Can the Low-Lying Electronic States of Benzenoid Hydrocarbons Be Described by the Semiempirical Valence Bond Approach?

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The low-lying excited states of benzenoid hydrocarbons with up to 22 π-electrons have been obtained from exact semiempirical valence bond (VB) calculations. The effective valence bond (EVB) model, which implements nonadjacent and cyclic six-body interactions on the basis of the classical valence bond (CVB) model, is shown to give satisfactory predictions of the low-lying excited spectra of small benzenoids with no more than 14 π-electrons. For larger benzenoid systems, the CVB model can account well for their lowest excited spectra, being in good agreement with the available experimental data and semiempirical PPP molecular orbital results. In addition, a good quadratic relationship between the energy difference between the ground and first excited states and the number of Kekulé valence structures is revealed among the isomeric benzenoid systems.

Introduction

There have been several threads of development concerning valence bond (VB) ideas[3−6] parallel to the prominent success of the molecular orbital (MO) theory in understanding many physical and chemical properties of conjugated molecules.[1,2] It has been seen that activity in applying π-electron's VB theory to benzenoid hydrocarbons has continued over the years with much widening interest during the last few years.[5−10] Recently, it has been demonstrated that some ground-state properties of benzenoid hydrocarbons can be successfully interpreted by the exact results of the classical VB (CVB) theory of Pauling and Wheland,[9,10] which had been thought to be the particular province of the MO theory. In addition to that, a question of common interest still remains unanswered: can the low-lying excited states of benzenoids be described by the valence bond approach?

Compared with ground states of benzenoid hydrocarbons, the low-lying excited states of these systems are less studied from the π-electron's semiempirical VB approaches. This is not accidental because even for benzene the descriptions of the nearest-neighbor CVB theory for its low-lying excited states are unsatifactory.[11] For example, the singlet−triplet (S−T) energy gap of benzene calculated from the CVB model is too small compared to the corresponding experimental value. Thus Malrieu and Maynau[11] pointed out that the CVB model should be improved by introducing nonadjacent and cyclic six-body contributions to describe the low-lying electronic states of benzenoid hydrocarbons. In fact, the effective valence bond (EVB) model,[11] which derived from the Hubbard model via the degenerate many-body perturbation theory, is an attempt toward this goal. As we know, the simplest (second-order) form of this model is essentially the CVB model, while nonadjacent and cyclic many-body interactions are included automatically in higher order corrections. For simplicity, the CVB model with higher order corrections will be termed as the EVB model throughout this paper. It has been shown that the low-lying electronic spectra of benzene calculated from the EVB model are in good agreement with experiments.[11] However, due to the computational complexity of the CVB and EVB models, the low-lying excited states of benzenoid systems other than benzene have not been investigated in this way. Recently, we show that for medium-sized conjugated systems the exact solutions of the CVB and even EVB model can be obtained by using the Lanczos algorithm.[10,12] In this work, firstly, we focus our attention on the low-lying excited spectra of a series of benzenoid species by exactly solving the CVB and EVB models. Our results are compared with the known experimental data and the corresponding MO values. Secondly, we want to investigate whether or not the EVB model is necessary in interpreting the low-lying excited spectra of benzenoid hydrocarbons larger than benzene. In addition, we try to correlate the calculated energy difference between the ground and first excited states with the number of Kekulé valence structures for benzenoid isomers, because this correlation may be very useful for predicting the band gaps of benzenoid polymers and the kinetic stability of larger carbon clusters like C_{60}.

Semiempirical Valence Bond (VB) Models

Classical Valence Bond (CVB) Model. For neutral benzenoid hydrocarbons, the semiempirical CVB model has long been extensively accepted and adopted (see recent review[3]). Supposing that all sites and bonds are identical,

$$H_{\mathrm{CVB}} = J\sum_{i-j}(2S_iS_j - {}^1/_2) \qquad (1)$$

the CVB Hamiltonian can be written as follows, where S_i is the spin operator for site i, J is an (positive) exchange parameter, and $i-j$ denotes nearest-neighbour sites. Obviously, this model is equivalent to the Heisenberg model used in solid-state physics.[13] This model has also proven to be the second-order effective Hamiltonian which can be derived from the Hubbard model via degenerate perturbation theory[11] and other methods.[14] These methods can lead to systematic procedures for introducing higher order corrections into the model Hamiltonian. For example, the effective valence bond (EVB) model,[11] developed by Malrieu and Maynau, is an improved CVB model which will be briefly introduced in the following.

