Dewar Resonance Energy
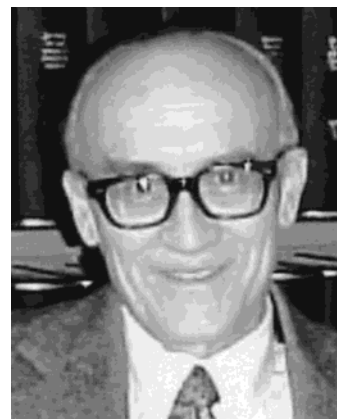
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Contents

I. Introduction

What has come to be called Dewar resonance energy was defined by Dewar and de Llano[1] in 1969, and we shall concentrate primarily on the development of this idea as a predictor of aromaticity through the 1970s.

Aromaticity has been a particularly contentious subject largely because it has no precise experimental definition that is agreed on by all who use the term. Most chemists though will agree that compounds called "aromatic" have the following physical properties: (1) The compounds have an odor, perhaps pleasant; (2) The molecule is cyclic (mono or poly) and conjugated; (3) The molecules have a special stability (but compared to what?); (4) The compounds react by electrophilic substitution rather than by addition to double bonds; (5) The C−C bonds of the molecule tend to have the same length in contrast to those of open-chain conjugated compounds which alternate in length; (6) Protons on the outer periphery of aromatic rings show downfield NMR chemical shifts.

Property 1 is included above only because of its historical precedence. We shall consider it no further. Property 2 has been used by Randić[2,3] in his "Method of Conjugated Circuits". Properties 3 and 4 are the

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classical experimental measures of aromaticity. Property 5, though more recent, is now standard. Property 6, as well as other magnetic effects, is also used. Schleyer and Jiao[4] give a quick and easily readable outline of these.

Unfortunately, while changes in one property roughly correlate with changes in the others, the

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correlation is not exact. Thus, it is possible for one person, having the property of bond equalization in mind, to argue that compound A is more aromatic than compound B while another, thinking of stability, to argue the reverse. The difficulty is, as Binsch[5] pointed out, that there appears little hope of chemists agreeing on any one of these physical properties as the defining measure of aromaticity. L.J.S. remembers moderating a theoretical discussion of aromaticity ("Bar facilities will be available during this session") at the ISNA 5 meeting[6] where at intermission he was surrounded by participants wanting to straighten out his ideas. While one on the right was saying "We must use NMR chemical shifts as the true measure of aromaticity", another on the left at the same time was saying with equal conviction "Whatever we do, we must not use NMR to define aromaticity". L.J.S. agrees with Professor Binsch's conclusion.

Theoretical predictors of aromaticity may be constructed by a computation of one or another, or even an average of several,[7] of these experimental measures. Energies or energy differences are probably the most commonly used, as in the original Hückel method[8−11] and in the Dewar[1] resonance energy to be discussed here. Reactivity, measure 4, has been used as in the free valence index, which is one of those included in Zahradník and Michl's average.[7] Julg and François[12] and later Kruszewski and Krygowski[13] in their HOMA model used bond-length equalization. NMR chemical shifts and other magnetic effects are the most recent physical measures of aromaticity to be used to construct theoretical predictors.[4] One might have expected that those who construct such predictors based on measurable physical properties would first check that the computational method used does accurately calculate the physical property before attempting the prediction of aromaticity. Strangely, this is not usually done, and our own work on Dewar resonance energy is guilty in this way. Further, it is obvious that this approach still leaves unsolved the problem of which physical property is to be considered the "true" measure of aromaticity.

Other theoretical predictors are based only in part, or not at all, on calculations of physical properties. As will be described in a little more detail below, the elegant graph-theoretical method of Trinajstić, Gutman, and co-workers[14,15] and of Aihara[16,17] is Dewar-like in spirit but uses a reference energy computed from the roots of a polynomial that corresponds to no actual molecule. Randić's theoretical predictor of aromaticity, the method of conjugated circuits, counts the number and size of conjugated rings in a compound and assigns an energy to each.[2,3] The success of these methods, too, must ultimately be judged by comparison with the yet-unagreed-upon defining experimental measure of aromaticity.

