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PARAMETERIZED VALENCE BOND CALCULATIONS FOR BENZENOID HYDROCARBONS USING CLAR STRUCTURES

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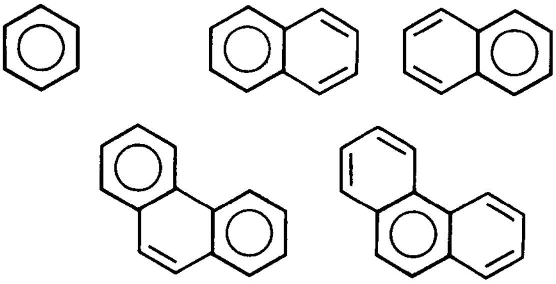
Abstract. SCF (Dewar-de Llano) calculations are used to parameterize a valence bond theory with a basis of Clar structures. A precise correlation of calculated resonance energies is found (corr. coeff. 0.9998). Graphtheoretic algorithms for carrying out the calculations are illustrated. It is suggested that this theoretical approach would be useful in considering structure and reactivity problems in very large polycyclic benzenoid aromatic hydrocarbons.

The concept of the aromatic sextet has been codified through the use of molecular diagrams that can be termed "Clar structures". In particular empirical structure-stability rules have been postulated by Clar[1,2] based on a large accumulation of qualitative experimental stability data. In this present paper we will test the quantitative use of Clar structures as valence bond (VB) basis functions for resonance energy (RE) calculations. The benchmark RE's of Dewar and de Llano[3] will be used to parameterize the VB calculations and for comparison purposes.

CALCULATIONS

Definitions and Procedures - In this paper Clar structures are defined to be structural diagrams in which all the carbon atoms of an aromatic hydrocarbon are spanned either by an aromatic sextet (designated by a circle) or by a π electron pair (designated by a double bond). Examples shown in 1 illustrate the fact that more than one Clar structure can be drawn for all condensed benzenoid systems except for that of benzene. One should note that the definition of a Clar structure is somewhat different from that of a "Clar pattern" as previously discussed by Hosoya and coworkers.[4,5]



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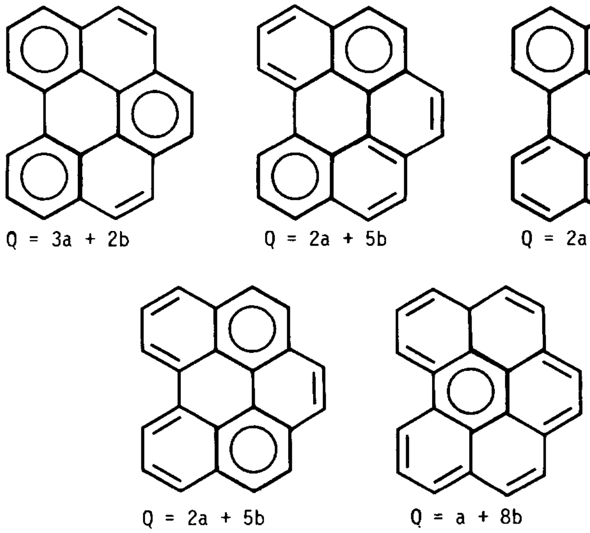
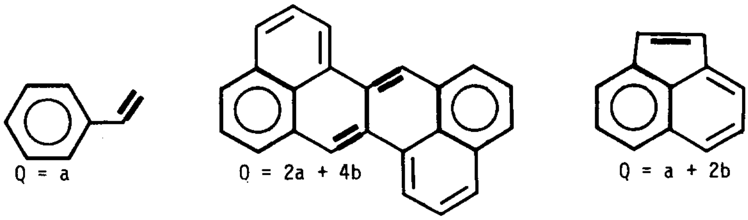
The canonical set of N Clar structures for a given aromatic hydrocarbon can be obtained using the rule that two circles cannot occupy adjacent annelated rings since this would signify two sextets = 12 electrons distributed over 10 π electron centers. The full (N = 5) canonical set of the Clar structures for benz[1,12]perylene is given in 2 as an example. Parameters a and b in 2 refer to Coulomb-type integrals for aromatic sextets and double bonds respectively, and both terms contribute to the total calculated RE of each Clar structure. However fixed, double bonds as in the molecules shown in 3 are assumed not to contribute to the calculated RE.