Effective Valence Bond (EVB) Model. It has been shown that in the strongly-correlated limit the Hubbard Hamiltonian can be reduced to the effective Hamiltonian operating solely on the space of neutral configurations by applying the degenerate

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many-body perturbation theory. The obtained effective Hamiltonian is essentially the zeroth-order Hamiltonian plus various order corrections. As mentioned above, the effective Hamiltonian up to second-order corrections is exactly the CVB Hamiltonian. The EVB Hamiltonian considered in this work means the effective Hamiltonian up to sixth-order corrections. Since there are no odd order terms for alternant systems,[15a] the EVB model, as displayed below, can be considered as a

$$H_{\mathrm{EVB}} = H_{\mathrm{CVB}} + H_{\mathrm{4th}} + H_{\mathrm{6th}} \tag{2}$$

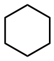
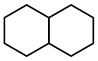
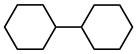
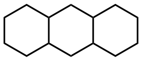
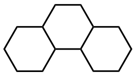
modified CVB model in which the fourth- and sixth-order corrections are implemented.

The spin operator form of the fourth-order correction H_{4th} has been given elsewhere.[12,15a] It has been verified that the fourth-order term, which introduces the second-nearest-neighbour interactions and cyclic four-body contributions, is crucial in treatments of conjugated hydrocarbons containing four-membered rings.[12a] However, the sixth-order formula is more sophisticated as shown below,

$$\begin{aligned}
\langle I|H_{\mathrm{6th}}|J\rangle = {}& \sum_{\alpha\beta\gamma\delta\epsilon} \frac{\langle I|V|\alpha\rangle\langle\alpha|V|\beta\rangle\langle\beta|V|\gamma\rangle\langle\gamma|V|\delta\rangle\langle\delta|V|\epsilon\rangle\langle\epsilon|V|J\rangle}{\Delta E_\alpha \Delta E_\beta \Delta E_\gamma \Delta E_\delta \Delta E_\epsilon} - \\
& \sum_{\alpha\beta\gamma\delta}\Bigg[\frac{\langle I|V|\alpha\rangle\langle\alpha|V|\beta\rangle\langle\beta|V|\gamma\rangle\langle\gamma|V|K\rangle\langle K|V|\delta\rangle\langle\delta|V|J\rangle}{\Delta E_\alpha \Delta E_\beta \Delta E_\gamma \Delta E_\delta} \times \\
& \left(\frac{1}{\Delta E_\alpha} + \frac{1}{\Delta E_\beta} + \frac{1}{\Delta E_\gamma}\right) + \\
& \frac{\langle I|V|\alpha\rangle\langle\alpha|V|\beta\rangle\langle\beta|V|K\rangle\langle K|V|\gamma\rangle\langle\gamma|V|\delta\rangle\langle\delta|V|J\rangle}{\Delta E_\alpha \Delta E_\beta \Delta E_\gamma \Delta E_\delta} \times \\
& \left(\frac{1}{\Delta E_\alpha} + \frac{1}{\Delta E_\beta}\right) + \\
& \frac{\langle I|V|\alpha\rangle\langle\alpha|V|K\rangle\langle K|V|\beta\rangle\langle\beta|V|\gamma\rangle\langle\gamma|V|\delta\rangle\langle\delta|V|J\rangle}{\Delta E_\alpha \Delta E_\beta \Delta E_\gamma \Delta E_\delta}\frac{1}{\Delta E_\alpha}\Bigg] + \\
& \sum_{\alpha\beta\gamma}\frac{\langle I|V|\alpha\rangle\langle\alpha|V|K\rangle\langle K|V|\beta\rangle\langle\beta|V|\mathrm{L}\rangle\langle L|V|\gamma\rangle\langle\gamma|V|J\rangle}{\Delta E_\alpha \Delta E_\beta \Delta E_\gamma} \times \\
& \left(\frac{1}{\Delta E_\alpha^2} + \frac{1}{\Delta E_\alpha \Delta E_\beta}\right)
\end{aligned} \tag{3}$$

where the roman letters I, J, and K represent neutral states belonging to the degenerate subspace, and the Greek ones α, β, ... , ϵ denote ionic states. ΔE_α, ΔE_β, ..., ΔE_ϵ reflect the energy difference between ionic and neutral determinants. The sixth-order terms are numerous and are difficult to simplify and to interpret. But it has been pointed out that the most important contribution comes from the cyclic six-body interaction terms.[11] As for the detailed discussions of the EVB model, one can refer to refs 11 and 12. As has been demonstrated, the EVB model can give quantitative agreement with the full CI PPP scheme when applied to calculating the low-lying spectra of benzene, greatly improving the results of the CVB model.[11] It is interesting to investigate whether or not this situation still holds in benzenoids larger than benzene.