We should like the idea of aromaticity to be both precise and of broad application. Unfortunately, these two requirements are to some extent antithetical. Too great an emphasis on precision may narrow the set of aromatics to benzene alone (see Heilbronner's question to Binsch[18]), while too much emphasis on broad application will lead to only a vague notion of aromaticity.[5] This problem is perhaps particularly severe in the area of aromaticity, but it is common throughout chemistry. Quantities such as aromaticity which are neither purely experimental nor purely theoretical are common in chemistry and can be troublesome. See ref 19 in which it was found that theoretical estimates of the hydrogen bond strength in hydrogen bifluoride were being compared to an "experimental" value that contained a theoretical component with as large an error as any of the theoretical estimates themselves.

In view of all these difficulties, what shall we take to be the experimental definition of aromaticity as we review the development of Dewar's theoretical predictor of aromaticity? We had not thought much about these problems when we began working with Dewar resonance energy. In retrospect, our timing was fortunate; since before Dewar's paper[1] there was no more successful theoretical predictor of aromaticity than Hückel's.[8] Dewar's results were so clearly superior, as judged by any measure of aromaticity, that it was not necessary to agree upon a single defining measure.

II. Early History of Resonance Energy

We give only a brief historical sketch here and refer readers to a thorough and readable pair of papers recently published by Brush[20,21] on this subject.

After the complications discussed in the Introduction, let us recall that after all the idea of aromaticity had its origin in simple and surprising chemical observations such as the well-known reactions in Scheme 1 which are easily demonstrated in a test

Scheme 1
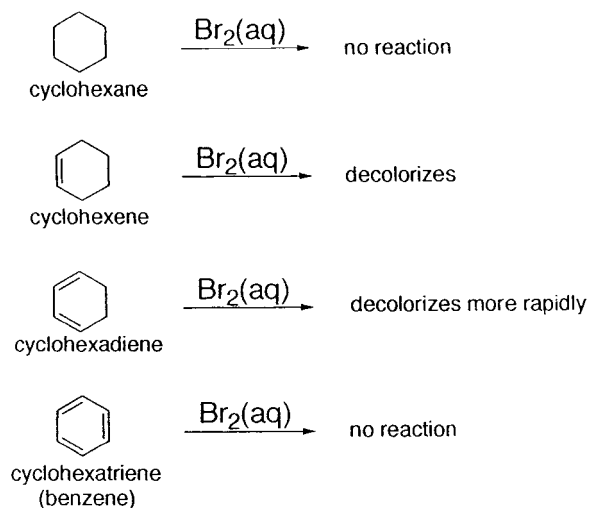
tube at room temperature. While one and two double bonds in a six-carbon ring react easily with Br_2, three conjugated double bonds as in benzene, which might be expected to react still faster, are inert. Why is this observed experimentally, and which compounds will behave in the one way and which in the other?

After Ladenburg pointed out that the original Kekulé structure for benzene predicted two *ortho* isomers of a disubstituted benzene, depending upon whether the two carbons are joined by a single or double bond, Kekulé proposed an oscillating variant that made all carbon bonds equal in a time average

and so implied only a single *ortho* isomer.[22,23] This gives the observed bond equalization and correct isomer count in benzene but does not explain the special stability or the lack of bromine addition.

This stability could not be explained until quantum mechanics allowed an understanding of the covalent chemical bond. Within a year of Schrödinger's paper, *Quantisierung als Eigenwertproblem*,[24] Heitler and London[25] applied his method to the hydrogen molecule and obtained two-thirds of the experimental bond energy $D_e = 108$ kcal/mol. A one-term wave function $\psi(1,2) = 1s_A(1)1s_B(2)$ with electron 1 in the 1s atomic orbital on atom A and electron 2 in such an orbital on atom B gives only 5% of this bond energy.[26] This approach in which electrons are put into atomic orbitals has come to be called the Heitler−London−Slater−Pauling (HLSP) or valence bond (VB) technique.

The key to Heitler and London's success, as we should explain it now, is that the identity of electrons requires the electron density $|\psi|^2$ of any state to be unchanged when the positions of electrons 1 and 2 are interchanged. Therefore, as a result of this exchange, the wave function itself must either be unchanged or change in sign. For particles with spin $^1/_2$, such as electrons, the sign must change. The $\psi(1,2)$ above does not have this symmetry, and it is necessary to look at the spin eigenfunctions in a little more detail. For a single electron there are only two possible eigenfunctions, call them α and β. The effect of spin on the energy of the system is fairly small. If this small energy is neglected, the wave function of the system may, but need not be, split into two factors, one depending on space and the other on spin. Each of these is either symmetric (retains sign) or antisymmetric (changes sign) under the exchange of a pair of electrons. The possibilities are

