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Critical Test for Resonance Energies[†]

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Abstract: The concept of conjugated circuits is used to formulate minimal conditions for theoretical models which have been designed to provide molecular resonance energies for benzenoid hydrocarbons. More than 20 available schemes have been tested and more than half were found to be deficient with respect to inherent consistency of the derived parameters R_n, signifying contributions from conjugated circuits of size $4n + 2$. The test is based on a graph-theoretical analysis which gives *expressions* for the molecular resonance energy and thus is independent of any computational errors or approximations in selection of the numerical parameters.

Despite some difficulties in giving a detailed definition of the molecular resonance energy and the fact that the computed quantity can only indirectly be related to experimental quantities such as the difference in the heats of atomization for hypothetical thermodynamic cycles, the notion of the resonance energy remains one of the central concepts in the chemistry of conjugated polycyclic systems. An important clarification is due to Dewar,[1] who identified the resonance energy (RE) with the difference in the total energy of the system and the reference energy derived from suitable bond additive terms.[2] Thus, the molecular RE represents the *departure* of the molecular energy in polycyclic conjugated systems from simple bond additivity, which is fully satisfied for acyclic conjugated structures.[1-3] A positive RE signifies that the polycyclic system is more stable than the acyclic reference structure, while a negative RE would indicate a system that is less stable than the corresponding acyclic reference system. The former can then be classified as aromatic or partially aromatic (i.e., with a dominant aromatic component) while the latter can be classified as antiaromatic.[4,5]

Aromaticity in the present paper is defined in terms of the presence or absence of *conjugated circuits*[6] of type $4n + 2$ or $4n$, respectively. A graph-theoretical analysis of Kekulê valence structures leads to the concept of conjugated circuits. This concept may be introduced in the following way. Imagine a particular Kekulê structure of some benzenoid hydrocarbon. Start with any carbon atom on the benzenoid hydrocarbon and traverse any path through bonds, returning finally to the starting position. If the path consists of alternating single and double bonds, the path is defined to be a conjugated circuit; otherwise it is not. In other words, the conjugated circuits are those circuits within the individual Kekulê valence structure for a molecule in which there is a regular alternation of the formal CC single and double bond.[6,7] Thus, conjugated circuits are necessarily of *even* length. The number of conjugated circuits characterize the system and provide a basis for discussion of the energetics of the conjugated structure.[8]

The circuit decomposition of individual Kekulê structures of polycyclic conjugated molecules leads to $4n + 2$ and/or $4n$ (linearly independent, linearly dependent, and disconnected) conjugated circuits. The $4n + 2$ circuits are denoted by R_n, while $4n$ circuits are denoted by Q_n. As an example we give the conjugated circuits count for anthracene in Figure 1.

The number of conjugated circuits for a molecule is $K - 1$,[9] where K is the number of Kekulê structures.

Besides the qualitative use of conjugated circuits for the classification of conjugated systems into aromatic (systems containing only $4n + 2$ conjugated circuits), partially aromatic (systems containing more $4n + 2$ than $4n$ conjugated circuits), partially antiaromatic (systems containing more $4n$ than $4n + 2$ conjugated circuits), and antiaromatic (systems containing only $4n$ conjugated circuits), the concept of conjugated circuits also leads to the *expressions* for the RE. One counts conjugated circuits[10] of different size within the collection of Kekulê valence structures and averages the sum (i.e., divides the sum by the number of Kekulê structures K for the molecule)

$$\mathrm{RE} = \frac{1}{K}\sum_{n\geq 1}(r_nR_n + q_nQ_n) \qquad (1)$$

where R_n and Q_n are parameters related to the $4n + 2$ and $4n$ conjugated circuits, while r_n and q_n are respectively the numbers of $4n + 2$ and $4n$ conjugated circuits belonging to a given polycyclic conjugated molecule. For several initial linear acenes one then obtains the RE expressions[6]

$$\text{benzene:} \quad \mathrm{RE} = (2R_1)/2 \qquad (2)$$

$$\text{naphthalene:} \quad \mathrm{RE} = (4R_1 + 2R_2)/3 \qquad (3)$$

$$\text{anthracene:} \quad \mathrm{RE} = (6R_1 + 4R_2 + 2R_3)/4 \qquad (4)$$

$$\text{tetracene:} \quad \mathrm{RE} = (8R_1 + 6R_2 + 4R_3 + 2R_4)/5 \qquad (5)$$

