# Bond Lengths, Reactivities, and Aromaticities of Benzenoid Hydrocarbons Based on the Valence Bond Calculations

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**Abstract:** The Lanczos method is employed to solve the valence bond model exactly for $\pi$-electronic systems of benzenoid hydrocarbons. The exact valence bond ground-state wave functions have been obtained for benzenoid hydrocarbons of up to 20 $\pi$ centers. By defining a set of local indices which can be easily calculated from these wave functions, bond lengths, reactivity, and local aromaticity of these benzenoid hydrocarbons have been discussed in a systematic way. The results are in excellent agreement with the known experimental facts and related predictions from molecular orbital theory.

It is commonly assumed that the molecular orbital (MO) theory, even the Hückel type, has made a prominent success in understanding some physical and chemical properties of conjugated molecules.[1–6] In the meantime, simpler versions of valence bond (VB) theory, as applied to benzenoid hydrocarbons (BHs) have been developed under the name of "structure-resonance theory"[7,8] and "conjugated-circuit theory".[9] They have been used to present valuable predictions in reasonably good agreement with chemical facts.[7–16] However, some limitations or discrepancies still remain in certain cases. Let's review a few known results for instance. The relative weight of each benzene ring in the enumeration of Kekulé structures[8b,14,16] often correlates very well with the relative aromatic character of the component rings but fails to differentiate between the local aromaticity of polyacene-like hydrocarbons. On the other hand, Pauling bond orders defined in terms of Kekulé structures give a good prediction on C–C bond lengths, yet equal value of bond orders occurs quite often in a given molecule which correlates to different bond lengths.[10] Over the past years, various approximate VB schemes[17,18] have also been developed to investigate ground-state properties of BHs, but some results still seem unsatisfactory.[18c,d] Obviously, exact VB calculations are required to justify those results obtained from various approximate VB schemes. It is well-known that the exact solution of the VB eigenproblem appears to increase rapidly in difficulty due to the dimension of the Hamiltonian-space being in exponentially proportional to the size of the chemical system. Although the spin and space symmetry are usually utilized to block-diagonalize the VB matrix, yet the solution of blocks remains formidable for medium size molecules by the standard diagonalization technique. More efficient computational techniques are essential. Recently, Alexander and Schmalz[19] have applied the unitary group approach to solve the VB model exactly for BHs with up to about 24 $\pi$ electrons. The exact VB ground-state energy has been obtained for these molecules, and the relative aromatic character of these molecules has been discussed by using these energies. Cioslowski[20] has presented another efficient computational algorithm to exactly solve the ab initio VB Hamiltonian and obtained the optimized geometry of several BHs having up to 18 carbon atoms. In this paper, we demonstrate that within the framework of VB theory molecular ground-state properties such as bond lengths, site reactivities, and local ring aromaticities can be interpreted in a systematic way based on a set of suitably defined local indices which are calculated from ground-state wave functions. We employ the Lanczos method,[21] which has been becoming a powerful tool to the treatment of many-body problems,[22] to diagonalize the VB Hamiltonian and calculate the VB ground-state wave functions (also including the corresponding ground state energies). In this way, all BHs having up to 20 $\pi$ centers

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have been discussed in detail. The results are compared with the experimental facts along with previous VB and related MO results.

The organization of this paper is as follows. In section II we describe the VB model and the computational method. In section III we employ the VB ground-state wave functions calculated with the computational method described in section II to discuss bond lengths, reactivities, and local aromaticities for a set of benzenoid hydrocarbons, respectively.

## The Valence Bond Model and the Computational Method

**The Valence Bond Model.** For neutral benzenoid hydrocarbons, the semiempirical VB model has long been extensively accepted and adopted (see recent review[23]). Supposing that all sites and bonds are identical, the nearest-neighbor VB Hamiltonian can be written as follows[23]

