

Kekulé-based Valence Bond Model.

II. Diels-Alder Reactivity of Polycyclic Aromatic Hydrocarbons[†]

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The Kekulé-based valence bond (VB) method was employed to study the ground state properties of 52 polycyclic aromatic hydrocarbons. The reactivity indices defined upon our VB calculations were demonstrated to be capable of quantitatively interpreting the second order rate constants of the Diels-Alder reactions. The qualitative trends of the reactivities of many homologous series can be also explained based on the local aromaticity index defined in this work.

Keywords valence bond model, Diels-Alder reaction, polycyclic aromatic hydrocarbons

Introduction

It is well known that molecular orbital (MO) theory has played an important role in understanding various chemical reactions of polycyclic aromatic hydrocarbons.¹ Especially, the Diels-Alder reactions of many polycyclic benzenoid hydrocarbons with maleic anhydride have been systematically studied² and discussed with several MO models, such as Brown's *para*-localization concept,³ Dewar's PMO treatment,⁴ a free valence index,^{1,5} Fukui's frontier orbital theory,^{6,7} complete second-order perturbation treatment,² and Hess-Schaad's model.⁸ On the other hand, within the framework of Herndon's structure-resonance theory,⁹ which is a simple parameterized version of valence bond (VB) theory, the empirical logarithm of the Kekulé structure count (SC) is demonstrated to be highly correlated with the kinetic data of the Diels-Alder reactions of polycyclic benzenoids. Herndon's method has a

strong appeal to the experimental chemists,² because it can yield the same accurate correlations and predictions of reactivities as various MO methods without involving any cumbersome calculations. However, few attempts have been made to give a quantum mechanical interpretation and justification of the SC/reactivity relationship from the actual VB calculations.^{9c} Because the complexity of valence bond calculations rises very rapidly as a function of the size of the chemical system, the exact solution of the VB model has been limited to those conjugated molecules with no more than 28 π -centers.¹⁰⁻¹² Recently, we demonstrated that the Kekulé-based VB model,¹³ in which the classical VB model is solved based on the covalent Kekulé structures, is capable of presenting reasonable predictions of some ground-state properties of a large number of benzenoid hydrocarbons. In this paper, we primarily focus on the application of this model to the Diels-Alder reactions of polycyclic aromatic hydrocarbons. We will show that the second order rate constants of the Diels-Alder reactions of a large quantity of benzenoid hydrocarbons can be correlated well with the reactivity indices defined upon our VB calculations. In addition, the qualitative trend of reactivities and regioselectivities of many homologous series can be understood in terms of the analysis of their characteristic component substructures, which can be easily obtained within the present model. Finally, we will illustrate that Herndon's SC index can be directly derived from the present VB calculations, indicating that there is a firm quantum mechanical background underlying this

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empirical method.

The organization of this paper is as follows. In section II, we briefly introduce the Kekulé-based VB model. In section III, we employ several reactivity indices based on the Kekulé-based VB calculations to correlate with the second-order rate constants of the Diels-Alder reactions for a large number of polycyclic aromatic hydrocarbons.

Computational details

In the preceding paper of the series,¹³ the Kekulé-based VB method was demonstrated to provide satisfactory predictions on the relative order of thermodynamic stabilities for a large number of benzenoid hydrocarbons, being in good agreement with exact VB calculations. The only approximation involved in the Kekulé-based VB method is that the wave function of a molecule is assumed to be approximately a linear combination of its Kekulé structure functions, *i. e.*,

$$\Psi = \sum_i C_i K_i \quad (1)$$

where K_i signifies the basis function corresponding to the i th Kekulé structure, and C_i is the coefficient associated with K_i to be determined variationally. This approximation greatly enlarges the scope of VB treatments, and makes it possible to account for some chemical properties of a number of conjugated molecules from VB viewpoints. In the next section, we will use some indices derived from Kekulé-based VB calculations to interpret the second order rate constants of the Diels-Alder reactions of polycyclic aromatic hydrocarbons.

Results and discussion

Quantitative correlation of the Diels-Alder reactivity

Within the Hückel MO (HMO) theory, both Brown's *para*-localization energy P ,³ which is the difference in π -electron energies of the product and the starting hydrocarbons, and Hess-Schaad resonance energy differences between the product and reactant ($\Delta RE = RE_{\text{product}} - RE_{\text{reactant}}$)⁸ are demonstrated to be well-behaved reactivity indices for the Diels-Alder reactions of benzenoid hydrocarbons. Here, based on the same definitions, these two indices are calculated with the Kekulé-based VB method.