Of significance, however, is the fact that the above RE expressions 2–5, with a *suitable* choice of numerical values for the parameters R_n, can reproduce the REs for all kinds of benzenoid hydrocarbons[6,11b,13] and this agrees exceedingly well with reported

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(10) Conjugated circuits of polycyclic conjugated hydrocarbons can be enumerated and generated in several ways.[7,9,11] A powerful approach appears to be the method based on the transfer matrix.[12]

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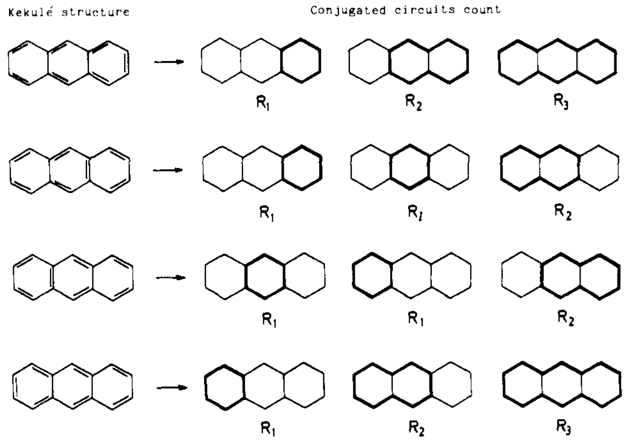

Figure 1. The conjugated circuits count for anthracene.

results based on SCF π-MO calculations.[14] Thus, the simple graph-theoretical approach reveals that the molecular RE, which represents a departure from bond additivity of the molecular energy, is itself an *additive* quantity: The additivity is in terms of qualified (i.e., conjugated) circuits contained in the collection of Kekulē valence structures.

Derivation of the Numerical Values for the R_n Parameters

The systems of linear eq 2–5 are results of a mathematical analysis of (molecular) graphs. In order to "inject" chemistry into this analysis one has to adopt some *outside* source. The parameters R_n are derived from the resonance energies reported by Dewar and de Llano[14] with use of Dewar's original variant[1] of the SCF π-MO theory of Pople.[15] One could use the least-squares approach to find the best set of parameters for R_n using the available SCF π-MO resonance energies for a dozen or more compounds, or alternatively one could use benzene (B), naphthalene (N), anthracene (A), and tetracene (T) as *standards* to which the R_n are adjusted accurately. The latter approach has some advantages for the present critical examination of available results. Equations 2–5 could more usefully (and just as concisely) be written as

$$R_1 = \mathrm{RE(B)} \qquad (6)$$

$$R_2 = \tfrac{3}{2}\mathrm{RE(N)} - 2\mathrm{RE(B)} \qquad (7)$$

$$R_3 = \mathrm{RE(B)} - 3\mathrm{RE(N)} + 2\mathrm{RE(A)} \qquad (8)$$

$$R_4 = \tfrac{3}{2}\mathrm{RE(N)} - 4\mathrm{RE(A)} + \tfrac{5}{2}\mathrm{RE(T)} \qquad (9)$$