Q = 3a + 2b Q = 2a + 5b Q = 2a + 5b

Q = 2a + 5b Q = a + 8b

2



Q = a Q = 2a + 4b Q = a + 2b

3

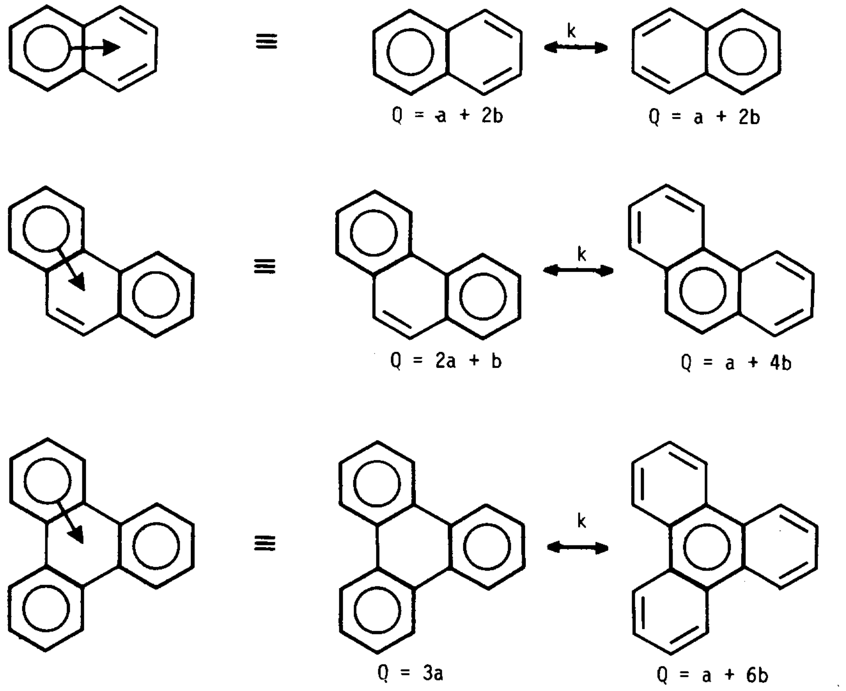
The Clar structures are to be taken as a basis set for an empirical VB calculation of RE. To obtain the total RE one must solve the effective VB Hamiltonian secular equation

$$\det|Q - XI| = 0 \tag{1}$$

where I is the N x N unit matrix, and the off-diagonal exchange elements of the Q matrix are enumerated and evaluated according to the following assumptions.

N-, P-, and T-type Resonance: The pairs of Clar structures depicted in 4 can be related to single particular Kekulé structures by alternate placement of the sextet circle in the available rings.[4,5] This type of sextet migration was originally symbolized with a corresponding number of arrows impinging on a single (central) ring by Clar.[2] However, since two circles cannot occupy adjacent annelated rings in a Clar structure, a single arrow or a single VB exchange integral k can be used to denote each resonance interaction depicted in 4. In these cases we say the Clar structures are k-related.

W- and O-type Resonance: It is possible to relate pairs of Clar structures to one another by simultaneous migration of two or more electron sextets. The examples of chrysene (W-type) and coronene (O-type) are depicted in 5 and 6 respectively. The relative decreasing sizes of the



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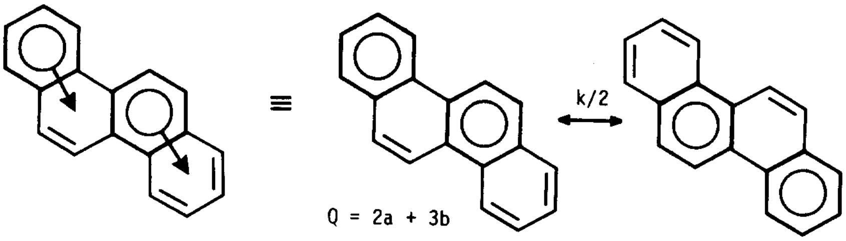

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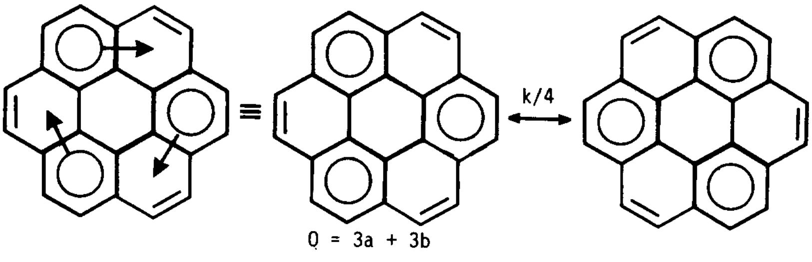