$$H = J\sum_{i-j}(2S_i\cdot S_j - {}^1/_2) \tag{1}$$

where $S_i$ is the spin operator for site i, $J$ is an (positive) exchange parameter, and i−j denotes nearest-neighbor sites. This model has proven to be the second-order effective Hamiltonian which can be derived from the quasi-degenerate perturbation theory[24] and other methods,[25,26] being equivalent to the Heisenberg model Hamiltonian used in solid-state physics.[27] Although this model can be further improved by introducing higher order corrections according to the above methods for deriving it, it seems to work so well for benzenoid hydrocarbons, because the two most important corrections tend to cancel in six-membered rings but not in rings of other size in which this spin Hamiltonian should be used cautiously.[19] Obviously, such a model Hamiltonian operates solely on the space of covalent VB structures, which consists of all possible ways of distributing spin-up or spin-down to these singly occupied orbitals consistent with the required total spin of the molecular state. Due to the commutativity of total spin $S$ or the $z$ component $S_z$ of $S$ with $H$, namely, $[S,H] = 0$ (or $[S_z,H] = 0$), one can diagonalize the VB model-(1) in the subspace in which $S$ (or $S_z$) is conserved. One straightforward way to obtain the VB ground-state wave function is to diagonalize the VB matrix in the basis of neutral Slater determinants. An efficient technique for the diagonalization of large matrices is the Lanczos method[21] which we give an outline in the following.

**The Computational Method.** The central idea of the Lanczos method is to transform a general quantum model to a chain model or, in matrix language, to transform a general symmetric matrix to a tridiagonal matrix.

First, this technique requires the selection of an initial state $\psi_0$ (normalized to one). If $\psi_0$ has a nonzero projection over the true ground state $\psi$ of the Hamiltonian (1), the method can give a good approximation to the ground state of $H$ as accurate as possible. Otherwise it will converge to an excited state. In the present work, the classical Néel state is usually chosen as an initial state to determine the ground state of $H$, but for other low-lying excited states, the lowest energy determinants (having the maximum number of spin alternation) occurring in various $S_z$ subspaces can be taken as starting states to obtain the low-lying states in these subspaces, after comparing the energies of these states, the first excited state and other low-lying excited states can be picked out.

By operating with $H$ on $\psi_0$, we define a state $\psi_1$ as follows:

$$\psi_1 = (H\psi_0 - a_0\psi_0)/b_1 \tag{2}$$

where constants $a_0$ and $b_1$ are calculated by

$$a_0 = \langle\psi_0|H|\psi_0\rangle \tag{3}$$

$$b_1^{\,2} = \langle(H\psi_0 - a_0\psi_0)|(H\psi_0 - a_0\psi_0)\rangle \tag{4}$$

It is obvious that $\psi_1$ is normalized to one and orthogonal to $\psi_0$.

Once we have obtained $\psi_0$ and $\psi_1$, we can construct a set of orthonormal states $\{\psi_2,\psi_3,...,\psi_n\}$ in succession with the following relation

$$\psi_n = (H\psi_{n-1} - a_{n-1}\psi_{n-1} - b_{n-1}\psi_{n-2})/b_n \tag{5}$$

where

$$a_{n-1} = \langle\psi_{n-1}|H|\psi_{n-1}\rangle \tag{6}$$

$$b_n^{\,2} = \langle(H\psi_{n-1} - a_{n-1}\psi_{n-1} - b_{n-1}\psi_{n-2})|(H\psi_{n-1} - a_{n-1}\psi_{n-1} - b_{n-1}\psi_{n-2})\rangle \tag{7}$$

Obviously, all $\psi_i$ ($i \le n$) span a tridiagonal symmetric matrix of $H$ with diagonal entries $\{a_0,a_1,...,a_{n-1}\}$ and their nearest-neighbor off-diagonal entries $\{b_1,b_2,...,b_n\}$ represented by a chain-graph.[22c] Then the secular equation for the chain model is prepared to solve the eigenvalues instead of the original Hamiltonian matrix. If we limit ourselves to the ground state and a few low-lying excited states, the recursion procedure can terminate at some earlier stage with a tridiagonal matrix of less dimension which is steady to give the stable numerical results for these low-lying eigenvalues. In other words, these low-lying eigenvalues within a given precision are no longer changed on increasing the dimension of the tridiagonal matrix. This has been discussed in detail elsewhere.[22c] It should be pointed out that the solution of the tridiagonal matrix allows us to evaluate the corresponding eigenvectors in the tridiagonal basis. In order to obtain the eigenvectors in the original Hilbert space, we must repeat the tridiagonalization technique accumulating the basis vectors with their corresponding weights.

