A COMPARISON OF RECENT THEORETICAL AROMATICITY INDICES

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Abstract – In the past decade REPE [B. A. Hess, Jr., and L. J. Schaad, J. Am. Chem. Soc., 93, 305 (1971)], Herndon's valence bond method [J. Am. Chem. Soc., 95, 2404 (1973)], the graph theoretical method of Trinajstić, Gutman and colleagues [MATCH, 1, 171 (1975)] and of Aihara [J. Am. Chem. Soc., 98, 2750 (1976)] and the conjugated circuits method by Randić [Chem. Phys. Lett., 38, 68 (1976)] have been developed for the prediction of aromatic character. These new methods are all quite simple to use; and, although minor differences can be found, for neutral conjugated molecules they tend to agree and to give results which are remarkably good compared to those of earlier techniques. The structures of the four methods are compared, and they are shown to be similar.

INTRODUCTION

Theoretical methods developed in the last ten years for the prediction of aromatic character are definitely more successful than those used earlier. This statement can be made without agreement on a quantitative experimental definition of aromaticity. It is enough to agree to the qualitative statement that aromatic compounds are especially stable and react by electrophilic substitution rather than addition. The reason that this is sufficient is that predictions from earlier theoretical treatments, in particular the Hückel delocalization energy, fail so badly that they disagree with even the most qualitative notions of aromaticity.

In the present paper we shall describe and compare four of the newer theoretical methods:

1. REPE of Hess and Schaad (Refs. 1-3)
2. The Valence Bond Method of Herndon (Refs. 4,5)
3. The Topological Resonance Energy of Trinajstić and coworkers (Refs. 6,7) and Aihara (Ref. 8).
4. Randić's method of conjugated circuits (Refs. 9,10).

The comparisons we wish to make are not so much in terms of the quality of predictions. There are differences, but on the whole the four give similar predictions for neutral conjugated molecules. To make a finer comparison would require a quantitative definition of aromaticity. This could be given, but here we want rather to compare the formal structure of the methods themselves.

Most theoretical indices of aromaticity are computed as differences between the actual molecular energy and the energy of some reference structure. This is not universally true; Julg (Refs. 11,12) and Kruszewski and Krygowski (Refs. 13,14) follow a suggestion of Albert (Ref. 15) and express aromaticity in terms of bond length equalization; but the four methods to be compared here can all be formulated as the difference between actual and reference energies. It will be crucial to keep the reference structure explicitly in mind. Much

confusion in the literature can be traced to a failure to do this.

Another point of confusion has arisen because often resonance or delocalization energies
have not been normalized to take into account the varying size of the conjugated system. In
comparing, for example, thermodynamic heats of formation of benzene and acetylene one of
course compares the ΔH_f of 1 mole of benzene with that of 3 moles (not 1 mole) of acetylene.
A similar normalization should be made in comparing resonance energies. If total resonance
energies are compared for conjugated molecules with a wide range of size, the dominating
effect is likely to be simply that large molecules have more resonance energy than small.
To illustrate this, Fig. 1 shows total resonance energy computed as in Ref. 1 compared with
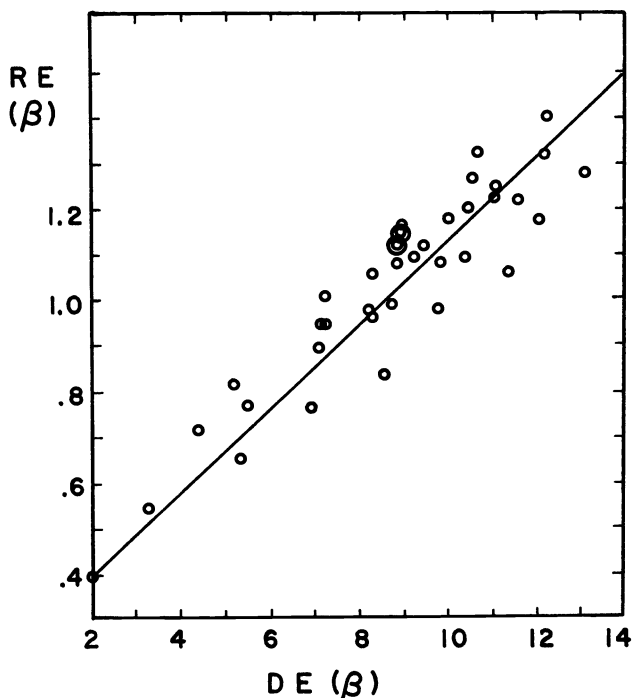

Fig. 1. A comparison of total resonance energy computed using the usual
ethylene reference (DE) and with the reference of Ref. (1) (RE).