TABLE 1: Low-Lying Electronic Spectra (in eV) of Some Small Benzenoid Hydrocarbons. Comparison of CVB and EVB Calculations with Experimental Data and MO Results Is also Given

compd	state	CVB[a]	EVB[a]	exptl	MO
benzene 	$^3B_{1u}$	2.67	3.72	3.94[b]	4.0,[c] 3.92[d]
	$^1B_{2u}$	5.08	5.49	4.90[e]	5.4[c]
naphthalene 	$^3B_{2u}$	1.96	2.61	2.64[f]	3.04,[g] 2.522[h]
	$^3B_{1g}$	4.37	4.56	3.94−3.99[i]	4.59[g]
biphenyl 	$^3B_{3u}$	2.05	3.12	2.84[j]	3.81[k]
	^3A_g	4.66	4.66	4.65[l]	
antracene 	$^3B_{2u}$	1.52	1.81	1.82[j]	1.660[m]
	$^3B_{1g}$	3.42	3.38	3.22[n]	2.844[m]
phenanthrene 	$^3B_2$	1.71	2.53	2.70[o]	2.90[p]
	$^3A_1$	3.49	3.96	3.45[o]	3.74[p]

[a] Parameters of the CVB and EVB models come from ref 11. The computed low-lying excitation energies for each molecule refer to its ground state energy. Within the CVB and EVB models, the ground-state energies (in eV) are, −16.7809 and −16.0853 ($^1A_{1g}$, benzene), −29.3280 and −27.8434 (^1A_g, naphthalene), −34.9389 and −33.3431 (^1A_g, biphenyl), −41.8285 and −39.5082 (^1A_g, anthracene), and −41.9689 and −39.8682 ($^1A_1$, phenanthrene), respectively. [b] Reference 26. [c] CASSCF+MRCI calculations from ref 27. [d] PPP full CI calculations from ref 28. [e] Reference 29. [f] Electron energy-loss spectra (EELS) from ref 30. [g] CASPT2 results from ref 31. [h] PPP full CI calculations from ref 32. [i] T_1-T_n with $E(T_1) = 2.64$ eV Meyar et al. (ref 33) have predicted this state based on T−T absorption spectra of anthracene and tetracene and semiempirical calculations. [j] 0−0 transition of phosphorescence from ref 34. [k] CNDO/SDCI results when twist angle $\Phi = 10°$ from ref 35. [l] T_1-T_n with $E(T_1) = 2.84$ eV from ref 36. [m] Results of Pariser from ref 37. [n] 0−0 transition in gas phase from ref 38. [o] 0−0 transition from EELS, ref 39. [p] CS-INDO results from ref 40 and references therein.

In the next section, we will first answer the above question and study the applicability of the EVB and CVB models to predict the low-lying excited spectra of a series of benzenoid hydrocarbons. By employing the Lanczos method, which proved to be very efficient for the diagonalization of large matrices in our previous works,[10,12] we can exactly solve the EVB model for benzenoid hydrocarbons with up to 14 π-electrons (the numerous off-diagonal elements included in this model hinder the extension of our treatments to larger molecules) and the CVB model with up to 22 π-electrons. The details of the computational method have been introduced in ref 10 and 12b.

Finally, it should be emphasized that, for those higher excited states, where the ionic configurations will become increasingly important, both the EVB and CVB models will gradually lost their effectiveness. Accordingly, we shall limit our applications of both models to the low-lying states with the energies about 0−5 eV above the ground states. In addition, all considered molecules are assumed to be planar because of the topological essence of these two models. We have carried out the calculations on an SGI R8000 workstation.