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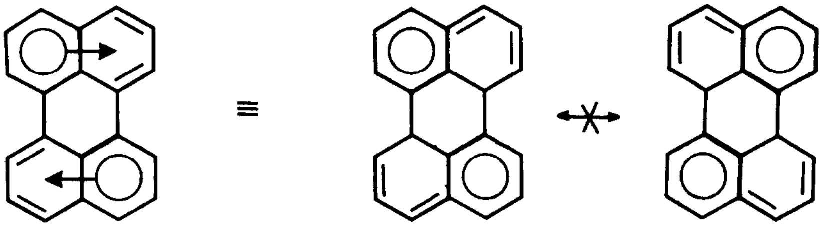
exchange parameters in 4, 5, and 6 are assigned in analogy to the relative sizes of exchange integrals for overlapping bond eigenfunctions calculated using Rumer-Pauling diagrams.[6,7] In any event, the values chosen lead to precise agreement of LCAO-MO-SCF[3] and VB resonance energies to be given in the results section.

Z-type Resonance: The resonance interaction depicted in 7 for perylene involves double sextet migration as in 5, but here the migrations take place in two separate subsystems interconnected by essential single bonds. In cases of this type we say that the structures are not k-related. The reason is that several different kinds of theoretical calculations [3,8-11] agree in assigning the RE of perylene as exactly twice the RE of naphthalene inferring that this type of resonance interaction should have no effect on RE. Heats of formation [3,12] and bond length data[13] are also in agreement with the argument that resonance of this type should be neglected in a VB structure-resonance theory calculation. However in 8 and 9, the bonds joining the subsystems are not essential single bond; a k-relationship exists, and appropriate resonance terms (k/2 in these cases) should be counted.



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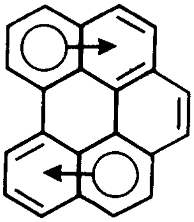

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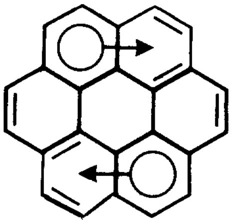

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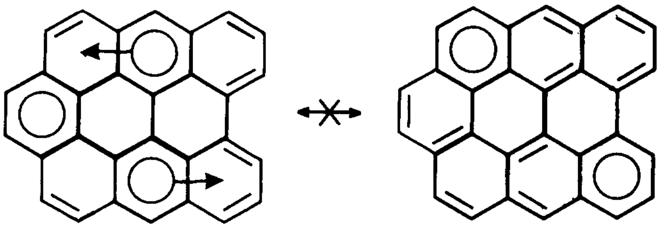
Finally, we also neglect double sextet migration resonance integrals and higher order terms if the resonance interactions leads to a change in the number of Clar sextets. An example is given in 10, and resonance terms of this type are numerous in the larger pericondensed polycyclic aromatic systems. Leaving out these terms leads to an easier computational procedure, and their inclusion gives calculated RE's in poor agreement with the SCF RE's. At present, we can adduce no further justifications for their exclusion.



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Parameterization- The trial VB wavefunction is taken as a linear combination of all allowed Clar structural diagrams. The secular equation that must be solved to obtain the state energies is given in eq. 1. In the VB approach the principal eigenvalue, with associated totally symmetric eigenfunction, represents the ground state energy.

In the case of the linear catacondensed acenes (benzene, naphthalene, anthracene, etc.) it is possible to write general explicit linear equations for the state energies in terms of the parameters a, b, k, and the number of 6-membered rings, n. The ground state energy, j = 1, is

$$E_j = a + 2b(n-1) + \left(2k \cos \frac{j\pi}{n+1}\right) \tag{2}$$

$$E(\text{ground state}) = RE = a + 2b(n-1) + 2k\left(\cos \frac{\pi}{n+1}\right) \tag{3}$$

equal to the RE. Linear equations in a, b, and k can also be obtained for pericondensed molecules in which linear acene fragments are separated only by essential single bonds as in perylene. Dewar and de Llano[3] studied 10 molecules within these types. Their RE's in terms of the Clar VB parameters and the LCAO-MO-SCF calculated values are given in Table 1. These 10 linear equations were subjected to a linear regression analysis to obtain the values of the parameters, also given in Table 1. We could have optimized the parameter values[14] using the entire Dewar-de Llano[3] data set of RE's. However we chose not to do this because of the precise correlation finally obtained, and because of the possibility that we might be able to use large deviations from future calculated values to help identify important structural features that could require empirical modifications of the theory.