## Results and Discussions

Using the standard Lanczos method described above we have calculated the VB ground-state wave functions for a series of benzenoid hydrocarbons with up to 20 $\pi$-electrons, altogether with their ground-state energies. Among them, we have neglected the little nonplanarity for benzophenanthrene for simplicity. As expected, the ground-state energies for these molecules reproduce the results previously given by Alexander and Schmalz.[19] We have carried out these calculations on a SUN SPARC 2 workstation which is incapable of dealing with those molecules of 24 $\pi$ sites that probably represent the calculable limit of our program even if a supercomputer is implemented. It should be stressed that the Lanczos method can be easily programmed and requires less storage and computational time so that the ground-state calculations even for a molecule of 18 $\pi$ sites can be finished on 486 personal

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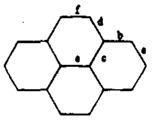
**Table 1.** Experimental and Calculated Bond Lengths (Å)

| compd | bond | singlet probability | bond length exptl[a] | bond length calcd | calcd-exptl |
|---|---|---|---|---|---|
| benzene | | 0.717 | 1.397 | 1.395 | −0.002 |
| pyrene | a | 0.718 | 1.395 | 1.395 | 0.00 |
| | b | 0.666 | 1.406 | 1.411 | 0.005 |
|  | c | 0.616 | 1.425 | 1.427 | 0.002 |
| | d | 0.586 | 1.438 | 1.437 | −0.001 |
| | e | 0.615 | 1.430 | 1.428 | −0.002 |
| | f | 0.807 | 1.367 | 1.367 | 0.00 |

[a] Values are from ref 10 and references therein.

computer within 1 h. In the following we will interrelate these results and certain physical and chemical properties of these BHs.

**Bond Lengths.** Through a simple transformation, the VB model (1) can be expressed as the sum of the diagonal operator $H_D$ and the off-diagonal operator $H_I$, i.e.

$$H = H_D + H_I \tag{8}$$

where

$$H_D = -J\sum_{i-j}(a_{\bar{i}}^{+} a_j^{+} a_j a_{\bar{i}} + a_i^{+} a_{\bar{j}}^{+} a_{\bar{j}} a_i) \tag{8a}$$

$$H_I = J\sum_{i-j}(a_{\bar{i}}^{+} a_j^{+} a_{\bar{j}} a_i + a_i^{+} a_{\bar{j}}^{+} a_j a_{\bar{i}}) \tag{8b}$$

In eqs 8a and 8b $a_{\bar{i}}^{+}$ and $a_i$ are the creation operator of the spin-down and the annihilation operator of the spin-up at site $i$, respectively. If one defines the probability of finding a singlet arrangement between atoms $i$ and $j$ through[28]

$$P_{ij}^{s} = \langle\Psi|1/2(a_i^{+} a_{\bar{j}}^{+} - a_{\bar{i}}^{+} a_j)(a_{\bar{j}} a_i - a_j a_{\bar{i}})|\Psi\rangle \tag{9}$$

where $\psi$ represents the ground state of Hamiltonian (1), then the total energy of the ground state in the VB scheme can be expressed as

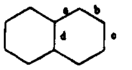
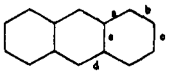
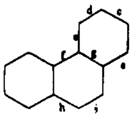
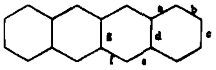
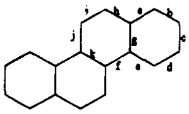
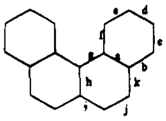
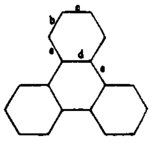
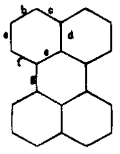
$$E_\pi = \langle\Psi|J\sum_{i-j}(2S_iS_j - {}^1/_2)|\Psi\rangle = \langle\Psi|H_D + H_I|\Psi\rangle$$

$$= -2J\sum_{i-j}P_{ij}^{s} \tag{10}$$

Equation 10 shows that the VB energy of a molecule can be partitioned into the sum of the probabilities of finding local singlet arrangements on its various bonds. This result is analogous to the well-known result of the Hückel MO theory where the total energy is proportional to the sum of the bond orders. The analogy between the bond order in the MO approach and local singlet probability in the VB approach suggests that $P_{ij}^{s}$ may be used to measure the strength of the i−j bond and correlate with the $i-j$ bond length. In the following, we call $P_{ij}^{s}$ as ground-state singlet probability (SP) of $i-j$ bond in short.