In the following, they will be applied to correlate with the second order rate constants of a large number of polycyclic benzenoid systems.

The calculated *para*-localization energies together with the rates of the Diels-Alder reactions for 52 benzenoid systems are listed in Table 1. In the meanwhile, the real reaction sites are indicated by heavy dots on the structural formulas. At first sight, one finds that the smaller the P value becomes, the faster the Diels-Alder reaction takes place. When the P values of the most reactive *meso* positions are plotted against the corresponding experimental data as shown in Fig. 1, an excellent correlation is obtained. The standard deviation of this fit is 0.282, being comparable to the results of the Hess-Schaad model and Herndon's SC method which are considered to do best among all known reactivity indices.^{2,8a} On the other hand, our calculations also reveal that the orientation phenomena are equally well handled with the Kekulé-based VB *para*-localization energies. Actually, the most reactive *meso* positions always correspond to the smallest P values, as seen from Table 1. Therefore, it can be concluded that the Diels-Alder reactivity and regioselectivity of polycyclic aromatic hydrocarbons can be reliably predicted from the present VB calculations. Interestingly, for two special coronoid species **60** and **61**, we have predicted their second-order rate constants from the well-behaved correlation displayed in Fig. 1, with the results also collected in Table 1. Further experiments are needed to verify our predictions (species **60** has been synthesized¹⁴ but species **61** is still unknown).

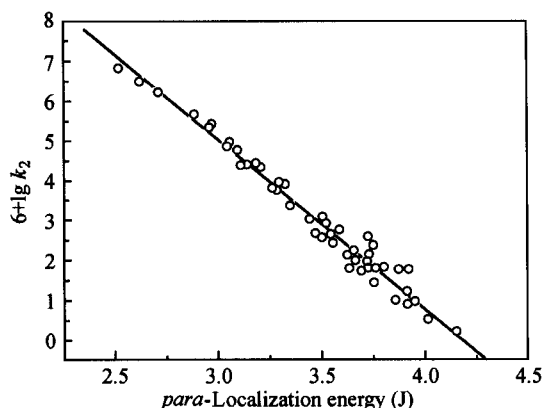


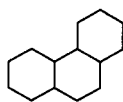
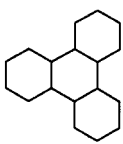
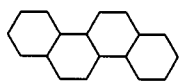
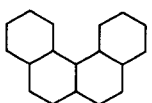
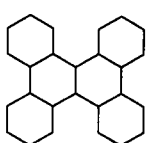
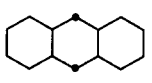
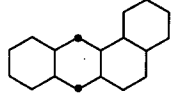
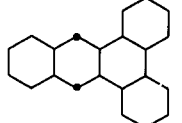
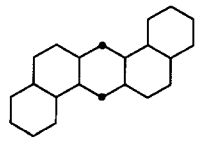
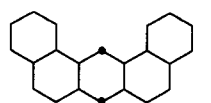
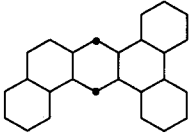
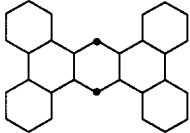
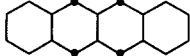
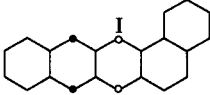
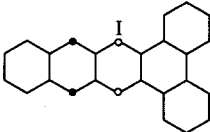
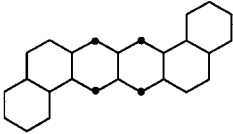
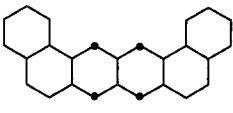
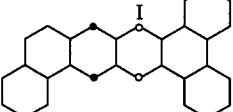
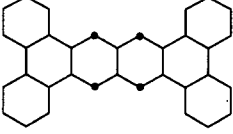
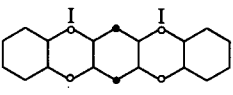
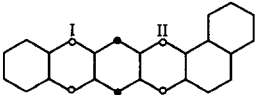


Fig. 1 Plot of second order rate constants with the *para*-localization energies P . Least-squares regression: $6 + \lg k_2 = 17.794 - 4.252P$.

