the latter proposal and confines electrons in various fragments of a molecule. Both energy values and geometrical parameters are consistent with experimental evidence and chemical hypotheses.

By comparison, we believe that the calculation results by van Lenthe and co-workers are greatly underestimated due to the improper use of delocalized orbitals or insufficiency of important resonance structures when the orbitals are local,[3] and both the geometries and energies cannot be justified by viable experimental proofs and computational results in literature. On one hand, delocalized orbitals (i.e., OEOs) are valuable to get the ground-state energy in a compact form, but they "intrude" on the wave function for the most stable resonance structure, i.e., the Kekulé structure for benzene. On the other hand, using limited resonance structures (two Kekulé structures in ZL's work) with block-localized orbitals cannot describe the ground state reasonably. In both cases, the resonance energy will be greatly underestimated. For instance, ZL's VRE in benzene varies broadly from 18.03 to 48.63 kcal/mol,[3] but all appear too low. The BLW approach provides an efficient way to explore the electron delocalization effect via the optimization of the strictly localized structure (namely the most stable resonance structure) and to derive the resonance energy following the original Pauling−Wheland definition. Computations at the DFT level with basis sets from 6-31G(d) to cc-pVTZ on the hypothetical 1,3,5-cyclohexatriene, where the single or double bonds resemble ethane or ethylene, respectively, demonstrated that the BLW results not only are in agreement with the available ab initio VB and experimental data but also show insignificant basis set dependency.[52]

Acknowledgment. The author thanks the reviewers for their constructive suggestions to improve the presentation of this work. In particular, one reviewer pointed out the correlation of the electronic excitation from the ground to 1^1B_{2u} state with the resonance energy of benzene.

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(52) As for the limitation of the BLW method, we recognized that, "as in other partition schemes, there is an element of arbitrariness, since it is not possible to decide a priori to which subgroup certain basis functions belong if basis functions are centered off the nuclei (e.g., bond functions) or if the basis set become complete".[1] The concept of basis set was introduced well behind the VB and MO theories and, particularly, the presently popular Gaussian-type basis function was introduced by Boys in 1950.[53] The VB theory is established on the understanding that a molecule is composed of individual atoms. Thus, when the atomic characteristics get vague or even disappear, i.e., using a complete (and unphysical) basis set centered on one point of the whole molecule, the VB theory will have difficulty to define individual resonance structures and so will the BLW method. Furthermore, all present basis sets have been devised within the MO theory, and the basis set artifact has been well known. However, we maintain that as long as the atomic characteristics are well retained in the basis functions, the BLW will generate stable results as demonstrated in this work.

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JP808941H