By using the VB ground state wave functions obtained above, we have calculated the ground-state SPs on various bonds for these BHs. To investigate whether it is possible to apply these SPs to predict carbon−carbon bond lengths in BHs, we depict the correlation between experimental bond lengths and ground-state SPs for ten molecules listed in Tables 1 and 2 of Figure 1.

**Table 2.** Bond Lengths in Benzenoid Hydrocarbons (Å)

| compd | bond | singlet probability | bond length exptl[a] | bond length calcd | calcd-exptl |
|---|---|---|---|---|---|
| naphthalene | a | 0.628 | 1.422 | 1.423 | 0.001 |
| | b | 0.766 | 1.371 | 1.380 | 0.009 |
|  | c | 0.661 | 1.412 | 1.413 | 0.001 |
| | d | 0.619 | 1.420 | 1.426 | 0.006 |
| | | | ±0.008 | | ±0.004 |
| anthracene | a | 0.613 | 1.444 | 1.428 | −0.016 |
| | b | 0.775 | 1.375 | 1.377 | 0.002 |
|  | c | 0.649 | 1.418 | 1.417 | −0.001 |
| | d | 0.673 | 1.405 | 1.409 | 0.004 |
| | e | 0.594 | 1.433 | 1.434 | 0.001 |
| | | | ±0.008 | | ±0.005 |
| Phenanthrene | a | 0.646 | 1.423 | 1.418 | −0.005 |
| | b | 0.751 | 1.386 | 1.385 | −0.001 |
| | c | 0.678 | 1.394 | 1.408 | 0.014 |
| | d | 0.748 | 1.401 | 1.386 | −0.015 |
|  | e | 0.655 | 1.409 | 1.415 | 0.006 |
| | f | 0.557 | 1.465 | 1.446 | −0.019 |
| | g | 0.634 | 1.420 | 1.422 | 0.002 |
| | h | 0.588 | 1.453 | 1.436 | −0.017 |
| | i | 0.807 | 1.350 | 1.367 | 0.017 |
| | | | ±0.008 | | ±0.011 |
| tetracene | a | 0.608 | 1.420 | 1.430 | 0.010 |
| | b | 0.777 | 1.381 | 1.376 | −0.005 |
| | c | 0.646 | 1.459 | 1.418 | −0.041 |
|  | d | 0.586 | 1.420 | 1.437 | 0.017 |
| | e | 0.681 | 1.390 | 1.407 | 0.017 |
| | f | 0.655 | 1.404 | 1.415 | 0.011 |
| | g | 0.574 | 1.460 | 1.441 | −0.019 |
| | | | ±0.010 | | ±0.017 |
| chrysene | a | 0.640 | 1.428 | 1.420 | −0.008 |
| | b | 0.754 | 1.363 | 1.384 | 0.021 |
| | c | 0.673 | 1.394 | 1.409 | 0.015 |
| | d | 0.751 | 1.381 | 1.385 | 0.004 |
| | e | 0.649 | 1.409 | 1.417 | 0.008 |
|  | f | 0.571 | 1.468 | 1.442 | −0.026 |
| | g | 0.629 | 1.409 | 1.423 | 0.014 |
| | h | 0.599 | 1.421 | 1.433 | 0.012 |
| | i | 0.792 | 1.369 | 1.372 | 0.003 |
| | j | 0.611 | 1.428 | 1.429 | 0.001 |
| | k | 0.655 | 1.401 | 1.415 | 0.014 |
| | | | ±0.010 | | ±0.011 |
| benzophenanthrene | a | 0.628 | 1.431 | 1.423 | −0.008 |
| | b | 0.642 | 1.391 | 1.419 | 0.028 |
| | c | 0.754 | 1.374 | 1.384 | 0.010 |
| | d | 0.673 | 1.409 | 1.409 | 0.000 |
| | e | 0.753 | 1.378 | 1.384 | 0.006 |
|  | f | 0.646 | 1.433 | 1.418 | −0.015 |
| | g | 0.578 | 1.446 | 1.439 | −0.007 |
| | h | 0.656 | 1.412 | 1.415 | 0.003 |
| | i | 0.603 | 1.430 | 1.431 | 0.001 |
| | j | 0.795 | 1.342 | 1.371 | 0.029 |
| | k | 0.598 | 1.443 | 1.433 | −0.010 |
| | | | ±0.010 | | ±0.011 |
| triphenylene | a | 0.665 | 1.410 | 1.412 | 0.002 |
| | b | 0.739 | 1.381 | 1.388 | 0.007 |
|  | c | 0.688 | 1.397 | 1.405 | 0.008 |
| | d | 0.646 | 1.413 | 1.418 | 0.005 |
| | e | 0.531 | 1.458 | 1.454 | −0.004 |
| | | | ±0.006 | | ±0.005 |
| perylene | a | 0.687 | 1.418 | 1.405 | −0.013 |
| | b | 0.748 | 1.370 | 1.386 | 0.016 |
|  | c | 0.631 | 1.400 | 1.423 | 0.023 |
| | d | 0.617 | 1.424 | 1.427 | 0.003 |
| | e | 0.614 | 1.425 | 1.428 | 0.003 |
| | f | 0.702 | 1.397 | 1.400 | 0.003 |
| | g | 0.523 | 1.471 | 1.457 | −0.014 |
| | | | ±0.004 | | ±0.011 |