Table 1. Resonance Energy Parameter Equations

Compound	VB equation	RE(SCF)^3(eV's)
Benzene	a	= 0.869
Naphthalene	$a + 2b + k$	= 1.323
Anthracene	$a + 4b + 1.4121k$	= 1.600
Tetracene	$a + 6b + 1.61803\,k$	= 1.822
Pentacene	$a + 8b + 1.73205\,k$	= 2.004
Perylene	$2a + 4b + 2k$	= 2.619
Zethrene	$2a + 4b + 2k$	= 2.694
Quarterrylene	$4a + 8b + 4k$	= 5.309
Acenaphthylene	$a + 2b + k$	= 1.335
Fluoranthene	$2a + 2b + k$	= 2.141

$a = 0.8590$

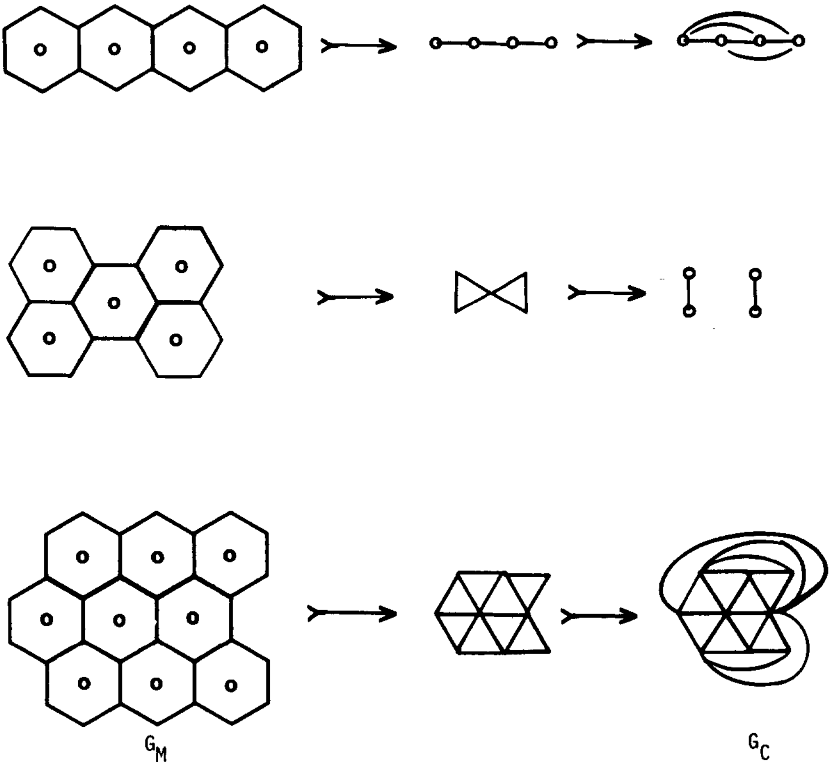
$b = 0.0744$

$k = 0.3176$

Correlation Coefficient 0.9993

The Number of Clar Structures - We use graph-theoretical concepts and algorithms to help count and verify the Clar structures. Several examples are given below to clarify and illustrate this approach.

To count Clar structures we use the concept of a modified C-graph (Clar graph, G_C)[15,16] which is a graph easily derived from the π-system molecular graph G_M. First the dual inner graph[17,18] is obtained by joining all the centers of neighboring hexagons as shown in 11. Then a



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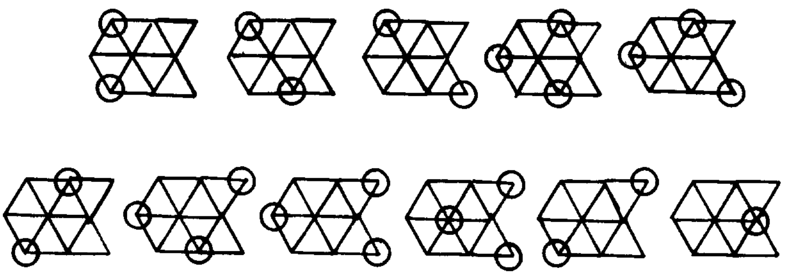
modified C-graph is drawn by deleting vertices corresponding to rings which cannot contain a sextet (empty rings[1,2]), and by also connecting those pairs of vertices which designate two rings in which sextets of electrons cannot be simultaneously present.[15]