Using the values for the SCF π-MO REs of benzene, naphthalene, anthracene, and tetracene by Dewar and de Llano[14]

$$\mathrm{RE(B)} = 0.869 \text{ eV}$$

$$\mathrm{RE(N)} = 1.323 \text{ eV}$$

$$\mathrm{RE(A)} = 1.600 \text{ eV}$$

$$\mathrm{RE(T)} = 1.822 \text{ eV}$$

we obtained[6]

$$R_1 = 0.8690 \text{ eV}$$

$$R_2 = 0.2465 \text{ eV}$$

$$R_3 = 0.100 \text{ eV}$$

$$R_4 = 0.1395 \text{ eV}$$

However, the value of the R_4 parameter appears to be unsatisfactory for a large range of benzenoids. Hence, in order to improve the agreement Dewar's REs, we determined the value of R_4 by a least-squares fit of our REs to the SCF π-MO REs for a score of randomly selected benzenoid hydrocarbons. The value obtained was $R_4 = 0.041$ eV.

The values of the R_n, $n = 1, 2, 3, 4$ parameters (with $R_4 = 0.041$ eV) appear very acceptable: As the ring size increases, so the contribution from the corresponding circuit decreases. This is in full agreement with expectation.[2,16] Larger $4n + 2$ annulenes are less aromatic then the smaller ones, a prediction already known from Hückel calculations.[17] The trend suggests that the role of even larger conjugated circuits may be ignored. Full mathematical equivalence of the above additivity of contributions from the conjugated circuits and the qualitative valence bond method (the structure–resonance theory) as developed by Herndon[18] can be established.[19] The conjugated circuits R_3 and R_4, which Herndon chose to neglect, make some small change to the computed REs for individual polycyclic systems.

The system of eq 6–9 propagate an error in the estimation of R_1 to R_2, and error in R_2 to R_3, and so on. Hence the values for the larger R_n will be sensitive to the accuracy of the estimates for the REs of benzene and naphthalene. A minor change in the numerical values for the various REs of the standard molecules can produce visibly different, even if not dramatically different, predictions for the parameters R_n. For example, slightly revised values for the standards used by Dewar and Trinajstič,[20] and by Herr,[21] produce the following SCF π-MO resonance energies

$$\mathrm{RE(B)} = 0.869 \text{ eV}$$

$$\mathrm{RE(N)} = 1.322 \text{ eV}$$

$$\mathrm{RE(A)} = 1.609 \text{ eV}$$

$$\mathrm{RE(T)} = 1.826 \text{ eV}$$

which in turn lead to the following set of R_n parameters

$$R_1 = 0.869 \text{ eV}$$

$$R_2 = 0.245 \text{ eV}$$

$$R_3 = 0.121 \text{ eV}$$

$$R_4 = 0.112 \text{ eV}$$

The above values seem to suggest that R_3 may have already approached its limiting constant value for the stabilizing contribution to larger conjugated circuits. Observe the significant variations in the new and old R_3 and R_4 parameters. We are not interested here in suggesting a novel parametrization, rather in indicating the limitations of a given set of parameters. If we were to recalculate the REs for a number of benzenoid hydrocarbons using $R_4 = 0.1395$ eV, rather than the least-squares value $R_4 = 0.041$ eV, we would only *increase* the differences between the predicted REs and those obtained by the SCF π-MO approach, because, as observed earlier,[6a] all the differences between the two sets of values are positive. Hence, $R_4 = 0.041$ eV is found to fit the overall data better, and hence, it can be viewed as empirical, even though not yet optimum. All this suggests that eq 6–9 themselves may provide the framework for *testing* various computed RE values for internal consistency, providing some assumptions on the relative trends for R_n are adopted.

Testing Criteria for Resonance Energies

First, we observed that the R_n values decrease with n, and we will allow for either R_n tending to zero or to some relatively small value, not necessarily much different from the values of R_3, R_4, and R_5. Second, we will demand, as the minimum criterion, that RE(B), RE(N), and RE(A) be accurately reproduced—reproduction here refers to the theoretical values, which may differ