the usual Hückel delocalization energy (Ref. 16) for the 40 benzenoid compounds of Ref. 17.
There appears to be fair agreement between the two methods, but this is entirely spurious.
Benzene lies in the lower left of the figure and the points correspond to molecules of
increasing size up to 32 carbon atoms in the upper right. If instead the two resonance
energies are compared per pi electron (or per carbon atom) as in Fig. 2, no correlation is
seen between the two methods. The best normalization is not yet certain. We at first
divided by the number of pi electrons (Ref. 1), but now by the number of carbon atoms
(Ref. 3). The two are equivalent for neutral ground-state hydrocarbon molecules, but differ
somewhat for ions and some hetero-systems. Division by the number of bonds has also been
used (Ref. 18), though Trinajstić (Ref. 19) finds no significant difference between this and
the division by number of pi electrons. In this paper we shall primarily use division by
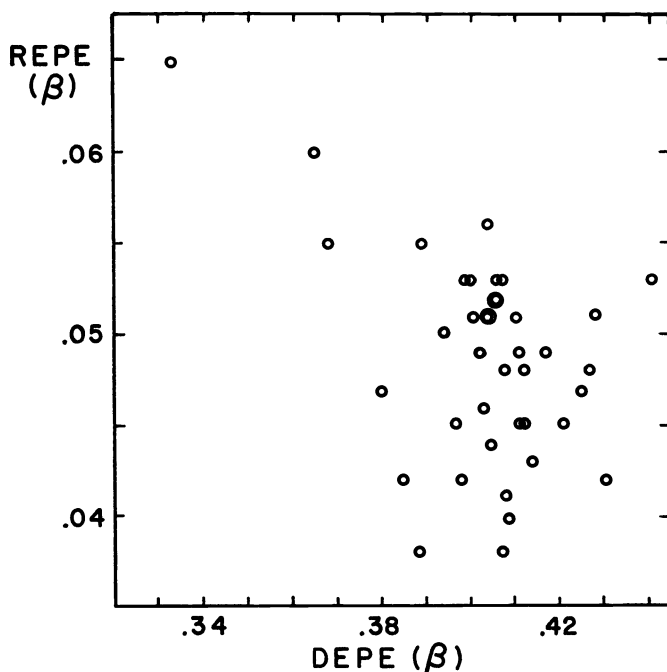number of pi electrons.

Fig. 2. The data of Fig. 1 normalized by dividing by the number of pi electrons.

THE FOUR THEORETICAL METHODS

REPE. In the Hückel calculation the pi energy of all acyclic conjugated hydrocarbons can be approximated accurately as the sum of bond energy terms (Ref. 1)

$$E_\pi(\text{acyclic}) = \sum_{i=1}^{8} n_i E_i \tag{1}$$

where n_i is the number of bonds of type i with energy E_i contained in the molecule. The 8 bond types used are listed with their energies in Table 1 of Ref. 1 where they are specified by a double subscript, the first of which is 1 or 2 for single or double bonds and the second gives the number of attached hydrogen atoms.

The same bond types occur in cyclic conjugated hydrocarbons, but in these compounds the Hückel pi energy is not accurately given as the sum of bond energy terms. The difference is defined as the resonance energy

$$RE = E_\pi - \sum_i n_i E_i \ . \tag{2}$$

For example in benzene there are 3 single bonds each with 2 attached hydrogen atoms and 3 double bonds each with 2 hydrogens
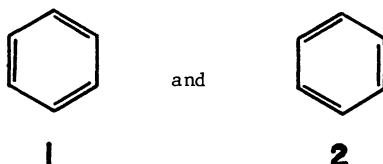
$$
\begin{aligned}
RE &= E_\pi(\text{benzene}) - (3E_{12} + 3E_{22}) \\
&= 8.00\beta - 7.61\beta = 0.39\beta \ .
\end{aligned}
\tag{3}
$$

Dividing by the number of pi electrons gives

$$REPE(benzene) = +0.065 \beta \; .$$

(4)

The difference (in units of β) between E_π and the sum of bond energies may be positive (= aromatic), zero (= nonaromatic) or negative (= antiaromatic).

Valence Bond Method. Consider the two Kekulé structures of benzene.

Suppose the corresponding wavefunctions are ψ_1 and ψ_2. If these two are assumed to be orthonormal, the energy of benzene, a linear combination of $\underline{1}$ and $\underline{2}$, is

$$E(benzene) = E[(\psi_1 + \psi_2)/\sqrt{2}]$$

$$= \frac{1}{2}[E(\psi_1) + E(\psi_2)] + \frac{2}{2}\int \psi_1 H \psi_2 d\tau.$$

(5)

The two Kekulé structures are of equal energy so that

$$\frac{1}{2}[E(\psi_1) + E(\psi_2)] = E(\psi_1).$$

(6)

The last term in Eq. (5) is the difference between the benzene energy and the energy of a single Kekulé structure. This is defined as the resonance energy in the valence bond method.

$$RE = \frac{2}{2}\int \psi_1 H \psi_2 d\tau$$

(7)

The integral in Eq. (7) is given the symbol H_{12} and is assigned the numerical value $\gamma_1 = 0.841$ eV (Ref. 5). For a molecule with N Kekulé structures a similar analysis gives

$$RE = \frac{2}{N}\sum H_{ij}.$$

(8)

Thus naphthalene has the 3 Kekulé structures
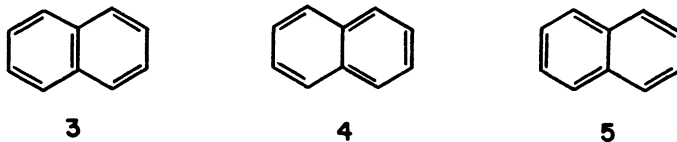
and

$$RE = \frac{2}{3}[H_{34} + H_{35} + H_{45}].$$

(9)

Herndon (Refs. 4,5) then reasoned as follows to obtain his successful and easily applied method. Naphthalene structures $\underline{3}$ and $\underline{4}$ differ in the 6-membered ring on the right; structures $\underline{5}$ and $\underline{3}$ differ in the left ring. This difference is like that between benzene structures $\underline{1}$ and $\underline{2}$. Therefore assume

$$H_{34} = H_{35} = \gamma_1. \qquad (10)$$

The difference between $\underline{4}$ and $\underline{5}$ extends over both rings and is taken to be the same as the difference between the two Kekulé structures of [10]-annulene. The corresponding resonance integral is given the value $H_{45} = \gamma_2 = 0.336$ eV so that for naphthalene

$$RE = \frac{2}{3}(2 \times 0.841 + 0.336) = 1.345 \text{ eV}. \qquad (11)$$

Herndon and Ellzey (Ref. 5) also list $\omega_1 = -0.650$ eV for the resonance integral between the two Kekulé structures of cyclobutadiene and $\omega_2 = -0.260$ eV for that of [8]-annulene. Resonance integrals for larger rings are neglected, though they could be included in the method.