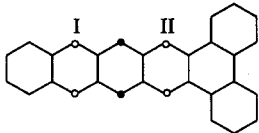
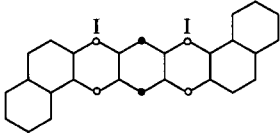
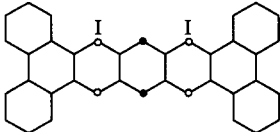
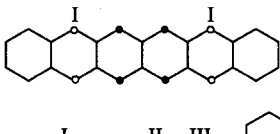
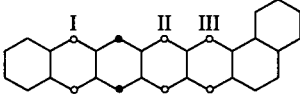


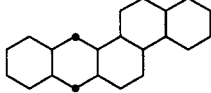
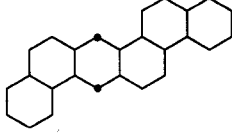
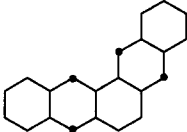
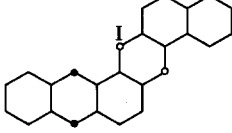
Table 1 The logarithms of the second order rate constants k_2 ($\text{L}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$), the ground-state π -electron energies E_π (-J), the *para*-localization energies P (J) of polycyclic aromatic hydrocarbons, the resonance energies RE (-J) and the logarithms of the number of the Kekulé structures $\ln K$

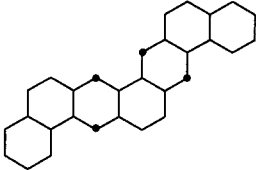
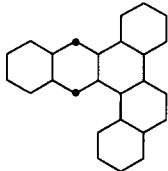
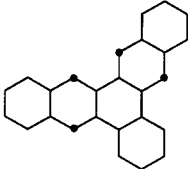
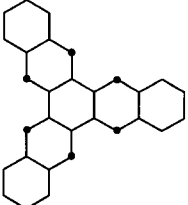
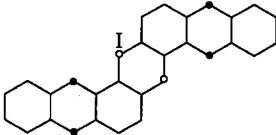
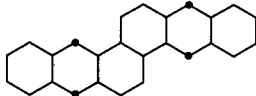
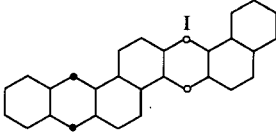
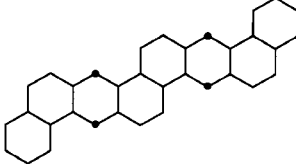
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1			8.400		0.900	0.693
2			14.370		1.370	1.099
3			20.524		2.025	1.609
4			26.806		2.807	2.197
5			26.593		2.594	2.079
6			26.593		2.594	2.079
7			39.014		4.014	3.178
8		3.36	20.150	3.350	1.650	1.386
9		2.13	26.398	3.627	2.398	1.946
10		1.83	32.731	3.806	3.231	2.565
11		1.02	32.598	3.858	3.098	2.485
12		1.02	32.598	3.858	3.098	2.485

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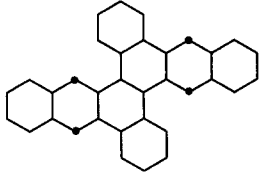
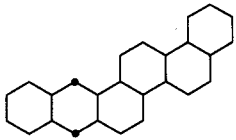
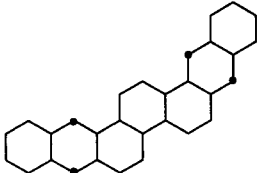
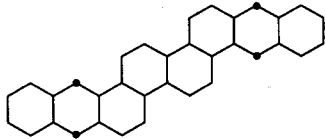
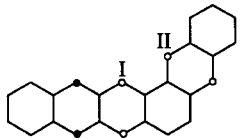
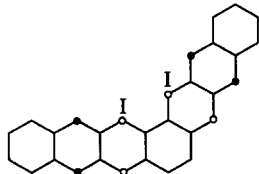
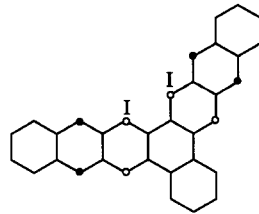
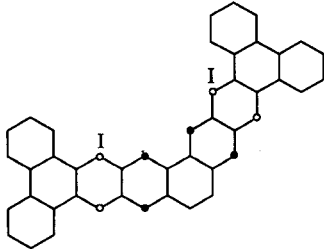
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13		0.53	38.907	4.012	3.907	3.091
14		0.24	45.201	4.152	4.702	3.689
15		4.97	25.830	3.060	1.830	1.609
16		4.23	32.129	3.205 (I, 3.389)	2.629	2.197
17		3.77	38.488	3.281 (I, 3.592)	3.488	2.833
18		3.09	38.402	3.507	3.402	2.773
19		3.08	38.402	3.507	3.402	2.773
20		2.76	44.765	3.588 (I, 3.715)	4.265	3.401
21		2.38	51.086	3.754	5.086	4.025
22		6.22	31.453	2.712 (I, 2.903)	1.952	1.792
23		5.65	37.783	2.888 (I, 2.985) (II, 3.263)	2.783	2.398