$$\psi_s(1,2) = [1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)] \quad (1)$$

or

$$\psi_a(1,2) = [1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)] \quad (2)$$

for the space factor. The first of these is symmetric under electron exchange and the second antisymmetric. Similarly for spin

$$\phi_{s1}(1,2) = \alpha(1)\alpha(2) \quad (3)$$

$$\phi_{s2}(1,2) = \beta(1)\beta(2) \quad (4)$$

or

$$\phi_{s3}(1,2) = [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (5)$$

are symmetric and

$$\phi_a(1,2) = [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (6)$$

is antisymmetric in particle exchange.

The symmetric space functions $1s_A(1)1s_A(2)$ and $1s_B(1)1s_B(2)$ analogous to ϕ_{s1} and ϕ_{s2} were not included in the set of space functions above. A more complete treatment would include them, but they

were neglected here since they are high-energy ionic terms corresponding to H^-H^+ and H^+H^-.

The proper wave function for the ground state of H_2 can now be written as $\Psi_G(r_1,r_2) = \psi_s(1,2)\phi_a(1,2)$. It is the cross term in the space factor of the energy expression, $E = <\Psi_G|H|\Psi_G>$, that gives the main part of the bond energy.

In 1931 Hückel published the first[8] in a series of four papers in which he applied the new quantum mechanics to the benzene problem using for the first time the VB method for aromatic compounds. Little reference is now made to this part of Hückel's paper. In the second part of this same paper, he applied to aromatics a method that Bloch[27] had used for crystal lattices. In this method electrons are placed into orbitals that extend over the entire molecule instead of being localized on a single atom. These molecular orbitals may in turn be constructed as linear combinations of atomic orbitals, and such an approach is usually called the Hund−Mulliken−Hückel (HMH) or molecular orbital (MO) method. Hückel's work in this second part of the paper leads to the famous $4n + 2$ rule for monocyclic conjugated hydrocarbons, though we do not find it explicitly stated here.

The VB treatment of the π electrons in a conjugated compound makes a direct correspondence between the terms used in the wave function and the double bonds in a Kekulé structure. This allows convenient semiempirical and even pictorial versions of VB calculations on conjugated compounds that, with the energetic work of Pauling and of Wheland, came to dominate discussions of structure and bonding during the 1930s and 1940s.

At the end of the 1930s, Coulson and co-workers, including Rushbrooke and Longuet-Higgins, continued the development and application of Hückel's work so that by the 1950s the MO method had largely replaced VB treatments of conjugated compounds. During this time there was continuing discussion of whether the VB or MO method gave better results for these organic molecules. Comparisons by Wheland[28,29] were even-handed and fair. However, it is interesting that he was so convinced that cyclobutadiene must show the same kind of extra stability as benzene that when he found MO calculations did not predict this, he took it as a point favoring the VB over MO method. The comparisons then were between the rudimentary forms of both methods. It was expected that as the VB and MO calculations were improved by the inclusion of configuration interaction in the VB method and correlation energy in the MO method, the two would converge to agreement. In 1948 Longuet-Higgins proved that this must be true in all cases,[30] but such computations were out of reach at the time.

Finally, in 1986 Voter and Goddard[31] carried out a generalized resonating valence bond (GRVB) calculation for square cyclobutadiene. As perhaps expected, the function

$$\Psi(^1A_{1g}) = \quad \square \quad + \quad \square \quad \quad (7)$$

shows a destabilizing interaction between the two Kekulé structures. However, it then follows that

$$\Psi(^1B_{1g}) = \quad \square \quad - \quad \square \quad \quad (8)$$

has a stabilizing interaction that makes this state 22 kcal/mol more stable than a single Kekulé structure and causes square cyclobutadiene to be aromatic, as Wheland supposed. Voter and Goddard also found that a full π CI calculation agreed with these GRVB results and gave $^1B_{1g}$, $^3A_{2g}$, $^1A_{1g}$, and $^1B_{2g}$ to be the first four states of square cyclobutadiene, in order of increasing energy. A molecular orbital calculation by these same authors gave instead the order $^3A_{2g}$, $^1B_{1g}$, $^1B_{2g}$, and $^1A_{1g}$.