[a] Values are from ref 10 and references therein.

Clearly, there exists a good linear relationship between the bond length and the corresponding ground-state SP. In order to predict the C−C bond lengths in BHs from the viewpoint of VB theory, we must establish the appropriate empirical formula

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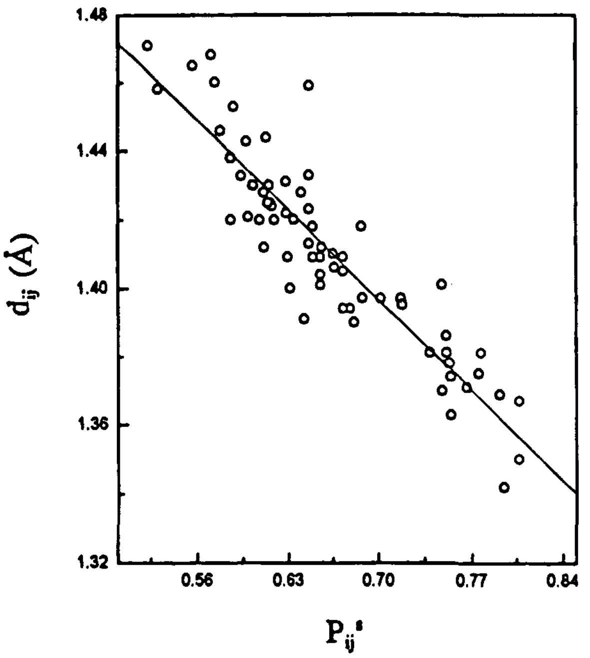

**Figure 1.** Relation between ground-state singlet probabilities and experimental bond lengths for all BHs listed in Tables 1 and 2.

between the bond length and the corresponding ground-state SP as is frequently done in the MO approach.[1] Because the VB model (1) homogenizes all sites and all bonds, it is suitable to select two typical species, benzene and pyrene, to determine this formula. In this way, both of the calculated ground-state SPs and experimental bond lengths for these two molecules are listed in Table 1 which are fitted to induce the good linear formula below

$$d_{ij}(\text{Å}) = 1.622 - 0.316\,P_{ij}^{s} \qquad (11)$$

where $d_{ij}$ denotes the length of $ij$ bond. Inversely, all bond lengths of benzene and pyrene calculated from eq 11 together with average deviations referring to experimental values are also collected in Table 1. At first sight, one immediately notes that average deviations listed in Table 1 are rather smaller than the corresponding deviations in fitting Conlson HMO bond orders with bond lengths and comparable to the deviations occurring in fitting Pauling bond orders with bond lengths.[10] In addition, the relative variations in bond lengths from bond to bond in pyrene are accurately predicted by their SP indices. It reveals that ground-state SP index defined by eq 9 and fulfilling the additivity relation eq 10 is probably a well-behaved local index which can be utilized to give reasonable predictions on bond lengths for other BHs.