A pair of Kekulé structure may differ in more than one ring. The two structures of phenanthrene


and
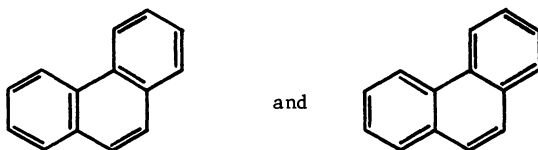
differ in both terminal rings. Resonance integrals between such structures are neglected in the Herndon method.

Topological Resonance Energy. The Hückel pi energy of a conjugated molecule is a sum of orbital energies which are the roots of the secular polynomial which in turn may be obtained by expanding the secular determinant. For example, benzene has nondegenerate orbital energies ±2 and degenerate orbital energies ±1 (in units of β). These are the roots of

$$P(x) = x^6 - 6x^4 + 9x^2 - 4 = 0. \qquad (12)$$

Trinajstić, Gutman and colleagues (Refs. 6,7) and Aihara (Ref. 8) developed their beautifully elegant topological energy scheme using a graph theoretical theorem of Sachs (Ref. 20) that shows how to compute the coefficients of P(x) directly from the molecular structural formula without requiring the secular determinant.

To use Sachs' result, start by drawing the structural formula of the conjugated hydrocarbon, omitting hydrogen atoms and double bonds. Thus, for benzene
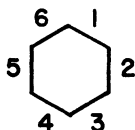
This structural formula, called the molecular graph, shows which carbon atoms are bonded to each other. The bonds are numbered for convenience in the following. It is first necessary to define what are usually called Sachs graphs. These are obtained from the original molecular graph by deleting bonds and atoms to leave disjoint bonds and/or rings with associated atoms. For example, the bonds 1 and 3 form a Sachs graph with 4 atoms. The bonds 1 and 2 do not constitute a Sachs graph since they are not disjoint (i.e. they touch). Sachs' theorem then says that if a_i is the coefficient of x^{N-i} in the secular polynomial of an N-carbon conjugated hydrocarbon

$$a_i = \sum_{S_i} (-1)^{c_i} 2^{r_i} \tag{13}$$

where S_i is a Sachs graph with i atoms, c_i is the number of components (i.e. disjoint parts) in S_i and r_i is the number of rings in S_i. Eq. (13) applies for i>0. The coefficient a_o always equals 1. In the case of benzene the coefficient a_1 is obtained from all Sachs graphs with 1 atom. There are no such in benzene or in any hydrocarbon so that one gets immediately $a_1 = 0$. To get a_2, construct all Sachs graphs with 2 atoms. These are simply the bonds 1 through 6. Each has 1 component and 0 rings. There are 6 of these; therefore

$$a_2 = 6 \times (-1)^1 2^0 = -6 \ . \tag{14}$$

the coefficient a_3 vanishes because benzene contains no 3-membered rings and therefore no Sachs graphs with 3 atoms. The 9 pairs of non-adjacent bonds (1,3), (1,4) ... (4,6) form the Sachs graphs with 4 atoms. Each has 2 components and no rings to give

$$a_4 = 9 \times (-1)^2 2^0 = +9 \ . \tag{15}$$

The coefficient a_5 is zero since benzene has no 5-membered rings. There are 3 Sachs graphs with 6 atoms. They are the two sets of three bonds (1,3,5) and (2,4,6) each with 3 components and 0 rings, and also the molecular graph itself with 1 component and 1 ring. Therefore

$$a_6 = 2 \times (-1)^3 2^0 + 1 \times (-1)^1 2^1 = -4 \ . \tag{16}$$

These results of Eq. (13) do agree with Eq. (12).

Sachs' theorem has been generalized to include heterocyclic molecules (Refs. 8,21,22), but this will not be considered here.

Trinajstić and Aihara then reasoned that if the cyclic contributions to the coefficients in Eq. (13) were dropped one would have a new set of coefficients for a polynomial corresponding to a system like (in some sense) the original molecule, but without cycles. They then defined this polynomial to be the secular equation of the reference structure. Summing these filled roots gives the energy of the reference structure which when subtracted from the pi energy of the original molecule gives what they have called the topological resonance energy (TRE).

In the case of benzene, only the last coefficient contains any cyclic contribution. Removing this gives the reference polynomial for benzene

$$R(x) = x^6 - 6x^4 + 9x^2 - 2 \quad . \tag{17}$$

The roots of eq. (17) are $\pm\sqrt{2}$, $\pm(2 \pm \sqrt{3})^{1/2}$ giving E_π (reference) $= 7.727\beta$ and TRE(benzene) $= (8.000 - 7.727)\beta = 0.273\beta$.

<u>Conjugated Circuits</u>. The most recent of the four methods, and the one of the four that is perhaps simplest in concept was developed by Randić (Refs. 9,10) out of his considerable graph theoretical work. To define the concept of conjugated circuit, imagine a particular Kekulé structure of some conjugated hydrocarbon. Start with any carbon atom, and traverse any path through bonds, returning finally to the original atom. If the path consists of alternating single and double bonds, the path is defined to be a conjugated circuit; otherwise it is not. In Kekulé structure <u>4</u> above for naphthalene the right-hand ring of 6 atoms and the perimeter of 10 atoms both form conjugated circuits; the left-hand ring of 6 atoms does not.