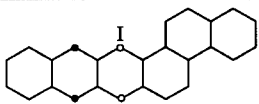
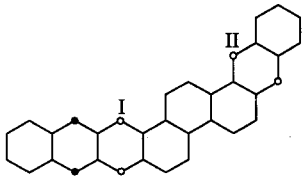
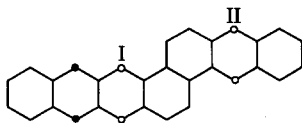
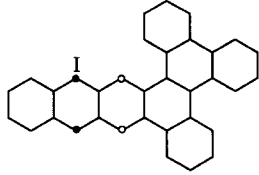
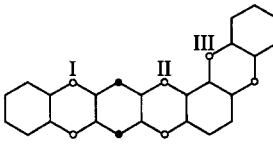
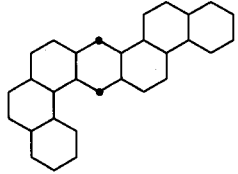
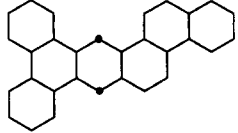
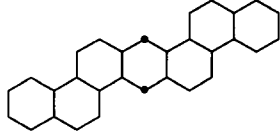
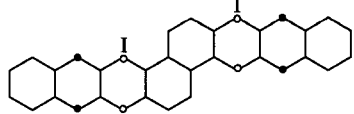
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No.	Hydrocarbon ^a	$6 + \lg k_2^b$	E_x	P	RE	$\ln K$
24		5.45	44.155	2.978 (I, 3.024) (II, 3.480)	3.655	3.044
25		4.88	44.097	3.047 (I, 3.329)	3.597	2.996
26		4.34	56.822	3.209 (I, 3.567)	5.322	4.277
27		6.82	37.040	2.519 (I, 2.810)	2.040	1.946
28		6.48	43.390	2.622 (I, 2.860) (II, 2.714) (III, 3.189)	2.900	2.565
29			32.701		3.201	2.565
30			38.791		3.791	3.044
31		2.58	32.427	3.502	2.927	2.398
32		1.45	38.647	3.752	3.647	2.944
33		1.82	32.311	3.761	2.811	2.303
34		1.74	38.492	3.695 (I, 3.972)	3.492	2.833

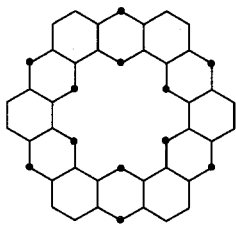
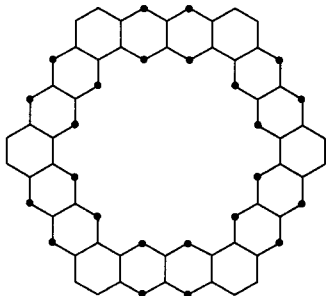
No.	Hydrocarbon ^a	$6 + \lg k_2^b$	E_π	P	RE	Continued
						$\ln K$
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36		2.15	38.727	3.733	3.727	2.996
37		1.78	38.675	3.877	3.675	2.944
38		1.77	44.630	3.920	4.140	3.332
39		2.00	44.378	3.666 (I, 4.078)	3.878	3.178
40		3.03	38.240	3.442	3.240	2.708
41		2.68	44.470	3.472 (I, 3.702)	3.970	3.258
42		1.82	50.696	3.727	4.696	3.807