Accordingly, calculated bond lengths and corresponding ground-state SPs, together with experimental values and average deviations defined before for several selected BHs are listed in Table 2. From Table 2, the average deviation of calculated and experimental values is ±0.009 Å, slightly larger than the average estimated experimental error of ±0.008Å[10] and comparable to the results given by Cioslowski based on the ab initio VB approach.[20]

One can see that the average deviation and the biggest error between the calculated and experimental bond lengths for a certain molecule depend on the approximate extent of Hamiltonian (1) in which equal $J$ for each C−C bond is assumed. For examples, in triphenylene almost all bond lengths are predicted in remarkable agreement with their experimental values presumably because this molecule can be regarded as being composed of three benzene rings joined together through approximate single bonds[1] thus in a larger extent it fulfills the assumption of Hamiltonian (1). While the correlation given by eq 11 is less perfect for tetracene probably owing to its diminished aromatic character described in the later section, such that equal $J$-value assumption is rather approximate.

**Orientation of Electrophilic Aromatic Substitution.** In the MO treatment, various indices such as free valence,[29] localization energy,[30] and other quantities[31,32] have been introduced to predict the orientation of electrophilic aromatic substitution. In the VB approach, sevaral indices have also been formulated.[12b,33] Here we give a treatment based on accurate VB calculations. According to eq 10, the total VB energy can be partitioned into the sum of the quantities with respect to each site, i.e.

$$\begin{aligned} E_\pi &= -2J\sum_i \sum_{j>i} P_{ij}^{s} \\ &= \sum_i E_i \end{aligned} \qquad (12)$$

where

$$E_i = -J\sum_{i-j} P_{ij}^{s} \qquad (12a)$$

Considering $P_{ij}^{s}$ is a well-behaved local index on i−j bond as indicated above, therefore $E_i$ (negative) can be feasibly understood as the local site-energy of the $i$th atom. When an electrophilic substitution occurs, one is primarily concerned with how the total energy changes as an electrophilic group attacks a certain carbon atom. Supposing lengths of those bonds bound to the $i$th atom are equally varied in the preliminary stage of the electrophilic attack, causing a change of exchange parameter $J$, the first-order change in the total $\pi$-energy of this molecule can be easily evaluated with

$$\Delta E_i = \Delta J(-2\sum_{i-j} P_{ij}^{s}) \qquad (13)$$

Thus $\Delta E_i$ (positive) is proportional to the site-energy $E_i$ of the $i$th atom defined by eq 12a, indicating that the site-energy $E_i$ can be anticipated to serve as a reactivity index for electrophilic aromatic substitution. i.e., the smaller the absolute value of site-energy is, the more reactive it will be. For a few selected BHs, calculated site-energy values and Hammett's $\sigma^+$ constants[1] obtained from the empirical fitting of experimental data are given in Table 3. Figure 2 shows the correlation of $E_i$ and $\sigma^+$. We see that $E_i$ correlates well with $\sigma^+$.

Remembering that those indices within the framework of MO theory also give good correlations with reactivities,[29−32] the good correlation between the site-energy index and reactivities does indicate there exists some inherent relationship between these two different theories.[18a,26c]

**Local Aromaticity.** Based on a large amount of experimental results and empirical rules, Clar[34] proposed the concept of the aromatic sextet to explain the relative stability of isomeric BHs and the local aromaticity of individual hexagons within a polycyclic benzenoid hydrocarbon. There have been many

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**Table 3.** Reactivity Indices for Selected BHs[a]

| compd | position | $E_i$[b] | $\sigma^+$ [c] | compd | position | $E_i$[b] | $\sigma^+$ [c] |
|---|---|---|---|---|---|---|---|
| **1** | 1 | 1.434 | −7.8 | **5** | 5 | 1.336 | 9.8 |
| **2** | 1 | 1.394 | 0.0 | **6** | 7 | 1.350 | 6.6 |
| | 2 | 1.427 | −3.4 | | | 1.355 | 6.6 |
| **3** | 1 | 1.388 | 1.1 | **7** | 6 | 1.391 | 2.6 |
| | 2 | 1.424 | 0.0 | **9** | 1 | 1.404 | −0.8 |
| | 9 | 1.346 | 8.1 | | 2 | 1.427 | −2.3 |
| **4** | 1 | 1.397 | −0.2 | **10** | 1 | 1.383 | 6.1 |
| | 2 | 1.429 | −2.5 | | 2 | 1.436 | |
| | 3 | 1.426 | −0.5 | | 4 | 1.393 | |
| | 4 | 1.403 | −2.7 | **11** | 3 | 1.377 | 8.4 |
| | 9 | 1.395 | 0.5 | **13** | 6 | 1.339 | 11.1 |

[a] The numbering of compounds and their positions (C atoms) are shown in Figure 3. [b] In units of $-J$. [c] Values are from ref 1.