Every Clar structure corresponds to a maximal independent set of vertices of the modified C-graph.[15] An independent set of vertices V(r) is said to be a maximal set if every vertex of the graph not included in V(r) is adjacent to at least one of the r vertices of V(r).[19] Applying this procedure to the molecular graphs in 11, one sees that each of the Clar structures of tetracene (or any linear polyacene) can only contain a single Clar sextet circle, and that all Clar structures of perylene must contain two and only two Clar circles. In general, however, Clar structures may contain varying numbers of Clar circles as illustrated in 12 where the maximal



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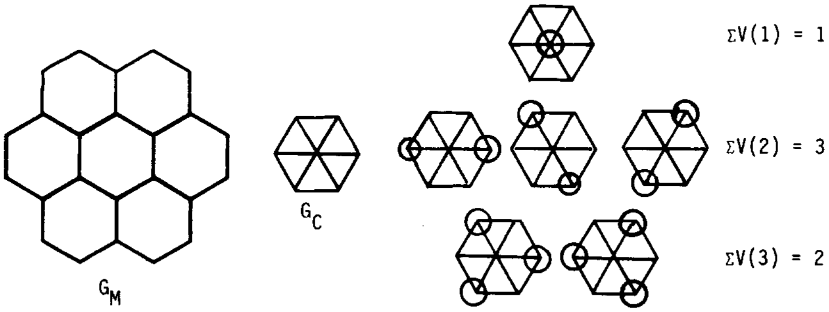
independent sets are schematically outlined for benzo[1,4]bisanthene, and r is equal to 1, 2, or 3. The drawings in 12 were systematically obtained using the benzobisanthene G_C of 11, but the curved lines of G_C have been omitted. In this case the Clar structure count (SC) is 11 and these eleven structures form the basis for the VB structure-resonance theory calculation.

Another example, coronene, is given is 13 to illustrate an additional complicating factor.

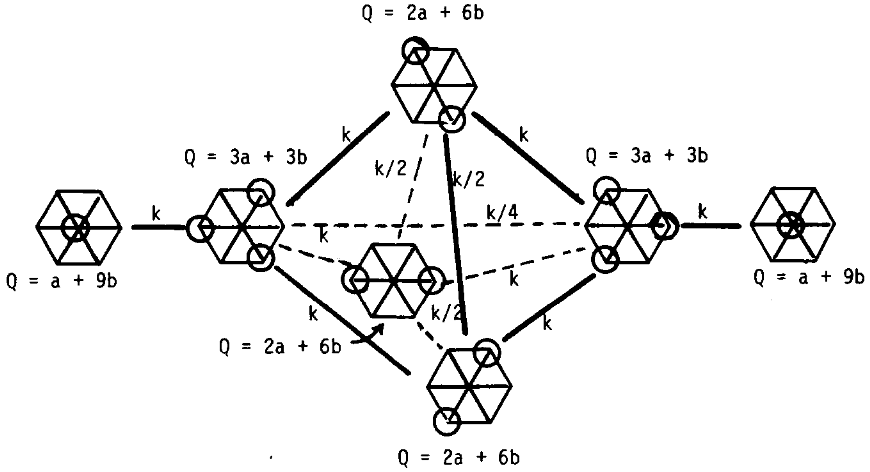


13

The G_C of coronene has $\Sigma V(1) = 1$, but the number of corresponding Clar structures is actually 2, due to the presence of a "super-ring"[4,5] in the framework of p-orbitals that remains after the central ring is deleted. In order to check for this structural feature and to confirm the Clar SC, the Clar structures can be explicitly drawn by using the V(r) of the C-graph as a guide. For coronene the Clar SC is 7 instead of 6 as would be obtained from simply counting the V(r).