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Table I. The Resonance Energies of Benzene (B), Naphthalene (N) and Anthracene (A) Taken as Source Data for Computation of the Graph-Theoretical Parameters R_n ($n = 1, 2, 3$) Which Represent the Contributions of the Conjugated Circuits of Size $4n + 2$[a]

	resonance energies (eV)			parameters for conjugated circuits (eV)			
method	RE(B)	RE(N)	RE(A)	R_1	R_2	R_3	ref
SPO	1.318	2.280	3.078	1.318	0.784	0.634	*e*
SCF π-MO	1.318	2.282	3.086	1.318	0.787	0.644	*e*
SCF π-MO	2.050	3.690	5.173	2.050	1.435	1.326	*f*
SCF π-MO	0.869	1.323	1.600	0.869	0.247	0.100	*g*
DRE	0.932	1.483	1.904	0.932	0.361	0.291	*h*
ring additivity	0.911	1.483	1.904	0.911	0.403	0.270	*i*
SCF π-MO	0.980	1.457	1.774	0.980	0.226	0.156	*j*
structure-resonance theory	0.84	1.35	1.60	0.84	0.35	−0.01	*k*
logarithmic formula[b]	0.821	1.302	1.643	0.821	0.311	0.201	*l*
ISE[c]	0.918	1.451	1.858	0.918	0.341	0.281	*m*
IMOSE[d]	0.925	1.458	1.813	0.925	0.337	0.177	*m*
HMOSE[d]	0.925	1.478	1.853	0.925	0.367	0.197	*m*

[a] All the approaches in this table satisfy the minimal conditions on the R_n. For details on the individual approaches and their acronyms (sometimes rather cryptic) the reader should consult the original literature. [b] $RE = a \ln K$; $A = 1.185$ eV, K = the number of Kekulé structures. [c] Based on heat of formation values taken from: Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970. [d] Based on SCF π-MO heats of atomization and resonance energies.[14] [e] Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685. [f] Lo, D. H.; Whitehead, M. A. *Can. J. Chem.* **1968**, *46*, 2027. [g] Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. [h] Baird, N. C. *Can. J. Chem.* **1969**, *47*, 3535. [i] Balaban, A. T. *Rev. Roumaine Chim.* **1970**, *15*, 1243. [j] Dewar, M. J. S.; Harget, A. J. *Proc. R. Soc. (London) A* **1970**, *315*, 443. [k] Herndon, W. C.; Ellzey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631. [l] Swinborne-Sheldrake, R.; Herndon, W. C.; Gutman, I. *Tetrahedron Lett.* **1975**, 755. [m] George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121.

from the values used for comparison. Because the individual RE are computed *independently* for each molecule the above conditions represent genuine constraints and, as will be seen, many schemes even widely used do not satisfy the critical conditions proposed here. One could impose additional conditions, such as the inclusion of RE(T) as one of the standards that ought to be reproduced accurately, but because of the nature of the corresponding equation, the solution of which is obtained by gradual substitution of smaller R_n values, the accumulation of minor errors in R_1, R_2, and R_3 may result in rather unreliable values for R_4. Hence, it seems sufficient to limit the testing to the most dominant contributions to the molecular RE, i.e., to R_1, R_2, and R_3 conjugated circuits.

In the following we will apply the above criteria to a number of reported theoretical methods for calculating the REs of benzenoid hydrocarbons. We have selected benzenoids rather than a more general collection of benzenoid and non-benzenoid hydrocarbons because the latter may introduce in addition to conjugated circuits of size $4n + 2$ those of size $4n$. This doubles the number of graph-theoretical parameters to be examined and, as discussed elsewhere,[6] parameters associated with $4n$ conjugated circuits are even less precise.[22]