To compute the resonance energy of a conjugated hydrocarbon by Randić's method:

1. Write down all Kekulé structures of the hydrocarbon.
2. List all conjugated circuits in each. Discard the largest circuit in any linearly dependent set (see below).
3. Add together R_n for each conjugated circuit of (4n + 2) atoms and Q_n for each of 4n atoms. Values of these parameters are given in Ref. 10.
4. Divide this sum by the number of Kekulé structures.

In the case of naphthalene, the three Kekulé structures above contribute $2R_1$, $R_1 + R_2$ and $R_1 + R_2$ respectively to give the resonance energy

$$RE = \frac{1}{3}[4R_1 + 2R_2] = \frac{1}{3}[4 \times 0.869 + 2 \times 0.246] = 1.323 \text{ eV.} \tag{18}$$

The one complication occurs when there are linearly dependent conjugated circuits as in the phenanthrene structure.
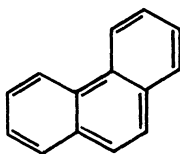
The central ring forms a 6-membered conjugated circuit; the two naphthalene fragments each are 10-membered conjugated circuits; and the perimeter is a 14-membered conjugated circuit. However the 14-membered circuit can be written as the sum of the two 10-circuits minus the 6-circuit. Randić therefore includes no contribution from the 14-circuit, the largest member of the linearly dependent set.

INTERRELATION OF THE FOUR METHODS

<u>REPE</u> and <u>Topological</u> <u>Resonance</u> <u>Energy</u>. Suppose TRE is divided by the number of pi electrons to give TREPE. REPE and TREPE are certainly similar in a general way. Both use a reference structure that is acyclic-polyene-like, but in somewhat different senses. The REPE

reference is like an acyclic polyene in that its energy is computed additively from bond energies. The TREPE reference is like an acyclic polyene in that the coefficients in its secular equation, when computed from Sachs' graph theoretical formula, contain no contributions from cyclic subgraphs. Because of the polyene reference structure for REPE and TREPE, both might be called Dewar resonance energies (Ref. 23) since he was the first to propose this reference (Ref. 24). However it is not easy to see the quantitative consequence of this similarity in spirit between REPE and TREPE.

The only more analytic investigation that we know is by Gutman (Ref. 25) who used Coulson's contour integral to express the sum of orbital energies. The orbital pairing theorem is built into this so the result applies strictly only to alternant hydrocarbons. Gutman also used only two bond energy terms – one for double and one for single bonds. Dewar and de Llano did use only two bond types in their original Pariser-Parr-Pople calculations (Ref. 24); and two bond types have been used in connection with Hückel calculations of aromaticity (Ref. 26); but 8 bond types (Ref. 1), two of which are arbitrary, seem required for accurate results (Ref. 27). It is not clear why 8 bond types are required with the Hückel method while the more elaborate PPP calculations need only 2.

Gutman's result, after normalization, is

$$\text{TREPE} \approx \text{REPE} + (0.69/N)\ln K \tag{19}$$

where N is the number of pi electrons and K the number of Kekulé structures. Rather severe approximations had to be made in Coulson's integral to get Eq. (19). The integral was divided into two ranges, and it is not clear that the lower limit of the upper range is large enough nor that the approximate integrand used in the lower range is accurate enough. Eq. (19) could of course be tested by example, but this has not yet been done.

Valence Bond and Conjugated Circuits. At first sight Herndon's valence bond method which involves resonance integrals between Kekulé structures and Randić's recipe in which one counts conjugated circuits within each Kekulé structure appear to be unrelated, but comparing the two methods in an actual application shows this is not true. Consider the case of phenanthrene in Fig. 3. The five Kekulé structures are shown with the conjugated circuit contribution to resonance energy under each structure and the valence bond integrals on the lines between structures. The R_3 in parentheses under structure 5 is the one discarded by Randić as linearly dependent. Summing the remaining conjugated circuits gives

$$\text{RE(Randić)} = \frac{1}{5}(10R_1 + 4R_2 + R_3), \tag{20}$$

and the valence bond integrals give

$$\text{RE(Herndon)} = \frac{2}{5}(5\gamma_1 + 2\gamma_2 + \gamma_3). \tag{21}$$

It may not be quite fair to call the result in Eq. (21) Herndon's resonance energy, since strictly Herndon would have dropped γ_3 as insignificant. However, had he included contributions through the same ring size as Randić, Eq. (21) would have been the result. Eqs. (20) and (21) are almost identical if corresponding parameters are equated (i.e. if $R_i = \gamma_i$, and also $Q_i = \omega_i$ for molecules with 4n rings).
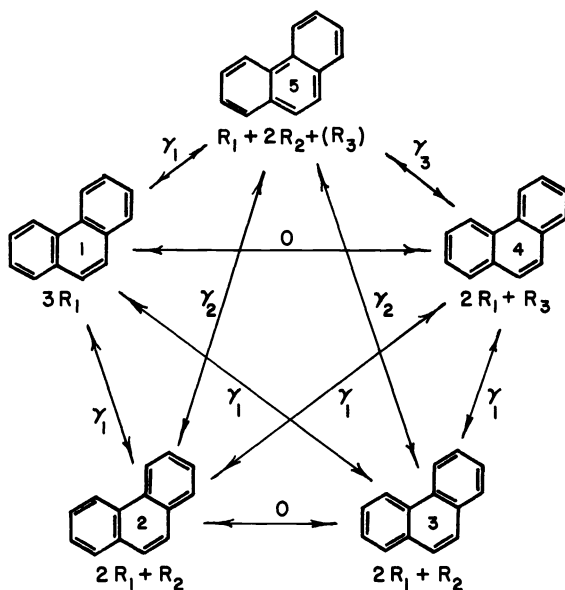
Fig. 3. Comparison of Randić's conjugated circuits and Herndon's valence bond methods in the case of phenanthrene.