Continued

No.	Hydrocarbon ^a	$6 + \lg k_2^b$	E_π	P	RE	$\ln K$
43		2.20	50.784	3.657	4.784	3.807
44		2.44	38.553	3.560	3.553	2.890
45		2.62	44.413	3.543	3.912	3.219
46		2.93	50.474	3.521	4.474	3.689
47		3.82	38.064	3.266 (I, 3.544) (II, 3.834)	3.064	2.565
48		3.97	43.827	3.297 (I, 6.686)	3.327	2.833
49		3.90	50.213	3.326 (I, 7.102)	4.213	3.496
50		2.59	69.020	3.726 (I, 3.730)	6.520	5.220

Continued						
No.	Hydrocarbon ^a	$6 + \lg k_2^b$	E_π	P	RE	$\ln K$
51		4.41	38.138	3.144 (I, 3.243)	3.138	2.639
52		4.43	50.138	3.186 (I, 3.298) (II, 3.601)	4.138	3.466
53		4.39	43.939	3.112	3.439	2.944
54		3.93	50.642	3.227 (I, 3.448)	4.642	3.784
55		5.37	43.729	2.961 (I, 3.018) (II, 3.429) (III, 3.877)	3.229	2.773
56		1.75	44.688	3.638	4.188	3.401
57		1.22	44.966	3.917	4.466	3.555
58		1.81	44.688	3.638	4.188	3.401
59		4.76	49.632	3.094 (I, 3.132)	3.632	3.178

Continued

No.	Hydrocarbon ^a	$6 + \lg k_2^b$	E_π	P	RE	$\ln K$
60		0.99 ^c	72.495	3.950	6.495	5.298
61		1.96 ^c	107.605	3.721	8.605	7.170

^a The heavy dots in the structural formulas indicate the most reactive *meso* positions, and the circles, which are labeled by the Roman numbers I, II, and III, denote other meso sites with their corresponding P values listed in parentheses for comparison. ^b Experimental data are from Ref. 2 for hydrocarbons 8–55, and Ref. 8 for species 56–59. ^c The rate constants of hydrocarbons 60 and 61 are theoretical predictions based on the Kekulé-based VB calculations.

Following the idea of Hess and Schaad,⁸ we can also define the resonance energy differences between the product and reactant, ΔRE , as an index for discussing the reactivity of the Diels-Alder reaction. As indicated by Hess and Schaad, within the HMO framework, ΔRE gives better correlation than the *para*-localization energy P in some benzenoid systems.^{8a} However, within the present VB treatment we will verify that the *para*-localization energy P and the ΔRE appear essentially equivalent for all cata-condensed benzenoid systems.

Considering an arbitrary cata-condensed benzenoid hydrocarbon (Scheme 1), the *para*-localization energy P for the heavily dotted sites is given by

$$P = E_I^\pi + E_{II}^\pi - E_{\text{reactant}}^\pi \quad (2)$$

and ΔRE by

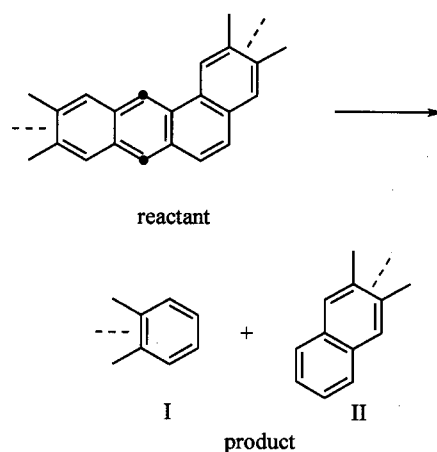
$$\Delta RE = RE_I + RE_{II} - RE_{\text{reactant}} \quad (3)$$

where

$$RE = E^\pi - E^{\text{ref}} \quad (4)$$

The reference energy E^{ref} is taken as the energy of a localized Kekulé structure, which can be directly obtained

Scheme 1



through

$$E^{\text{ref}} = -2n_{\text{double-bond}} - 0.5n_{\text{single-bond}} \quad (5)$$

where $n_{\text{double-bond}}$ and $n_{\text{single-bond}}$ are respectively the number of the double bonds and single bonds in a hydrocarbon. In the above equations, E^{ref} , E^π , RE and ΔRE are all in units of J.