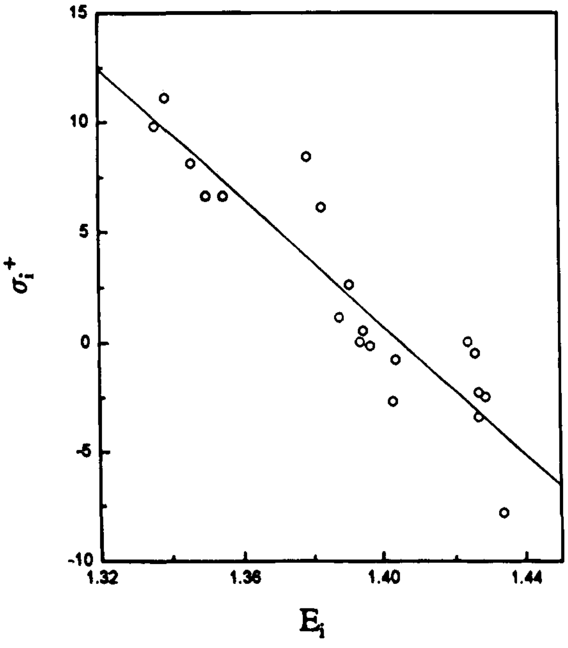

**Figure 2.** Correlation of $E_i$ values with experimental reactivities.

investigations[8b,14,35−39] in formulating the mathematical indices to quantify Clar's intuitive ideas. Here, we intend to discuss this problem from the exact VB model. Similar to Herndon−Ellzey's definition of local aromaticity,[8b] we define the relative local hexagon energy (RLHE) as the ratio of the local hexagon energy to the ground-state energy of benzene to measure the local aromaticity of individual rings. Due to the additivity of singlet probabilities on various bonds as indicated in eq 10, the local energy of each hexagon in the ground state of a given BH can be directly calculated by

$$E_r = -2J\sum_{i-j} P_{ij}^s \tag{14}$$

where the $i-j$ signifies the bond in the rth hexagon. In Figure 3, we give the results for all BHs containing up to 20 $\pi$ sites.

Obviously, our results are in good agreement with the qualitative ideas represented by the Clar structures. For example, the local aromaticity for each hexagon of the polyacene monotonously decreases from terminal toward the center analogous to the dilution of the aromatic sextet. The central ring in triphenylene and perylene shows least aromatic character compatible with the Clar's postulate of "empty" ring. From the viewpoint of MO theory, the PPP-BC index[16] is assumed to be capable of quantitatively figuring out the concept of the Clar's aromatic sextet. To compare results from these two