The two results become entirely identical if in addition the discarded R_3 contribution of structure 5 is reincluded. It is true that the problem of linearly dependent structures does arise in the valence bond method, but if the carbon atoms are numbered sequentially around the phenanthrene perimeter, a Rumer diagram then shows all 5 Kekulé structures of phenanthrene to be linearly independent (Ref. 28). Hence the linear dependence of valence bond structures is not the same as the linear dependence of Randić's conjugated circuits.

This equivalence of the Randić and Herndon methods can be seen to be general if Randić's rule for excluding linearly dependent cycles is dropped. Choose any Kekulé structure of the conjugated hydrocarbon under consideration, and pick out one of its conjugated circuits. There will be another Kekulé structure which differs only in the interchange of double and single bonds in that circuit. Each of the two contributes R_i (or Q_i) to the sum in Randić's method, and the interaction between the two contributes $2\gamma_i$ (or $2\omega_i$) to Herndon's sum. Thus every such pair that contributes $2R_i$ (or $2Q_i$) to Randić's sum contributes $2\gamma_i$ (or $2\omega_i$) to Herndon's. Conversely for each $2\gamma_i$ (or $2\omega_i$) in Herndon's sum the corresponding pair of structures contributes $2R_i$ (or $2Q_i$) in Randić's. Consequently, if linearly dependent cycles are included and if $R_i = \gamma_i$ and $Q_i = \omega_i$, the two method are identical.

Randić finds that after discarding linearly dependent circuits, there remains the same number of conjugated circuits in each Kekulé structure. This convenient result appears to be the main justification for the rule (Ref. 29). On the other hand bringing the method into agreement with Herndon's valence bond technique is at least as powerful a reason to retain the linearly dependent circuits. In practice the choice is not expected to make a large difference in computed resonance energies since it is only larger rings with relatively small resonance contributions that are in question.

The exact equivalence of the Herndon and Randić methods which at first appear so different is a pleasing result and causes each method to constitute a further justification of the other.

REPE and Valence Bond. Since resonance energy in Herndon's valence bond method is the difference between the actual energy and the energy of a single Kekulé structure, all of which are assumed to be isoenergetic, the reference structure here is actually a single Kekulé structure. A Kekulé structure perhaps looks polyene-like as it is usually pictured, and this might lead one to expect a connection between REPE and Herndon's method, but in a more exact way what is the energy of such a reference structure? This question is examined in the Appendix, but its importance is diminished by the fact that Herndon's treatment differs in a crucial way from the standard valence bond method.

If a molecule has two isoenergetic Kekulé structures with orthonormal (lack of orthogonality would not affect the results here in any significant way) wavefunctions ψ_1 and ψ_2, the ground-state wavefunction is

$$\Psi = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2) \tag{22}$$

with energy

$$E = H_{11} + H_{12} \tag{23}$$

where the resonance energy H_{12} is negative. Should H_{12} turn out to be positive, as can always be made to happen by an arbitrary change of sign of functions for one of the Kekulé structures, then the ground-state wavefunction is instead

$$\Psi = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2) \tag{24}$$

with energy

$$E = H_{11} - H_{12}. \tag{25}$$

The point is that resonance between two Kekulé structures must always lower the energy by an amount $|H_{12}|$. It cannot raise the energy of the ground state.

This result applies to cyclobutadiene as truly as to benzene. In an early calculation Wheland (Ref. 30) decided the valence bond method to be better than the molecular orbital method because the VB method gives a resonance energy lowering for cyclobutadiene while the MO method does not. Now, when the chemistry of cyclobutadiene is better known, this result has become an embarrassment to the valence bond method. A key feature of Herndon's success is that he forces the resonance interactions of 4n rings to be destabilizing in spite of the standard VB result to the contrary. The exceptional instability of cyclobutadiene makes one feel that Herndon's choice is correct, and theoretical work by Dewar and Longuet-Higgins (Ref. 31) gives further support. Dewar and Longuet-Higgins found that if the Hückel secular determinant of an alternant hydrocarbon is arranged so that all starred atoms precede all unstarred, then the upper right quadrant is given by the number of Kekulé structures if these are given signs in a way that 4n rings contribute negative factors.

Nevertheless, Herndon's choice causes his technique to be quite unlike the original VB method so that seeking connections between REPE and his method through details of a rigorous VB calculation does not look profitable. Instead, in view of the equivalence between the Randić and Herndon methods, it might be more straightforward to look for relations between REPE and Randić's method in which resonance energy can be thought of as the average over all Kekulé structures of simple additive contributions from conjugated circuits in each. This additivity is reminiscent of the bond energy additivity in acyclic polyenes and might be analyzed in a similar way.

We have shown that an acyclic polyene can be treated as a set of mutually perturbing C=C units (Ref. 32). In zero order, the total energy contributions is 2β for each double bond. In first order, each orbital energy is greatly affected, but there is zero effect on total energy. Second-order terms give exactly $\beta/2$ for each single bond. The sum of third-order terms vanishes. At this point we were confounded by the complexity of the analysis, but computational examples showed small additive contributions in fourth order which resulted in bond energy terms very close to those used empirically for REPE reference structures. The sum of fifth-order terms vanishes, and there appears to be some breakdown of additivity in sixth order.

The same treatment has now been applied to cyclic conjugated hydrocarbons to see whether they can be described in terms of the same bond energies plus certain cyclic contributions. If they can, and if the cyclic contributions are like those in the Randić method, a connection between REPE and the methods of Randić and Herndon will have been demonstrated.