Factorization and Graph Theory - Using the above-described procedures it is straightforward to set up the secular matrix for any π-molecule, and readily available HMO computer programs can be employed to find eigenvalues and eigenvectors, the principal eigenvalue giving the RE. In all cases the Clar structure basis is much smaller than, for example, the Kekulé structure basis,[10] allowing one to obtain the RE's by rapid hand calculations or with the aid of a desk calculator. Moreover, our aim is only to obtain the largest root of the secular equation corresponding to the ground state energy, which means that only the totally symmetric factored determinant is required to be solved.

Toward this end, the resonance (k) relationships among the Clar basis structures are usefully depicted using the graph-theoretic concept of the graph of the effective Hamiltonian matrix G_H.[10,20] Taking again the example of coronene, the vertices and lines of G_H correspond to structures and resonance interactions respectively as shown in 14. In this figure the dual graphs



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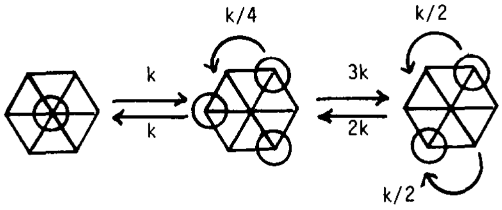
from 13 are used to represent the Clar structures and only k-relations are drawn. Using the symmetric character of the drawing in 14 allows one to obtain further symmetry-reduced graphs[20] that can be taken as equivalent to the block-diagonalized Hamiltonian matrix. The totally symmetric symmetry-reduced graph and the associated secular determinant is given in 15.



$$\begin{vmatrix} a+9b-x & k & \\ k & 2a+6b+k/4-x & \sqrt{6}k \\ & \sqrt{6}k & 3a+3b+k-x \end{vmatrix}$$

15

By substituting the optimized parameters into this determinant one obtains the largest root x = 3.516 (RE = 3.516 eV) which is close to the SCF RE value of 3.524 eV.[3]

RESULTS AND DISCUSSION

The Dewar-de Llano[3] and our Clar VB RE's are compared in Table 2 (next page). There are no significant discrepancies between the two calculated sets of values. The average deviation is ± 0.013 eV and the correlation coefficient is 0.9998. When one considers the ease of application, the Clar VB approach seems to provide a justifiable alternative to π-SCF-MO methods, and the results are tantamount to those obtained by the more complex procedures. Of the various simple schemes that have been tested to reproduce Dewar RE's,[8-11,21,22] the Clar VB structure-resonance theory seems to yield the most satisfactory correlation.

This Clar VB theory may be particularly suitable for investigating structure and reactivity problems in extremely large polycyclic benzenoid aromatic hydrocarbons. To illustrate this, note the Kekulé SC's (Table 2) for ovalene and quarterrylene, 50 and 81 respectively, as compared to the Clar SC's of 15 and 16. The numbers of p-orbitals, 32 and 40 respectively, are also larger then the Clar SC's, although these numbers of p-orbitals are well within current computational capacities. With even larger molecules the restricted size of the Clar basis set could prove to be an advantageous factor in a comparison with MO calculations or empirical VB calculations based on Kekulé structures.

The Clar structure basis also provides an easily visualized realization of the aromaticity of individual rings[10,23-26] within polycyclic benzenoid hydrocarbons. The eigencoefficients can lead directly to a numeric evaluation of benzenoid character, and one can postulate that benzenoid character is closely related to aromaticity. Problems of this type are under investigation.

Acknowledgment

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REFERENCES

[1] E. Clar, "Polycyclic Hydrocarbons," Vol. I and Vol. II, Academic Press, New York, N.Y., 1964.
[2] E. Clar, "The Aromatic Sextet," Wiley, London, 1972.
[3] M.J.S. Dewar and C. de Llano, J. Am. Chem. Soc. 91, 789 (1969).
[4] H. Hosoya and T. Yamaguchi, Tetrahedron Letters, 4659 (1975).
[5] N. Ohkami, A. Motoyama, T. Yamaguchi, H. Hosoya, and I. Gutman, Tetrahedron 37, 1113 (1981).
[6] L. Pauling, J. Chem. Phys. 1, 280 (1933).
[7] J.H. Van Vleck and A. Sherman, Rev. Mod. Phys. 7, 167 (1935).
[8] M. Randić, Chem. Phys. Letters, 38, 68(1976); J. Am. Chem. Soc. 99, 444(1977); Tetrahedron 33, 1905(1977).
[9] I. Gutman, M. Milun, and N. Trinajstić, MATCH 1, 171(1975); J. Am. Chem. Soc. 99, 1692(1977).
[10] W. C. Herndon and M. L. Ellzey, Jr., J. Am. Chem. Soc. 96, 6631 (1974).
[11] J. Aihara, J. Am. Chem. Soc. 98, 2750 (1956): Ibid. 99, 2048 (1977).
[12] W. C. Herndon, Thermochimica Acta 8, 225 (1973).
[13] W. C. Herndon, J. Am. Chem. Soc. 96, 7605 (1974).
[14] W. C. Herndon and M. L. Ellzey, Jr., Chem. Phys. Letters 60, 510(1979).
[15] I. Gutman, Z. Naturforschung 37a, 69 (1982).
[16] I. Gutman and S. El-Basil, Z. Naturforschung 39a, 276 (1984).
[17] A.T. Balaban and F. Harary, Tetrahedron 24, 2505, (1968).