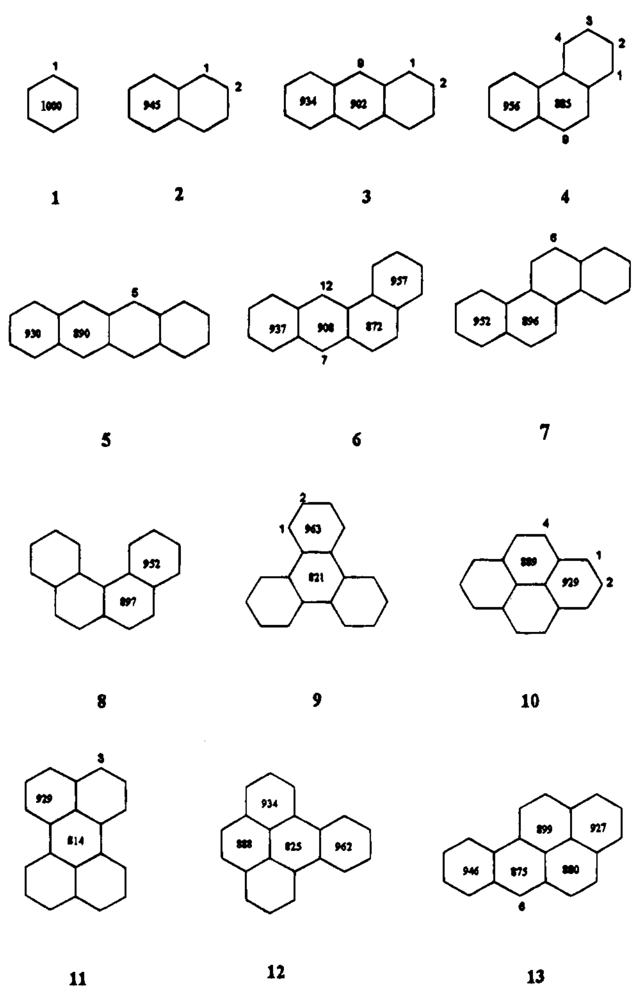

**Figure 3.** RLHE values of benzenoid hydrocarbons containing up to 20 $\pi$ centers. Values are given as 1000RLHE.

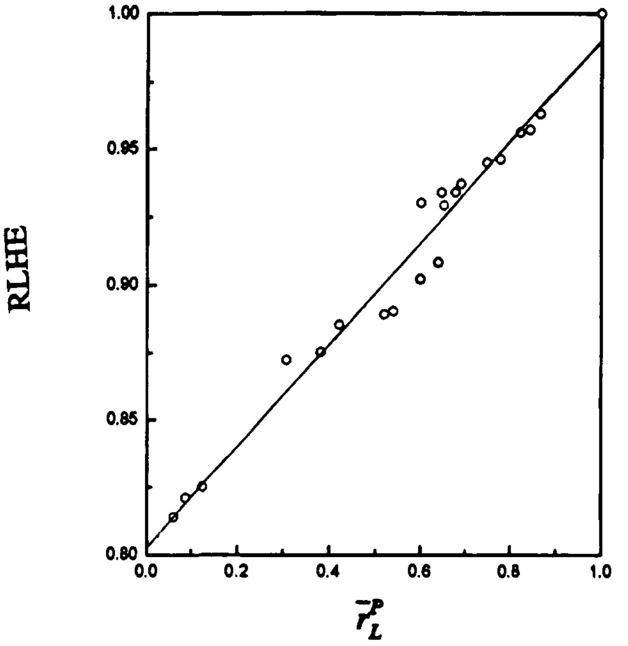

**Figure 4.** Relation between the RLHE and the normalized benzene character calculated by using PPP-MO method.

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different approaches, we plot the RLHE values against the $\bar{r}_{\mathrm{L}}^{\mathrm{P}}$ values (normalized benzene character in the PPP approach) for all BHs displayed above in Figure 4.

It is apparent that a linear relationship holds very well in Figure 4, again indicating the consistency of MO (PPP-scheme) and VB models in explaining the local aromaticity of BHs. Moreover, it is encouraged that RLHE index provides the correct predictions of local aromaticity for polyacene and benz[*a*]-anthracene, avoiding the limitation of those indices[8b,14,16] based solely on the enumeration of the Kekulé structures although for other molecules our calculations agree with them.

## Conclusions

We have employed the Lanczos method to solve the VB model exactly for $\pi$-electronic systems of benzenoid hydrocarbons with up to 20 carbon atoms. The exact VB ground-state wave functions have been obtained for these molecules. By introducing and defining local indices known as singlet probability, site-energy, and relative local hexagon energy which can be easily evaluated by using ground-state wave functions, thus bond lengths, orientation of electrophilic aromatic substitution, and local aromaticities for these BHs have been discussed systematically. The predictions from them agree very well with the corresponding experimental facts and the deductions of MO theory. The calculations presented in this paper may have been clarifying those questions arising from the approximations in previous VB schemes and justifying those results obtained from various types of approximate VB versions. Except for some special BHs like polyacene pointed out above, our calculations tend to support that those simple VB approaches like "structure-resonance theory" and "conjugated-circuit theory" can also provide reasonably good insight into some physical and chemical properties for those BHs beyond the capability of exact VB calculation.

In summary, our work leads one to draw a conclusion that VB theory can also make the same correct predictions for the $\pi$-electronic properties of benzenoid hydrocarbons as MO theory, being consistent with the relationship underlying these two different theoretical approaches.[18a,26c]

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