In the treatment of acyclic systems we worked with the 1-electron orbitals. We have since found that using the n-electron wavefunction is actually simpler. The reason is that in zero order the lower orbital from each ethylene unit is degenerate with all the others. The proper linear combination varies from system to system so it is necessary to continue without knowing the exact form of the zero-order 1-electron wavefunction; but if the n-electron wavefunction is used instead, all lower orbitals are completely filled, there is no degeneracy, and the exact form of the zero-order function is known. A further advantage is that, while the 1-electron treatment was restricted to cases where all orbital degeneracy is removed in first order and where empty and filled zero-order orbitals do not interchange in first order, these restrictions are removed in the n-electron treatment. Using the n-electron wavefunction does not allow one to follow perturbation effects in individual orbitals, but these are not needed.

Imagine first a chain of C-C units each with a pair of $p\pi$ orbitals ϕ and a pair of pi electrons

$$C = C \ \ldots \ C = C \ \ldots \ C = C \ \ldots$$
$$\phi_1 \ \phi_2 \quad \phi_3 \ \phi_4 \quad \phi_5 \ \phi_6$$
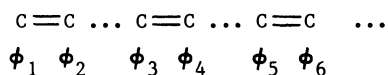
The solid lines become double bonds and the dotted lines single bonds in the resulting polyene. The Hamiltonian H is a sum of 1-electron operators in the Hückel approximation

$$H(1,2\ldots N) = \sum_{i=1}^{N} h(i) \tag{26}$$

and each of these will be written as a zero-order part plus a perturbation

$$h = h_0 + h' .$$ (27)

So that

$$\langle \phi_i | h_0 | \phi_j \rangle = \beta$$ (28)

if atoms i and j are connected by a solid line in the drawing above, and

$$\langle \phi_i | h' | \phi_j \rangle = \beta$$ (29)

if atoms i and j are connected by a dotted line, and

$$\langle \phi_i | h_0 | \phi_j \rangle = \langle \phi_i | h' | \phi_j \rangle = 0$$ (30)

otherwise. Eq. (26) implies that the total wavefunction will factor into 1-electron orbitals, and it does not matter whether a simple or antisymmetrized product is used. It will be simpler to work with the simple product

$$\Psi(1,2...N) = \psi_1(1)\alpha(1)\psi_1(2)\beta(2) \; . \; . \; . \; \psi_{N/2}(N)\beta(N)$$ (31)

where

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \; ; \; \psi_2 = \frac{1}{\sqrt{2}}(\phi_3 + \phi_4) \; ; \; \text{etc} .$$ (32)

The zero-order energy is

$$E^{(0)} = \langle \Psi | \sum_i h_0(i) | \Psi \rangle = N\beta$$ (33)

where the β in Eq. (33) is the usual resonance integral of Hückel theory and not to be confused with the spin function β in Eq. (31). The result in Eq. (33) of 2β for each ethylene unit is as expected.

In first order

$$E^{(1)} = \langle \Psi | \sum_i h'(i) | \Psi \rangle .$$ (34)

A typical term in Eq. (34) is

$$\langle \psi_1(1)\alpha(1) \psi_1(2)\beta(2) \; ... \; | h'(1) | \psi_1(1)\alpha(1) \; ... \rangle$$

$$= \langle \psi_1(1) | h'(1) | \psi_1(1) \rangle \langle \psi_1(2) | \psi_1(2) \rangle \; ... \; \langle \psi_{N/2}(N) | \psi_{N/2}(N) \rangle$$

$$= \frac{1}{2} \langle \phi_1(1) + \phi_2(1) | h'(1) | \phi_1(1) + \phi_2(1) \rangle = 0 .$$ (35)

The integral in Eq. (34) vanishes because of Eqs. (28)-(30). In a similar way all other terms in Eq. (35) vanish to give

$$E^{(1)} = 0 \tag{36}$$

The second-order energy is

$$E^{(2)} = \sum_i{}' \frac{|\langle \Psi|H'|\Psi_i\rangle|^2}{E^{(0)} - E_i^{(0)}} \tag{37}$$

where the excited states Ψ_i are obtained by replacing one or more ground state orbitals in Ψ by the excited orbitals

$$\psi_1' = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \quad ; \quad \psi_2' = \frac{1}{\sqrt{2}}(\phi_3 - \phi_4) \quad ; \quad \text{etc.} \tag{38}$$

For example replacing $\psi_1 \alpha$ by $\psi_1' \alpha$ gives

$$\frac{1}{2\beta}|\langle \psi_1'(1)\alpha(1)\psi_1(2)\beta(2) \cdots |h'(1) + \cdots + h'(N)|\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\cdots\rangle|^2$$

$$= \frac{1}{2\beta}\Big[\langle \psi_1'(1)|h'(1)|\psi_1(1)\rangle + 0 + \cdots + 0\Big]^2$$

$$= \frac{1}{8\beta}\Big[\langle \phi_1 - \phi_2|h'|\phi_1 + \phi_2\rangle\Big]^2 = 0 \tag{39}$$

but replacing $\psi_1 \alpha$ by $\psi_2' \alpha$ gives in a similar way

$$\frac{1}{8\beta}\Big[\langle \phi_3 - \phi_4|h'|\phi_1 + \phi_2\rangle\Big]^2 = \frac{1}{8\beta}\beta^2 = \beta/8 \quad . \tag{40}$$

A nonvanishing integral is obtained only if a ground orbital on one ethylene unit is replaced by an excited orbital of the same spin from a neighboring unit. For each pair of neighbors this can be done in four ways: replace

$$\psi_i \alpha \quad \text{by} \quad \psi_{i+1}' \alpha \qquad \psi_{i+1} \alpha \quad \text{by} \quad \psi_i' \alpha$$
$$\psi_i \beta \quad \text{by} \quad \psi_{i+1}' \beta \qquad \psi_{i+1} \beta \quad \text{by} \quad \psi_i' \beta \quad . \tag{41}$$

To give a contribution of

$$4(\beta/8) = \beta/2 \tag{42}$$

for each single bond in the polyene. All multiple excitations give only vanishing integrals.