Voter and Goddard's paper was followed in 1994 by Balková and Bartlett's high-level multireference coupled cluster calculations, including single, double, and triple (in varying ways) excitations.[32] These gave the same order of states as found by Voter and Goddard in their VB calculations. Mo, Wu, and Zhang[33] also reported VB calculations on this system and also find it to be slightly aromatic. More recently Filatov and Shaik[34] published density functional studies of square cyclobutadiene and found states in the same order as in Voter and Goddard's MO calculation. However, this disagreement of Voter and Goddard's VB and π CI and Balková and Bartlett's MRCC order, on the one hand, with Voter and Goddard's MO and Filatov and Shaik's density functional order, on the other, is not numerically large since Balková and Bartlett find that the two pairs of states that interchange in the two orderings are both within 10 kcal/mol of each other.

Three further comments should be made about square cyclobutadiene. First, Karadakov et al.[35] and Zilberg and Hass[36,37] showed that cyclooctatetraene and all other $4n$ monocyclic conjugated hydrocarbons behave as Voter and Goddard found for cyclobutadiene, using the singlet rather than triplet ground state. Second, Shaik, Hiberty, and co-workers[38] examined these systems using their interesting separation of σ and π contributions to aromatic energies. Third, the fact that the ground state of cyclobutadiene is a singlet, despite the HOMOs of the system not being filled, is an apparent violation of Hund's rules. Gallup[39] examined this question for systems with 4-fold symmetry, as have Hrovat and Borden[40] more recently.

It is now reasonably certain that cyclobutadiene has a rectangular rather than square equilibrium geometry, both from calculations of the equilibrium structure[41-43] and from the agreement between observed[44] and calculated[45-47] IR spectra of the compound. However, the square form remains of interest first because it is the geometry treated in the original VB and MO calculations and also because it is now considered to be the transition structure between the two rectangular forms.

What is to be made of this important work on cyclobutadiene? Voter and Goddard described cyclobutadiene as aromatic since, as in benzene, interaction between the two Kekulé structures lowers the molecular energy below that of a single Kekulé structure. This appears to be a reasonable definition of aromaticity, yet, as is well-known, cyclobutadiene is extremely unstable. The resolution of this apparent dilemma lies in the choice of reference structure, and we return to this after reference structures are discussed in section III.B.

After this discussion of Voter and Goddard's relatively recent and quite significant paper and of others in response to it, we return to the history of the prediction of aromaticity at about 1950. During the following decade, more and more researchers carried out MO calculations for molecules of special interest to them. A particularly influential paper by Roberts, Streitwieser, and Regan[48] gave Hückel resonance energy, or delocalization energy as it is often called, for 32 unusual, conjugated cyclic hydrocarbons. This and other papers stimulated much synthetic effort, but the result was that many compounds computed to have significant Hückel delocalization energy (DE) were found after difficult syntheses to be unstable. Something was badly wrong with the Hückel predictions of aromaticity!

III. Dewar Resonance Energy

At the start, two simple but important points should be made. The first is that total resonance energies are not as useful as those "normalized" to take account of molecular size. A sheet of graphite has more total resonance energy than benzene but is not less reactive. Second, most resonance energies, including the Hückel DE, are differences between a computed energy and the energy of some reference structure. A faulty resonance energy may be the result of a poor computation method and/or a poor choice of reference.

A. Normalization of Resonance Energy

Hückel DEs of 40 benzenoid hydrocarbons[49] are shown in Figure 1 plotted against the number of carbon atoms in each. Although there is some deviation from a straight line, the dominant effect shown in Figure 1 is a linear increase of Hückel DE with size of the hydrocarbon.

We thank Professor W. C. Herndon for permission to quote a second example. Over 25 years ago we refereed the manuscript of Herndon's successful
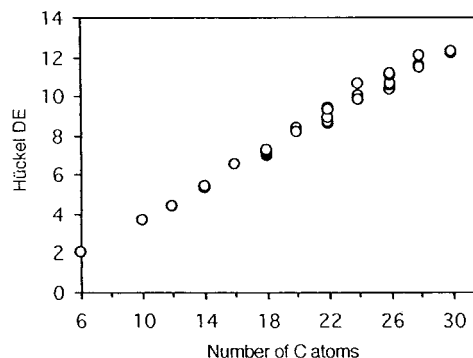