So from the Eqs. (2)–(4), we obtain

$$\Delta RE = P + E_{\text{reactant}}^{\text{ref}} - E_{\text{I}}^{\text{ref}} - E_{\text{II}}^{\text{ref}} \quad (6)$$

Supposing there are n_1 double bonds and n_2 single bonds in product I, and m_1 double bonds and m_2 single bonds in product II, then the Kekulé form of the reactant should have $(n_1 + m_1 + 1)$ double bonds and $(n_2 + m_2 + 3)$ single bonds. Substituting the reference energies into Eq. (6) gives

$$\begin{aligned} \Delta RE &= P - 2(n_1 + m_1 + 1) - 0.5(n_2 + m_2 + 3) + \\ &\quad 2n_1 + 0.5n_2 + 2m_1 + 0.5m_2 \\ &= P - 3.5 \end{aligned} \quad (7)$$

Obviously, from the present VB viewpoint these two reactivity indices are completely parallel to each other in fact.

Despite this, compared to the *para*-localization energy index, the index ΔRE seems to have more profound physical meanings because there is an excellent linear relationship between the Kekulé-based resonance energy RE and the logarithm of the number of the Kekulé structures $\ln K$ for benzenoids as depicted in Fig. 2. The least-square regression for 61 benzenoid systems leads to

$$RE(-J) = -0.103 + 1.258 \ln K \quad (8)$$

with the standard deviation of 0.100 and the correlation coefficient of 0.995.¹⁵ Consequently the ΔRE can be derived directly from counting the numbers of the Kekulé structures of the product and the reactant (denoted by K_{product} and K_{reactant} respectively) as shown below,

$$\Delta RE(-J) = 1.258 \ln(K_{\text{product}}/K_{\text{reactant}}) \quad (9)$$

This formula is reminiscent of Herndon empirical structure count method,⁹ which is obtained from fitting $\ln K$ to the Dewar's resonance energy. Therefore, a quantum mechanical interpretation of the empirical SC method is given here. One should no longer be surprised at the excellent quantitative agreement between experimental and theoretical data from this simple method.

Qualitative analysis of reactivity in the homologous series

It is also meaningful to analyze some qualitative trends of the Diels-Alder reactivity in many homologous series. There are several such examples described as below (Scheme 2). In each homologous series, the rate

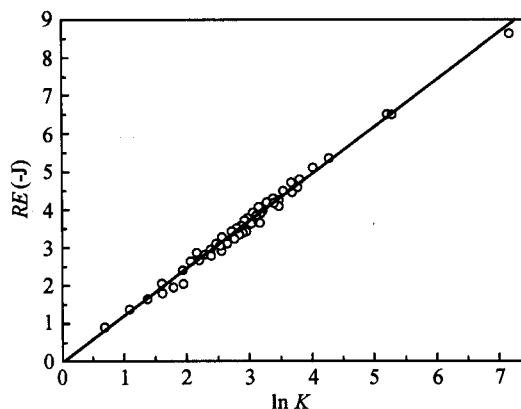


Fig. 2 The correlation between resonance energies of benzenoids calculated from the Kekulé-based VB and the logarithms of the numbers of Kekulé structures $\ln K$.

constants are very close and the most reactive *meso* positions (denoted by heavy dots in Scheme 2) also appear in the identical regions. This phenomenon suggests to us an examination of whether the reactivities of these homologous systems can be understood in terms of their component fragments. As it is well known, in the polycyclic benzenoid systems a local aromaticity index is usually employed to characterize the contributions of the localized substructures to the stability and reactivity of the whole system.^{10,16-19} Here based on the idea of Dewar and de Liano²⁰ a new local aromaticity index is developed for this purpose. For a given ring in a benzenoid system, the ratio of the resonance energy difference ΔRE from its analogous structure in which the ring is missing to the resonance energy of benzene as a dimensionless index of its local aromaticity (LA) is defined, *i. e.*,

$$LA_i = \frac{RE(\text{the whole system}) - RE(\text{the } i\text{th ring missing})}{RE(\text{benzene})} \quad (10)$$

where LA_i represents the local aromaticity of the i th ring. According to this definition, when the LA of a ring approaches 1.0, for example, 0.925 for the terminal ring of the first molecule listed in Scheme 2, this ring may be relatively stable like benzene, whereas if the LA is close to zero, like 0.068 for the annelated ring of this molecule, it means that this ring is nearly "empty" by Clar's terminology.¹⁵ In other words, this hydrocarbon can be viewed as a composition of one naphthalene and

two benzenes to the first approximation. Hence it is understandable that the reactivity of this species is actually determined by its naphthalene fragment. Extending this analysis to all other molecules listed in Scheme 2, we can find that in each of four homologous series, the logarithms of the second order rate constants, $6 + \lg k_2$, are very close, respectively depending on their characteristic fragments, *i. e.*, naphthalene, anthracene, tetracene, and pentacene (these fragments are denoted by bold lines in Scheme 2).