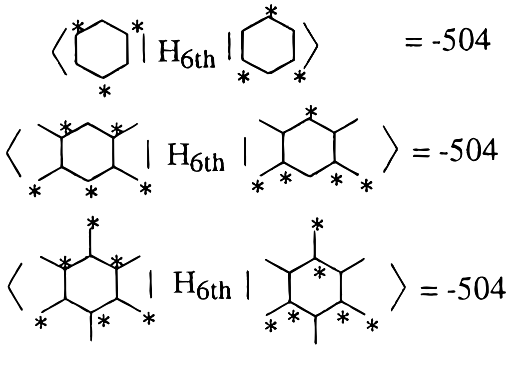
Results and Discussions

Low-Lying Excited Spectra of Benzenoid Systems with No More than 14 π-Electrons. Within the framework of both

CVB and EVB models, we have computed the low-lying transition energies for several small benzenoid systems, with results listed in Table 1. For comparison, a collection of experimental data and MO predictions are also given. Firstly, one can notice that the EVB model well reproduces the low-lying electronic spectra within an average deviation of 0.26 eV from experiments. The results obtained from this two-parameter Hamiltonian agree well with more complex full π configuration interaction Pariser–Parr–Pople (PPP) results and other semi-empirical or even ab initio MO calculations. Meanwhile, we can also find that the CVB model can correctly predict the order of low-lying states with the average error of 0.48 eV. This reflects that the inclusion of higher order corrections in the EVB model does improve the results of the CVB model for these small benzenoid systems. However, it seems that the effect of higher order corrections decreases gradually with increasing the size of benzenoids.

It is worthwhile analyzing how higher order corrections act in these systems. We take benzene for example. For the ground state ($^1A_{1g}$) of benzene, the calculated energy changes from -16.7809 eV (CVB) to -16.0853 eV (EVB) after including higher order corrections. As pointed out above, for benzenoid systems the two most important correction terms, i.e., the next-nearest-neighbor transpositions and cyclic permutations which permute the electrons around the circumference of the six-membered ring, are introduced by fourth- and sixth-order corrections, respectively. Our results agree with previous works[9] in showing that these two corrections are of comparable magnitude but opposite sign for the ground state of benzene. But for the first excited state ($^3B_{1u}$), its energies are respectively calculated to be -14.1104 and -12.3600 eV on the basis of the CVB and EVB models, implying that these two correction terms do not completely cancel. So higher order corrections are significant in the description of the energy gap between the ground and first excited states of benzene.

On the other hand, we want to know why higher order corrections appear less important in larger molecules. From **1** (where asterisks denote α spins), we note that in benzene the six-body operator couples two Neél determinats, giving the largest off-diagonal element of -504 (in units of -0.0008143 eV as given in ref 11). In fact, if one considers the same operator on an internal cycle of a fused benzenoid, it couples the Neél determinant with a determinant having 4 or 6 spin frustrations (cf. **1**), of much lower weight in the lowest states. Therefore, the effect of higher order corrections will remarkably decrease in large and even the medium-sized benzenoids. It should be pointed out that similar discussions have already been given by Malrieu and his co-workers.[16]



1

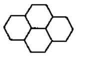
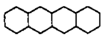
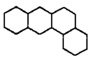
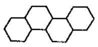
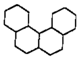
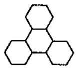
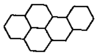
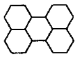
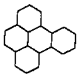
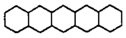
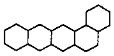
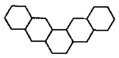
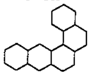
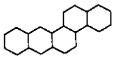
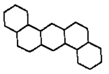
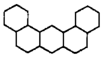
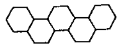
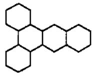
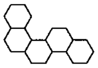
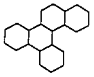
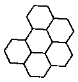
From the above discussions, we can conclude that the higher order corrections are necessary in describing the low-lying excited states of small benzenoids, while their effects will become gradually small with the increase in the size of benzenoid hydrocarbons. Consequently, it can be anticipated that the CVB model without higher order corrections may also work well for the low-lying electronic states of larger benzenoids, which will be demonstrated in the following.