Before considering a number of alternative estimates for the RE of benzenoid hydrocarbons, we should mention that comparisons of the results of different methods are given in a number of publications.[3,19,23] These usually consist of lists of the results of different methods and their differences and discuss the degree of congruence. In some cases the formal structures of the methods themselves are compared.[19] Such comparisons, useful as they are, are not likely to reveal subtle differences and deficiencies. This is especially true in the case of benzenoid hydrocarbons which represent a highly homogeneous collection of structures, although comparisons of this kind, particularly when extended to non-benzenoid systems, conjugated radicals and ions, heterocycles, etc., may point to some structures in which two theories differ significantly: one predicting the compound under consideration to be stable and the other predicting it to be unstable. An illustration of this is, for example, the different theoretical predictions obtained for heptalene. Hückel theory predicts the RE of heptalene per π electron (RE/e = 0.301β) which is comparable to that of benzene (RE/e = 0.333β),[24] whilst the Hess-Schaad model gives a value of the RE per π electron (RE/e = -0.002β) characteristics of a non-aromatic species.[3] Experimental findings are congruent with the Hess and Schaad prediction: Heptalene indeed represents a cyclo-polyenic system.[25]

Finally, before embarking on the application of our criteria, we do not want to leave an impression that this question of critical assessment of theoretical methods for calculating REs has not received attention in the chemical literature already. We should in particular mention the work by George et al.[26] They not only pointed to a number of limitations in the definition of the RE for conjugated hydrocarbons but also proposed a remedy in the form of a definition which appears to be susceptible to experimental verification. The fundamental idea of George et al. was to consider special reactions, called *homodesmotic*, in which the hybridization of carbon atoms and the number of CH bonds do not change in the course of the reaction. This allows cancellations of some invariant contributions and increases the accuracy of the predicted RE.

Examination of a Number of Available Theoretical Schemes for Calculating Resonance Energies

For each selected theoretical approach we have taken the reported REs of benzene, naphthalene, and anthracene and then solved the system of eq 6–8. The results are collected in Table I and Table II. In Table I are listed those cases that passed the test, and those that failed are given in Table II.

The number of theoretical computations of REs for benzenoid hydrocarbons is substantial and no effort was made to search for all of them. The selected ones are representative in that they cover the diversity of the theoretical methods: from simple HMO and its modifications to semiempirical SCF MO methods and VB-type computations. One of the factors in selecting the reported methods is the number of structures computed by the method. The purpose

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Table II. The Review of Methods Used to Compute R_n (n = 1, 2, 3) Which Fail To Satisfy the Constraints on the Monotonic Dependence of R_n on n[a]

	resonance energies (eV)			parameters for conjugated circuits (eV)			
method	RE(B)	RE(N)	RE(A)	R_1	R_2	R_3	ref
VB	1.561	2.654	3.630	1.561	0.846	0.859	*e*
HMO[b]	2.000	3.683	5.314	2.000	1.525	1.579	*f*
VB	1.561	2.875	4.206	1.561	1.191	1.348	*g*
HMO with S = 0.25	1.561	2.723	3.816	1.561	0.963	1.024	*g*
ring count formula[b,c]	1.561	2.602	3.643	1.561	0.781	1.041	*g*
additive DRE	0.911	1.435	1.995	0.911	0.331	0.596	*h*
reparametrized HMO[b]	0.390	0.550	0.658	0.390	0.045	0.056	*i*
reparametrized HMO[b]	0.440	0.563	0.634	0.440	−0.036	0.019	*j*
IMOSE[d]	0.918	1.335	1.670	0.918	0.167	0.253	*k*
HMOSE[d]	0.918	1.487	1.971	0.918	0.395	0.399	*k*
Z number[b]	0.278	0.366	0.464	0.278	−0.0007	0.108	*l*
TRE[b]	0.273	0.389	0.475	0.273	0.038	0.056	*m*
TRE[b]	0.276	0.390	0.476	0.276	0.033	0.058	*n*