It should be mentioned that because of the excellent correlation between the *RE* and the $\ln K$ as displayed in

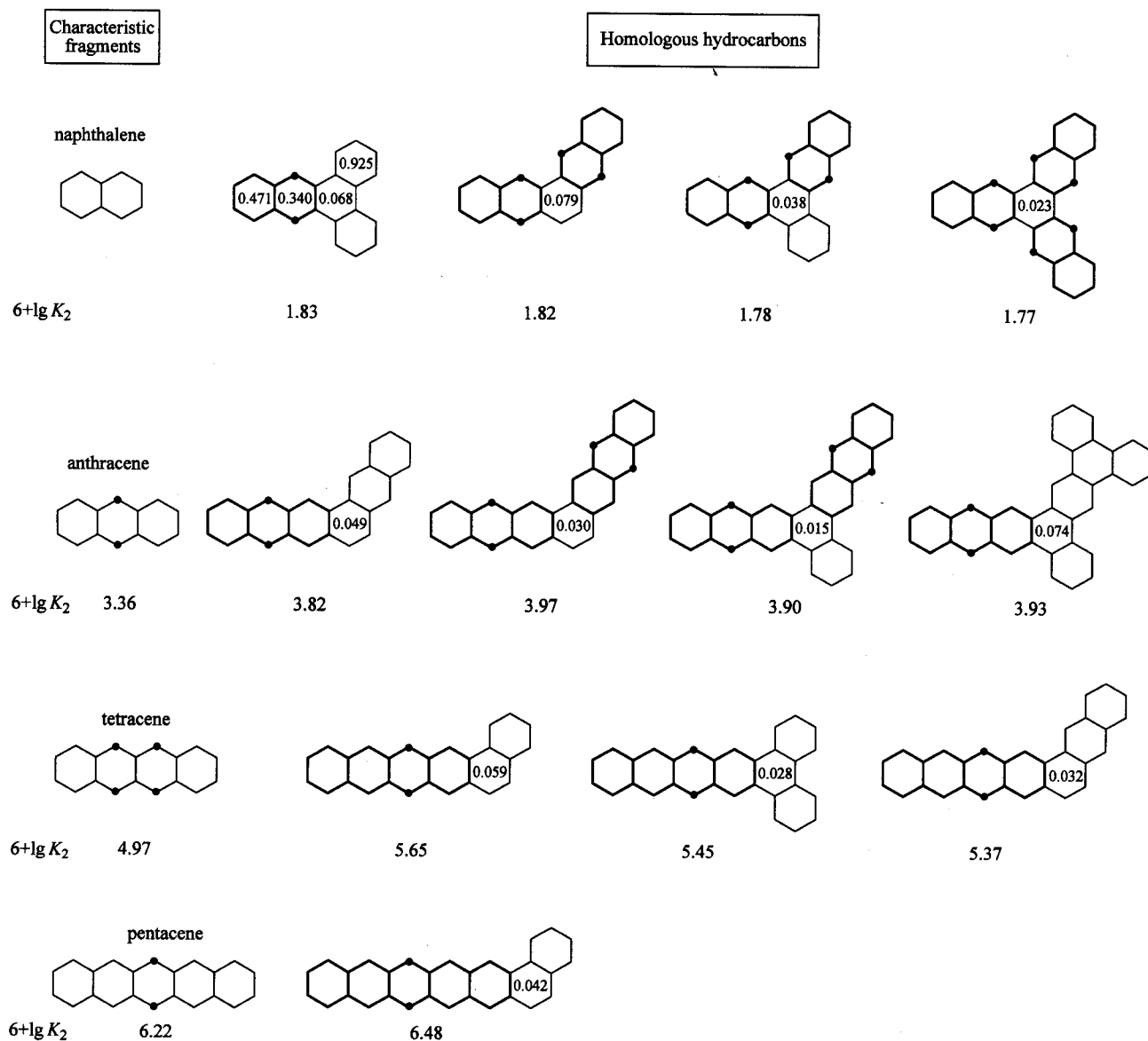
Eq. (8), the local aromaticity index considered above can also be approximately attained by directly counting the Kekulé structures through

$$LA_i \approx 1.398 \ln [K(\text{the whole system})/K(\text{the } i\text{th ring is missing})] \quad (13)$$

[the calculated *RE* of benzene (-0.9 J) is adopted in this formula]. Obviously, by using this formula, one can quickly estimate the local aromaticities of individual rings for a given benzenoid hydrocarbon.