The results so far simplify the analysis of the third-order energy (Ref. 33).

$$E^{(3)} = \sum_i{}'\sum_j{}' \frac{\langle \Psi|H'|\Psi_i\rangle \langle \Psi_i|H'|\Psi_j\rangle \langle \Psi_j|H'|\Psi\rangle}{(E_i^{(0)} - E^{(0)})(E_j^{(0)} - E^{(0)})} \tag{43}$$

The excited function Ψ_i in Eq. (43) must differ from Ψ by a single excitation across a single bond. Ψ_j would then interact with Ψ_i if it contained a second such excitation, but the resulting doubly-excited Ψ_j would have a zero matrix element with Ψ making the entire term in Eq. (43) vanish. Alternatively, if Ψ_i contains an excitation across the bond between ethylene units r and $r + 1$, the matrix element between Ψ_i and Ψ_j will be non-zero if this excitation is moved forward to ethylene unit $r + 2$ in Ψ_j. It cannot be moved back to unit r since that would give a Ψ_j that does not interact with Ψ. Even so, the Ψ_j with the single excitation moved foward can interact with Ψ only if ethylene units r and $r + 2$ are adjacent. This is true in the case of a 6-membered ring, but never for an open chain. Therefore for the linear chain

$$E^{(3)} = 0 \ . \tag{44}$$

The example of a linear chain has been used but the results so far are easily seen to apply to all acyclic polyenes. It can also be seen how the effects of ring formation will alter these results. Consider two ethylene units arranged in a cyclobutadiene ring. The zero- and first-order results above all apply, and the second-order analysis holds through Eq. (39), but in Eq. (40) there is an additional negative interaction between ϕ_1 and ϕ_4 that cancels the positive effect between ϕ_2 and ϕ_3. As a result all second-order terms vanish in cyclobutadiene; and, unlike all other cases, the single bonds in cyclobutadiene do not contribute $\beta/2$ to the pi-binding energy. Further, all integrals in all higher perturbation terms will vanish in exactly the same way. Cyclobutadiene appears as a very special molecule in which the perturbation series terminates at zero-order and in which the exceptional antiaromaticity is caused by vanishing of the single bond interactions that stabilize all other systems.

Third-order effects, which vanish in acyclics, explain the aromaticity of the benzene ring. There are 12 non-zero terms of the kind described above. Each equals

$$\frac{1}{4\beta^2}(-\beta/2)^2(\beta/2) = \beta/32 \tag{45}$$

giving a total of

$$3\beta/8 = 0.375\beta \tag{46}$$

in good agreement with our benzene resonance energy of 0.392β (Ref. 1). Higher order terms are also expected to contribute, but the first effect of the benzene ring in third-order appears to be dominant.

We have not yet extended the analysis past this point, but it looks as though it will be much easier to do than with our previous 1-electron treatment (Ref. 32). It can be seen that the effect of an N-carbon ring will first appear in $N/2$ order, and the sign of the effect does seem to alternate as the ring is increased by each 2-carbon unit.

In an acyclic hydrocarbon there is only one way to dissect the molecule into ethylene units. This is not true in cyclics where each Kekulé structure corresponds to a possible dissection, and conversely. The reference energies formed from additive acyclic bond contributions are very nearly identical for all Kekulé structures (and could be made

identical with no significant consequences - see Eq. (12) of Ref. (3)), but this may not be true for cyclic effects in all orders of perturbation. That is, while we expect each dissection to give the correct result in the infinite limit, certain cyclic effects may appear in lower order in some dissections than in others. This may suggest an averaging of the low-order effects over all Kekulé structures as in the Randić method.

CONCLUSION

Roughly, and prematurely since the perturbation analysis of the last section is far from complete, the four ways of calculating aromatic character examined are all interrelated and all may express the same simple physical fact that for conjugated, neutral, closed-shell hydrocarbons, but not necessarily for ions and radicals which were not considered, the pi energy of acyclic systems is approximately additive in terms of bond energies, and that ring formation makes further energy contributions, manifest as aromaticity or antiaromaticity, which are also additive, or perhaps additive to the energy of each of several Kekulé structures whose contributions are averaged.

APPENDIX

Cyclobutadiene has zero resonance energy in the MO method, but a negative (i.e. stabilizing) resonance energy in the VB method. This means that in the MO method cyclobutadiene is computed to be equal in energy to the reference of two ethylene molecules, while in the VB method it is lower in energy than the reference of a single Kekulé structure. This still leaves open the question of how the two reference structures compare in energy. The probable reason for this logical gap is that it is usual to express VB and MO results in terms of different parameters so that they are not directly comparable. We shall show that results from the two methods can be written in the same parameters and the comparison of reference structures made.