Lowest Triplet States of the Medium-Sized Benzenoid Hydrocarbons. By employing the Lanczos method to diagonalize the CVB model, we have calculated the energies of the lowest two states for a number of benzenoid hydrocarbons with up to 22 π-centers. Our results are presented in Table 2. For most of these benzenoids, their ground-state energies have been calculated by Alexander and Schmalz,[9] which have been exactly reproduced here. However, the energies of the first excited states of these systems are first obtained in this work. It can be found from Figure 1 that the calculated energy gaps (in J) between the ground and first excited states exhibit a linear correlation with the available experimental spectra (in eV) (two molecules, naphthacene and pentacene, are excluded here considering the reason discussed hereafter). From this good correlation, we obtain that for benzenoids the realistic value of the exchange parameter J, which occurs in the CVB model, is about 3.15 eV. By using this parameter, the calculated singlet–triplet energy separations within the CVB framework are also collected in Table 2. The predicted values compare well with the available experimental spectra with the average deviation of only ±0.13 eV, being comparable to the results of the semiempirical PPP MO calculations.[41] From Table 2, one can see that the biggest errors occur on triphenylene and perylene, which can be regarded as being respectively composed of benzene and naphthalene rings through an "empty" ring as postulated by Clar.[17] Consequently, the higher order corrections may be very important for these special molecules as in the cases of benzene and naphthalene. Interestingly, the speciality of these molecules has also been mentioned in the conjugated circuit model.[5e] For other species, the deviations between the calculated and experimental values tend to depend on the approximate extent of the CVB model in which equal J is assumed for each C–C bond. For instance, for benz[*ghi*]perylene our prediction is extremely close to the experimental data presumably because bond lengths of this molecule are almost equal.[18] Moreover, we notice that for most isomeric benzenoid systems the relative magnitude of S–T energy gaps predicted from our calculations is in agreement with the experimental measurements, as exemplified in isomeric species with 18 π-sites (cf. Table 2).

In addition, we'd like to give some comments on the parameter J obtained above. Let's consider a simple conjugated system, ethylene, in which its singlet–triplet gap is analytically obtained within the CVB model ($\Delta E_{ST} = 2J$). Remember that its experimental $\Delta E_{ST} = 3.5{-}3.6$ eV[6a], thus the corresponding J of a double bond is about 1.8 eV. While for benzenoid system with the average C–C bond length of 1.40 Å, a mean value of 3.15 eV obtained from the above fitting seems reasonable.

Summarizing above results, we see that the CVB model with the parameter J of 3.15 eV can give reasonable predictions of the lowest triplet spectra for most of the medium-sized benzenoid systems. However, it should be pointed out that, for naphthacene and pentacene of the polyacene series, the parameter $J = 3.15$ eV will give unsatisfactory predictions on their lowest triplet spectra. This may be attributed to the fact that there exist considerable variations of the bond lengths from bond to bond in these species,[20] so that equal J-value assumption is rather approximate. Nevertheless, the S–T energy separations of these two molecules are correctly predicted by the CVB theory to be the smallest among their respective isomeric

TABLE 2: Energies of the Two Lowest States for a Series of Medium-Sized Benzenoid Hydrocarbons

				lowest triplet spectra[c]		
benzenoids	E_S[a]	E_T[a]	$\Delta E_{S\text{-}T}$[b]	CVB[d]	exptl	MO[e]
pyrene 	-25.13256	-24.41103	0.72153	2.27	2.11[e]	1.79
naphthacene 	-27.85819	-27.22240	0.63579	1.26[f]	1.26[e]	1.24
benz[a]anthrancene 	-27.94444	-27.20543	0.73901	2.33	2.04[e]	2.03
chrysene 	-27.99497	-27.21658	0.77839	2.45	2.47[e]	2.20
benzophenanthrene 	-27.99314	-27.20919	0.78395	2.47	2.49[g]	
triphenylene 	-28.03939	-27.21988	0.81951	2.58	2.89[e]	2.76
benz[a]pyrene 	-31.59204	-30.96244	0.62960	1.98	1.82[h]	1.65
perylene 	-31.60319	-30.98949	0.61370	1.93	1.56[h]	1.67
benz[e]pyrene 	-31.65132	-30.94675	0.70457	2.22	2.29[h]	
pentacene 	-34.26652	-33.72357	0.54295	1.08[f]	<1.24[i]	
benz[a]naphthacene 	-34.35497	-34.24222	0.62558	1.97		
pentaphene 	-34.36970	-33.70609	0.66361	2.09	2.08[e]	2.07
dibenz[b,g]phenanthrene 	-34.41313	-33.73185	0.68128	2.15		1.89
benz[b]chrysene 	-34.41514	-33.73779	0.67735	2.13	2.23[g]	1.95
dibenz[a,h]anthracene 	-34.43483	-33.73365	0.70118	2.21	2.26[e]	2.29
dibenz[a,j]anthracene 	-34.43451	-33.73109	0.70342	2.22	2.30[g]	2.33
picene 	-34.47083	-33.75256	0.71827	2.26	2.49[h]	2.35
dibenz[a,c]anthracene 	-34.46838	-33.74775	0.72063	2.27	2.20[e]	2.13
benz[c]chrysene 	-34.46908	-33.74615	0.72293	2.28	2.52[g]	2.35
dibenz[c,g]phenanthrene 	-34.46809	-33.74483	0.72326	2.28	2.45[j]	
benz[g]chrysene 	-34.50282	-33.77033	0.73249	2.31		2.27
benz[ghi]perylene 	-35.28475	-34.65456	0.63019	1.99	1.99[e]	2.11