Table 2. Resonance Energies (eV's) for Benzenoid Aromatic Hydrocarbons

Compound	Clar SC	Kekulé SC	RE(SCF)	RE(VB)	Difference
Benzene	1	2	0.869	0.859	0.010
Naphthalene	2	3	1.323	1.325	-0.002
Anthracene	3	4	1.600	1.606	-0.006
Tetracene	4	5	1.822	1.819	0.003
Pentacene	5	6	2.004	2.004	0.0
Perylene	4	9	2.619	2.651	-0.032
Zethrene	4	9	2.694	2.651	0.043
Quarterrylene	16	81	5.309	5.302	0.007
Acenapthylene	2	3	1.335	1.325	0.010
Fluoranthene	2	6	2.141	2.184	-0.043
Phenanthrene	2	5	1.933	1.924	0.009
Pyrene	3	6	2.098*	2.099	-0.001
Benzo[c]phenanthrene	3	8	2.478	2.477	0.001
Benz[a]anthracene	3	7	2.291	2.313	-0.022
Chrysene	3	8	2.483	2.477	0.006
Triphenylene	2	9	2.654	2.652	0.002
Dibenz[a.c]anthracene	3	13	3.058	3.076	-0.018
Dibenz[a.h]anthracene	3	12	2.948	2.958	-0.010
Dibenz[a.j]anthracene	3	12	2.948	2.958	-0.010
Benzo[a]pyrene	4	9	2.584*	2.579	0.005
Benzo[d]pyrene	3	11	2.853*	2.842	0.011
Benzo[1,12]perylene	5	14	3.128	3.098	0.030
Coronene	7	20	3.524	3.516	0.008
Benzo[1,4]bisanthene	11	30	3.862	3.902	-0.040
Ovalene	15	50	4.539	4.526	0.013
Biphenyl	1	4	1.699	1.718	-0.019
Styrene	1	2	0.858	0.859	-0.001
Stilbene (trans)	1	4	1.712	1.718	-0.006

*Corrected values (personal communication, M.J.S. Dewar)

REFERENCES (Cont.)

[18] T. Yamaguchi, Z. Suzuki, and H. Hosoya, Natural Science Report of the Ochanomizu University **26**, 39(1975).

[19] N. Christofides, "Graph Theory, An Algorithmic Approach," Academic Press, New York, 1975. Chpt. 3.

[20] W.C. Herndon, J. Mol. Structure **103**, 219(1983).

[21] B.A. Hess, Jr., and L.J. Schaad, J. Am. Chem. Soc. **93**, 305(1971)

[22] Clar structural formulas and an associated sextet counting polynomial have been used to define and discuss RE's by J. Aihara, Bull. Chem. Soc. Jap. **50**, 2010 (1977). A practical objection can be raised since the sextet polylnomial has complexed valued roots in some cases. Therefore RE's calculated by Aihara may be without acceptable physical meaning. See also discussions of so-called "topological ring resonance energies" by W. C. Herndon, J. Am. Chem. Soc. **104**, 3541(1982) and I. Gutman and W. C. Herndon, Chem. Phys. Letts. **105**, 281 (1984).

[23] O. Polansky and G. Derflinger, Int. J. Quant. Chem **1**, 397(1967).

[24] M. Randić. Tetrahedron **31**, 1477(1975).

[25] H. Hosoya, M. Shobu, K. Takano, and Y. Fujii, Pure and Appl. Chem. **55**, 269(1983).

[26] M. Zander, Match **14**, 183(1983).