Figure 1. Total Hückel delocalization energy in units of β vs number of carbon atoms for the benzenoid compounds listed in ref 56.
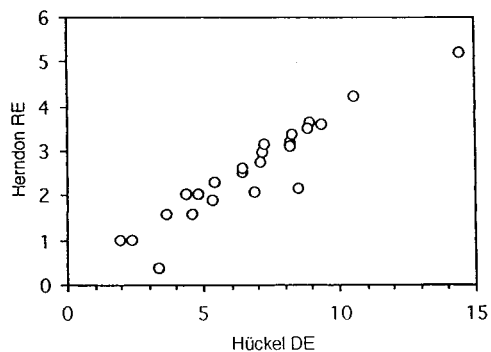
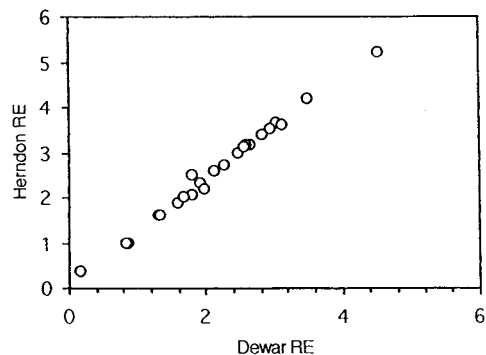**Figure 2.** Herndon's valence bond resonance energy in units of γ_1 vs Hückel delocalization energy in units of β.

Figure 3. Herndon's valence bond resonance energy in units of γ_1 vs Dewar's Pariser–Parr–Pople resonance energy in eV.
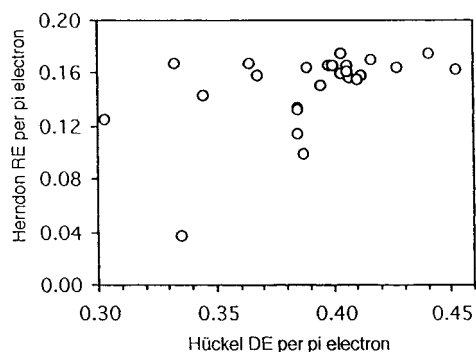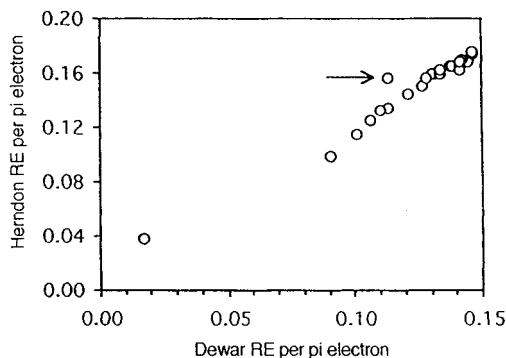

Figure 5. Same as in Figure 3 but with all resonance energies divided by the number of π electrons in the molecule.

Table 1. Hückel π-Bond Energy Terms Fit to 40 Acyclic Polyenes

type of bond	ij^a	E_{ij} (β units)
$H_2C=CH$	23	2.0000^b
$HC=CH$	22	2.0699
$H_2C=C$	22′	2.0000^b
$HC=C$	21	2.1083
$C=C$	20	2.1716
$HC-CH$	12	0.4660
$HC-C$	11	0.4362
$C-C$	10	0.4358

^{a} The first index gives the bond order, the second the number of attached H atoms. ^{b} Arbitrarily assigned.

When this correction is made, pyrene falls nicely on the curve of Figure 5, as can be seen in Figure 1 of Herndon's paper.

The comparison of total resonance energies can be misleading simply because the dominate factor there is molecular size. If total resonance energies are divided by the number π electrons in the molecule, the resulting normalized resonance energies are more sensitive and more useful predictors of aromaticity. Division by the number of atoms in the conjugated system has also been used[52,53] and might be significant for ions and heterosystems where each atom does not contribute one π electron. Zahradník, Michl, and Pancíř[7] and Aihara[54] used division by the number of bonds in the conjugated system, though Trinajstić[55] finds no significant difference between this and division by number of π electrons. In the following we shall divide by the number of π electrons and use resonance energy per π electron (REPE).

B. The Reference Structure

It will be seen that the choice of reference structure turns out to be crucial to the success of Dewar's computation of resonance energy. We show the predicted order of aromaticity of the set of 11 small conjugated hydrocarbons in Figure 6 using various reference structures. Readers may wish first to make their own rankings of these 11 for comparison with the results below. The annulenes, $(CH)_n$, will also be examined.