[a] Energies of the singlet ground states and the first excited (triplet) states are in units of J. [b] S−T energy gaps are in units of $-J$. [c] In units of eV and referring to their ground-state energies. [d] All molecules, except for naphthacene and pentacene, are calculated by taking $J = 3.15$ eV. [e] Reference 41 and references therein. [f] The detailed discussions on these two molecules have been given in the text. [g] Reference 42. [h] Reference 43 and references therein. [i] Reference 21. [j] Reference 44 and references therein.

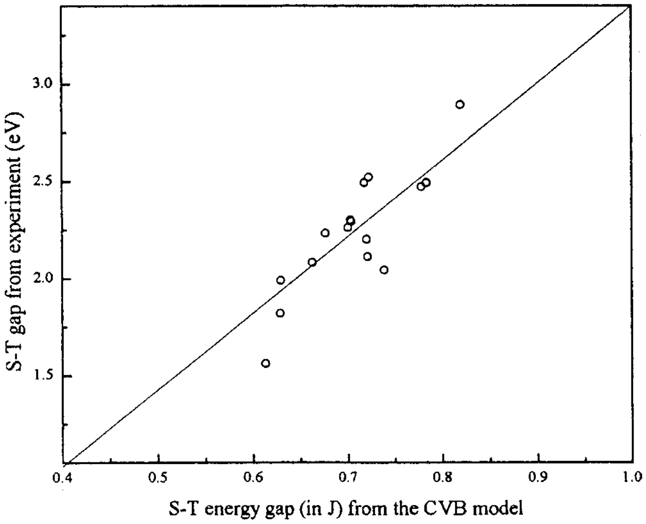


Figure 1. Correlation of the singlet−triplet energy gaps with experimental data.

species. Reasonably, the value of the averaged J for naphthacene can be obtained from its corresponding experimental data, giving $J = 1.99$ eV. Extending this parameter to pentacene, its lowest triplet state is predicted to lie only 1.08 eV above the ground state, being consistent with the fact that its lowest triplet spectrum is hardly observed experimentally until recently.[21] This result implies that for the long-chain polyacene its ground state may become nearly degenerate within the CVB theory and may undergo a Peierls distortion.[22,23]

The Correlation of the Singlet−Triplet Energy Gap with the Number of Kekulé Structures. It is believed that for benzenoid hydrocarbons the number of Kekulé valence structures K is an important structural parameter which may be closely related to some ground-state properties (for example, the relative aromatic stability[24,25]). Now, on the basis of the exact CVB calculations for finite benzenoids, we manage to find out which chemical properties can be correlated with the simple Kekulé counts.

For benzenoid isomers of 22 π-sites, the exact ground-state energies (per site) and singlet−triplet gaps are collected in Table 3, together with the number of Kekulé valence structures K and its logarithm ln K. At first sight, one can immediately notice that the exact ground-state energy is indeed proportional to both the number of Kekulé structures (correlation coefficient, 0.997) and the logarithm of K (correlation coefficient, 0.988). This

TABLE 3: Relation between the Number of Kekulé Structures (*K*) and the Singlet−Triplet Energy Gaps (ΔE_{S-T}) among Isomeric Benzenoids of 22 Sites

benzenoids	E_S/N^a	ΔE_{S-T}^b	K[c]	ln *K*
pentacene	1.557 57	0.542 95	6	1.791 8
benz[*a*]naphthacene	1.561 59	0.625 58	9	2.197 2
pentaphene	1.562 26	0.663 61	10	2.302 6
dibenz[*b,g*]phenanthrene	1.564 23	0.681 28	11	2.397 9
benz[*b*]chrysene	1.564 32	0.677 35	11	2.397 9
dibenz[*a,h*]anthracene	1.565 22	0.701 18	12	2.484 9
dibenz[*a,j*]anthracene	1.565 21	0.703 42	12	2.484 9
picene	1.566 86	0.718 27	13	2.564 9
dibenz[*a,c*]anthracene	1.566 74	0.720 63	13	2.564 9
benz[*c*]chrysene	1.566 78	0.722 93	13	2.564 9
dibenz[*c,g*]phenanthrene	1.566 73	0.723 26	13	2.564 9
benz[*g*]chrysene	1.568 31	0.732 49	14	2.639 1