In the VB method the two Kekulé structures and their wavefunctions are (see Chapt. 4 of Ref. 28)

$$\Phi_1 = \tfrac{1}{2}(\psi_2 - \psi_4 - \psi_5 + \psi_6)$$

$$\Phi_2 = \tfrac{1}{2}(\psi_1 - \psi_2 + \psi_3 - \psi_6) \tag{A1}$$

where the spin-state functions

$$
\begin{aligned}
\psi_1 &= (4!)^{-1/2}\; \det|\phi_1(1)\alpha(1)\; \phi_2(2)\beta(2)\; \phi_3(3)\beta(3)\; \phi_4(4)\alpha(4)|\\
\psi_2 &= (4!)^{-1/2}\; \det|\phi_1(1)\beta(1)\; \phi_2(2)\alpha(2)\; \phi_3(3)\beta(3)\; \phi_4(4)\alpha(4)|\\
\psi_3 &= (4!)^{-1/2}\; \det|\phi_1(1)\beta(1)\; \phi_2(2)\alpha(2)\; \phi_3(3)\alpha(3)\; \phi_4(4)\beta(4)|\\
\psi_4 &= (4!)^{-1/2}\; \det|\phi_1(1)\beta(1)\; \phi_2(2)\beta(2)\; \phi_3(3)\alpha(3)\; \phi_4(4)\alpha(4)|\\
\psi_5 &= (4!)^{-1/2}\; \det|\phi_1(1)\alpha(1)\; \phi_2(2)\alpha(2)\; \phi_3(3)\beta(3)\; \phi_4(4)\beta(4)|\\
\psi_6 &= (4!)^{-1/2}\; \det|\phi_1(1)\alpha(1)\; \phi_2(2)\beta(2)\; \phi_3(3)\alpha(3)\; \phi_4(4)\beta(4)|
\end{aligned}
\tag{A2}
$$

are constructed from $2p\pi$ atomic orbitals ϕ_i on carbon atom i as numbered in the Kekulé structures.

Solution of the secular equation

$$\begin{vmatrix} \langle\Phi_1|H|\Phi_1\rangle - E & \langle\Phi_1|H|\Phi_2\rangle - ES \\ \langle\Phi_2|H|\Phi_1\rangle - ES & \langle\Phi_2|H|\Phi_2\rangle - E \end{vmatrix} = 0 \qquad (A3)$$

together with the fact that

$$\langle\Phi_1|H|\Phi_1\rangle = \langle\Phi_2|H|\Phi_2\rangle \qquad (A4)$$

gives

$$E = \frac{\langle\Phi_1|H|\Phi_1\rangle \pm \langle\Phi_1|H|\Phi_2\rangle}{1 \pm \langle\Phi_1|\Phi_2\rangle} \qquad . \qquad (A5)$$

The overlap integral is given by

$$\langle\Phi_1|\Phi_2\rangle = \tfrac{1}{4}\langle\psi_2 - \psi_4 - \psi_5 + \psi_6|\psi_1 - \psi_2 + \psi_3 - \psi_6\rangle = -1/2 \qquad (A6)$$

using the fact that the spin-state functions (A2) are orthonormal. The remaining integrals in (A5) can also be experessed in terms of integrals over the spin-state functions such as

$$\langle\psi_2|H|\psi_2\rangle = \int \phi_1(1)\alpha(1) \ldots \phi_4(4)\beta(4) \, H \, \det|\phi_1(1) \ldots \phi_4(4)\beta(4)|d\tau \quad . \qquad (A7)$$

In the VB method this is left as the parameter Q, but if we make the MO assumption of Eq. (26) the Hamiltonian gives four 1-electron terms. Each of these, if we drop terms in S^2, $S^2\alpha$, $S^3\beta$ and higher, where S is the overlap integral between two ϕ_i's on adjacent carbon atoms, gives a nonvanishing integral with the identity permutation from the determinant in (A7). The result is

$$\langle\psi_2|H|\psi_2\rangle = 4\alpha \quad . \qquad (A8)$$

The α in (A8) and the β to appear below in (A9) are the Coulomb and resonance integrals of the MO method and must not be confused with the α and β spin functions in (A2). Similarly

$$\langle\psi_2|H|\psi_4\rangle = -2S\beta \quad , \text{ etc.} \qquad (A9)$$

Combining all required spin-state integrals gives the energy of the two cyclobutadiene Kekulé structures as

$$\langle\Phi_1|H|\Phi_1\rangle = \langle\Phi_2|H|\Phi_2\rangle = 4\alpha + 2S\beta \qquad (A10)$$

and

$$\langle\Phi_1|H|\Phi_2\rangle = -2\alpha - 4S\beta \quad . \qquad (A11)$$

The cyclobutadiene ground-state energy, corresponding to the negative sign in (A5) is then

$$E = 4(\alpha + S\beta) \ . \tag{A12}$$

A similar calculation on ethylene gives a ground state energy of $2(\alpha + S\beta)$. Thus in the VB method, just as in the MO method the energy of cyclobutadiene equals that of two ethylene molecules. In fact, the energy expressions are quite similar in the two methods with $S\beta$ in the valence bond method taking the place of β in the MO result. Hence the apparent disagreement between the VB and MO results for cyclobutadiene is caused by a different choice of reference in the two methods.

Unfortunately, this accord is lost if we repeat the same calculations on benzene where it is found that

$$
\begin{aligned}
E(\text{Kekul\'e structure}) &= 6\alpha + 3S\beta \\
E(\text{benzene}) &= 6\alpha + 24S\beta/5 \\
E(\text{3 ethylene}) &= 6(\alpha + S\beta) \ .
\end{aligned}
\tag{A13}
$$

As in cyclobutadiene the VB and MO references differ, but in the VB method benzene appears to be higher in energy than three ethylene molecules.

It might be argued that terms in $S^2\alpha$ should have been retained since, with $S = 0.25$, $\alpha = -11.16$ eV (Ref. 34) and $\beta = -1.4$ to -2.4 eV (Ref. 35), $S^2\alpha$ is of the same magnitude as $S\beta$. However repeating the calculations above with S^2 and $S^2\alpha$ terms retained gives no significant changes for reasonable values of S and β.

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