[a] One of Hakala's schemes can be classified as satisfactory, because we do not insist on the inclusion of R_4 in the testing procedure. Observe the undesirable large value of R_3 for HMO, the feature that persists to some degree for almost all schemes listed in this table. [b] In β units. [c] RE = 6(N_c + N_a + N_e) kcal/mol; N_c = the number of carbon atoms, N_a = the number of angular condensed rings, N_e = the number of fully enclosed rings. [d] Based on the HMO values taken from: Coulson, C. A.; Streitweiser, A., Jr. *Dictionary of π-Electron Calculations*; Freeman: San Francisco, 1965. [e] Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955. [f] Streitweiser, A., Jr. *Molecular Orbital Theory for Organic Chemists*, 4th ed.; Wiley: New York, 1967. [g] Hakala, R. W. *Int. J. Quantum Chem.*: *Quantum Chem. Symp.* **1967**, *1*, 187. [h] Baird, N. C. *Can. J. Chem.* **1969**, *47*, 3535. [i] Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305. [j] Milun, M.; Sobotka, Ž.; Trinajstič, N. *J. Org. Chem.* **1972**, *37*, 139. [k] George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121. [l] Aihara, J.-i. *J. Org. Chem.* **1976**, *41*, 2488. [m] Aihara, J.-i. *J. Am. Chem. Soc.* **1976**, *98*, 2750. [n] Gutman, I.; Milun, M.; Trinajstič, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.

of this work is not to judge alternative schemes but rather to point to a need for some improvement.

The examination of Tables I and II reveals a significant difference between the schemes analyzed. In Table I, which contains the methods that passed the test for intrinsic consistency of the parameters, we find the following: (a) several variants of the SCF MO approach and (b) few schemes based on some kind of *additivity* or *relationship*. In contrast the methods in Table II, classified as deficient (as far as the test for innate consistency is concerned), are variants of the Hückel MO approach, or schemes based on HMO, even when they use different reference procedures. Thus, it appears very clear that HMO-based approaches have some unresolved difficulty.

The analysis of the results by George et al.[26] is instructive. When their REs are based on the SCF π-MO schemes or on the empirical heats of formation, then they belong to Table I. When their REs are based on Hückel theory, then they are classified as not satisfactory because they do not pass the test and appear in Table II.

Concluding Remarks

The ultimate test of any model is comparison with experiment. The testing that we propose here is not to replace the ultimate validation whose aim is to reproduce experimental results when known. Rather it can assist a model in extending its applicability, possibly reducing standard error, revise some underlying assumptions, even perhaps help in determining some hitherto unknown parameters, or put some bounds on their magnitude. With more *precise* and more reliable results for the standard structures (such as benzene, naphthalene, and anthracene used in this study), one can attempt a more critical selection of parameters relating to non-benzenoid systems, non-alternants, cations, and anions of conjugated molecules, and one can even contemplate a quantitative approach to RE in heterocyclic systems.[27] Already with a more precise set of parameters for benzenoid systems one can resolve the dilemma of neglecting some terms in the enumeration of conjugated circuits and see what possible influence these additional terms may have. Gomes has also pointed out the need to include linearly dependent conjugated circuits, but he still advocates ignoring contributions from disjoint conjugated circuits.[8c] If one constructs all possible superpositions of various Kekulé valence forms, as implied in the computations of the various VB integrals, then disjoint conjugated circuits also emerge.[28] In large polycyclic systems the number of such contributions may be quite large, as has been illustrated for coronene.[29] Hence it would be important to know if such contributions have a significant effect on the molecular RE. But, while these questions may be somewhat detailed, the major problem that remains unanswered is the limiting behavior of contributions from higher conjugated circuits: Do such contributions approach some limiting finite nonzero value, or do they decay to zero after some threshold value of n? In other words, is the resonance stabilization local, not extending beyond a certain radius, as the zero-convergence for large R_n would imply, or is it perhaps global, extending over all the molecular structure, regardless of its size? It may happen, once again, that the simple Hückel method offers the correct answer, but we may not know this until and unless very reliable REs are obtained for smaller benzenoid systems, particularly our standards: benzene, naphthalene, and anthracene (and tetracene). Or the answer may come from other sources, such as experimental work on larger annulenes or theoretical work on long-range spin coupling in hexagonal lattices.[30]

Registry No. Benzene, 71-43-2; naphthalene, 91-20-3; anthracene, 120-12-7.

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