1. Hückel Reference Structure

The Hückel delocalization or resonance energy of a conjugated hydrocarbon X with n double bonds is

Figure 4. Same as in Figure 2 but with all resonance energies divided by the number of π electrons in the molecule.

resurrection of the semiempirical valence bond method.[51] There Herndon compared total resonance energies computed by his method with those of the standard Hückel method and of Dewar's method. Figures 2 and 3 show these comparisons. There is reasonable agreement among all three though Herndon and Dewar agree better with each other than with Hückel. To eliminate the effect of molecular size shown in Figure 1, dividing the total resonance energy by the number of π electrons was suggested. These results are shown in Figures 4 and 5. It is now seen that there is little correlation, except that caused by molecular size, between the Herndon and Hückel results, while the Herndon and Dewar energies still agree well. In fact, one wonders why pyrene, indicated by the arrow in Figure 5, lies off the curve. Looking further, it is found that the pyrene value in Table 2 of Dewar and de Llano's paper[1] was copied incorrectly from Table XX of de Llano's dissertation.[51]

Hückel (β)	Chung, Dewar (eV)	Dewar, de Llano (eV)	Hess, Schaad (β)		Gutman, Milun, Trinajstic (β)	Milun, Sobotka, Trinajstic (β)
0.368	0.243	0.145	0.065	prototype of aromaticity	0.046	0.073
0.367	0.220	0.132	0.055	well-known aromatic	0.043	0.056
0.336	0.137	0.054	0.043	simple derivatives isolated, undergo electrophilic subst	0.039	0.043
0.333	0.092	0.025	0.023	generally considered aromatic	0.015	0.024
0.307	0.070	0.017	0.002	typical polyene	0.003	-0.002
0.302	0.069	0.011	-0.002	isolated but reactive	0.000	-0.012
0.298	0.023	0.008	-0.004	isolated but reactive	-0.012	-0.016
0.280		0.008	-0.018	observed in Ar matrix, dimerizes above 80K	-0.027	-0.018
0.244		0.003	-0.027	observed in matrix, dimerizes above 75K	-0.030	-0.028
0.118		0.001	-0.033	prepared in very dilute soln., extremely reactive	-0.049	-0.032
0.000		-0.193	-0.268	observed at 8K, vanishes at 35K	-0.307	-0.260

Figure 6. Comparison of resonance energies per π electron. The Hückel results in the first column are standard and can easily be obtained from the data in Tables 2 and 3 in ref 56. The modified Pariser−Parr−Pople results in the second column are from ref 57; those in the third column are from ref 1 except for calicene, cyclobutadiene, and fulvalene which are from ref 51 and benzcyclobutadiene from ref 58. Our Hückel results in the fourth column are from ref 56, and those in the sixth column are from ref 59. The graph-theoretical results in column 5 are from ref 13. Experimental properties are from the following references: calicene, refs 60−63; fulvene, ref 64; heptalene, ref 65; pentalene, refs 66 and 67; benzocyclobutadiene, ref 68; cyclobutadiene, refs 69 and 70.

defined by eq 9.

$$\text{RE}\ (X) = E_\pi(X) - nE_\pi(CH_2{=}CH_2) = E_\pi(X) - 2n$$

$$(9)$$

That is, Hückel resonance energies (in units of β) are computed with the HMO molecular orbital method to get the π energies (E_π) of X and of ethylene, and the reference energy of n times the ethylene π energy (2β) is subtracted from that of X. Hückel resonance energies per π electron for 11 conjugated hydrocarbons are in the first column of Figure 6, and Figure 7 shows this quantity for the annulenes.

Let us examine the order of aromaticity in column 1 of Figure 6 as predicted by the Hückel computational method together with the Hückel reference. Do this using the properties of these compounds listed in the fourth column of that figure. Given the lack of a precise definition of aromaticity discussed above, at best only broad features can be picked out in the columns of Figure 6. First, most would probably agree that the top four compounds in column 1 are all more aromatic than the bottom seven, but the order within the two sets looks poor. Most would put benzene above azulene, calicene, and probably naphthalene. Butadiene, certainly, and fulvene, probably, would be moved above pentalene, heptalene, benzocyclob-
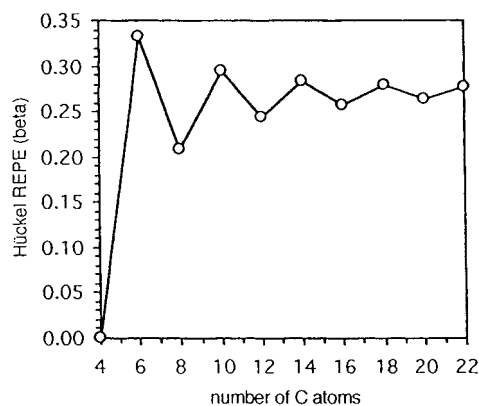
Figure 7. Hückel delocalization energies per π electron in units of β for the conjugated monocyclic hydrocarbons using the Hückel reference structure and the Hückel computational method.