It seems that the reactivity of a large benzenoid hy-

Scheme 2



drocarbon can be qualitatively evaluated in terms of the analysis of its characteristic localized components, which is easily performed within the present scheme.

Conclusions

This work presents a valence bond viewpoint for understanding reactivities of the Diels-Alder reactions of benzenoid hydrocarbons. In quantitative correlations with the experimental data, the *para*-localization energy index based on our VB calculations is comparable to or superior to previous theoretical models. In the meantime, another quantity, the resonance energy difference between the product and reactant, is exhibited to be parallel to the *para*-localization energy index within the Kekulé-based VB framework. More importantly, it was showed that the widely used Herndon structure/reactivity relationship can be naturally attained from the present work. Therefore, a quantum mechanical evidence of Herndon's simple method is revealed. On the other hand, it was demonstrated that for homologous benzenoid systems, the reactivities of their Diels-Alder reactions qualitatively depend on their characteristic localized fragments, which can be recognized without any difficulty by the local aromaticity defined in this work.

References and note

- 1 Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961.
- 2 (a) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163.
(b) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3173.
(c) Biermann, D.; Schmidt, W. *Israel J. Chem.* **1980**, *20*, 312.
- 3 (a) Brown, R. D. *J. Chem. Soc.* **1950**, 691.
(b) Brown, R. D. *J. Chem. Soc.* **1950**, 3249.
(c) Brown, R. D. *J. Chem. Soc.* **1951**, 1612.
(d) Brown, R. D. *J. Chem. Soc.* **1951**, 3129.
- 4 Dewar, M. J. S.; Pyron, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 3098.
- 5 Pullman, B.; Pullman, A. *Prog. Org. Chem.* **1958**, *4*.
- 6 Fukui, K. *Fortschr. Chem. Forsch.* **1970**, *15*, 1.
- 7 Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.
- 8 (a) Hess, B. A.; Schaad, L. J.; Herndon, W. C.; Biermann, D.; Schmidt, W. *Tetrahedron* **1981**, *37*, 2983.
(b) Hess, B. A.; Schaad, L. J. *J. Chem. Soc., Chem. Commun.* **1977**, 243.
(c) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305.
- 9 (a) Herndon, W. C. *J. Chem. Soc., Chem. Commun.* **1977**, 817.
(b) Herndon, W. C. *J. Org. Chem.* **1975**, *40*, 3583.
(c) Herndon, W. C. *J. Org. Chem.* **1981**, *46*, 2119.
- 10 Li, S. H.; Jiang, Y. S. *J. Am. Chem. Soc.* **1995**, *117*, 8401.
- 11 Alexander, S. A.; Schmalz, T. G. *J. Am. Chem. Soc.* **1987**, *109*, 6933.
- 12 Wu, J.; Jiang, Y. S. *J. Comput. Chem.* **2000**, *21*, 856.
- 13 Li, S. H.; Ma, J.; Jiang, Y. S. *Chin. J. Chem.* **2002**, *20*, 1168.
- 14 (a) Diederich, F.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 372.
(b) Krieger, C.; Diederich, F.; Schweitzer, D.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 699.
- 15 This result also suggests that the Kekulé-based VB method is nearly size-consistent, because complete size-consistency demands $RE = A \ln K$ (A is a parameter). See:
(a) Carter, P. G. *Trans. Faraday Soc.* **1949**, *45*, 597.
(b) Swinborne-Sheldrake, R.; Herndon, W. C. *Tetrahedron Lett.* **1975**, 755.
(c) Seitz, W. A.; Klein, D. J.; Schmalz, T. G.; Garcia-Bach, M. A. *Chem. Phys. Lett.* **1985**, *115*, 139.
- 16 Clar, E. *The Aromatic Sextet*, Wiley, New York, 1972.
- 17 (a) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.
(b) Randić, M. *Tetrahedron* **1975**, *31*, 1477.
- 18 Herndon, W. C.; Ellzey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631.
- 19 Moyano, A.; Paniagua, J. C. *J. Org. Chem.* **1991**, *56*, 1858.
- 20 Dewar, M. J. S.; de Liano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.