[a] Ground-state energies per site (in $-J$). [b] In units of $-J$. [c] From ref 5b.

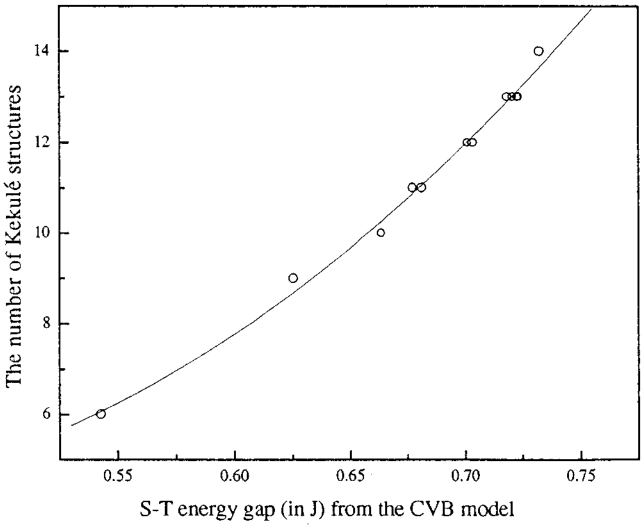


Figure 2. Relation between the singlet−triplet energy gaps and the number of Kekulé structures for the isomeric benzenoids of 22 π-electrons.

indicates that the simple Kekulé counts can be used to directly correlate with the relative thermal stability of the isomeric benzenoid systems, which will be further discussed in another paper.

In this work, our primary concern is whether or not there exists a definite correlation between the S−T energy gap and the number of Kekulé structures. From Figure 2, we can find that there exists a good quadratic relationship between them. It should be emphasized that this correlation also exists among other isomeric benzenoids listed in Table 2. Considering that the real benzenoid systems lie intermediate between the MO and VB antipodes,[15b] the correlation of the S−T energy gap with *K* can be utilized to give a reasonable estimate on band-gaps of these polymers. Similarly, this simple VB approach can also be used to deduce the kinetic stabilities of large fullerenes. This may open a new field for the application of the simple VB methods based on Kekulé counts.[10]

Conclusions

In the present work, the low-lying electronic states of benzenoid hydrocarbons with up to 22 sites have been obtained from exact semiempirical VB calculations, with the emphasis on the low-lying excited spectra of these systems. It seems that the nearest-neighbor CVB model gives unsatisfactory predictions of the low-lying excited states of small benzenoids with no more than 14 π-electrons. While the EVB model, which implements higher order corrections (nonadjacent and cyclic six-body interactions) on the basis of the CVB model, works well for these systems. For larger benzenoids, our calculations suggest that the effect of higher order corrections may become increasingly smaller with the increase in the size of molecules, and therefore the CVB model can yield reasonable predictions on the lowest triplet spectra of these species, agreeing well with the available experimental data and semiempirical PPP MO results. Finally, we find that the energy difference between the ground and first excited states is quadratically related to the number of Kekulé structures among isomeric benzenoid systems. Accordingly, the band gaps of benzenoid polymers and the kinetic stabilities of large fullerenes may be deduced simply based on the simple counts of Kekulé valence structures.

In summary, we conclude that semiempirical VB models can give reasonable descriptions of the low-lying electronic states of benzenoid hydrocarbons. Furthermore, we'd like to point out that the semiempirical VB models have been improved in several ways.[6,19] For example, the EVB model can be further modified by introducing renormalized four- and six-body terms as demonstrated in ref 19. The CVB model can be developed into a geometry-dependent version.[6a] With this geometry-dependent VB model, the potential energy surfaces of the low-lying electronic states have been investigated for a series of conjugated hydrocarbons.[6,45] These improvements offer new possibilities for our future work.

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