utadiene, and fulvalene. Cyclobutadiene is at the bottom where most would put it, but it is now usually considered to be antiaromatic and so should have a negative resonance energy instead of zero as predicted by the Hückel method. The conjugated monocyclic hydrocarbons (annulenes) in Figure 7 alternate about and seem to be converging to a value of about 0.027β. That is, instead of going from aromatic to antiaromatic or nonaromatic as one goes from $4n$ +
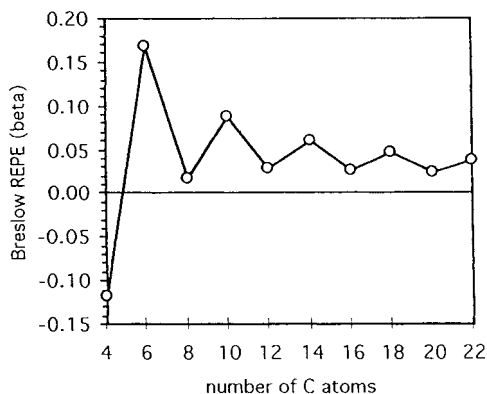
Figure 8. Resonance energies per π electron in units of β for the conjugated monocyclic hydrocarbons using the Breslow reference structure and the Hückel computational method.

Figure 9. Resonance energies per π electron in units of electronvolts for the conjugated monocyclic hydrocarbons using the Chung−Dewar reference structure and the Pariser−Parr−Pople computational method.

2 to $4n$ cycles as one would expect if the reference correctly represents a typical nonaromatic polyene, the results alternate between aromatic and not-so-aromatic. All in all, the Hückel order is not very satisfactory.

2. Mullikan–Parr Reference Structure

In 1951 Mulliken and Parr[71] published π-electron calculations of the resonance energy of benzene and butadiene. Here the energy of benzene with all carbon−carbon bonds equal was compared to that of a cyclic reference structure with three single (1.54 Å) and three double (1.34 Å) bonds and with localized π bonds. The authors called this a Kekulé structure, but of course in a VB calculation any given bond must be of the same length in all Kekulé structures. Although the Mulliken and Parr method was not widely applied at the time, their reference structure is certainly a direct precursor of the later Dewar reference, and Dewar and de Llano did use a modified Mulliken−Parr reference. Results using this reference structure are not shown in Figure 6.

3. Breslow Reference Structure

Breslow and Mohacsi[72] in 1963 reported studies of the 1,3-dithiepinyl anion in which they concluded that this system behaved like a nonaromatic, in contrast to Hückel predictions. They suggested the corresponding open chain might be a more appropriate reference structure than Hückel's. That is, benzene should be compared to n-hexatriene instead of to three isolated carbon−carbon double bonds. They tried this for several monocyclic ions and found results in better agreement with their expectations. Figure 8 shows the computed REPE of the first several neutral annulenes using the Breslow reference. Comparison with the results using the Hückel reference in Figure 7 shows a considerable improvement in that all predicted REPEs have been decreased by use of the Breslow reference so that cyclobutadiene is now strongly antiaromatic (REPE < 0) and the other $4n$ compounds are weakly aromatic. No results with the Breslow reference are shown in Figure 6, but this reference is close to Dewar's below.

4. Chung–Dewar Reference Structure

What has come to be called the Pariser−Parr−Pople (PPP) method is an amalgam of the π-electron SCF treatment of Pople[73] with his point charge integral approximations replaced by the parameter values of Pariser and Parr.[74] In 1965 Chung and Dewar examined the annulenes using the Hückel, the PPP, and Dewar's own "split p-orbital" (SPO) method to compute π energies.[57]

Each was used with two reference structures. The first was like the Mulliken−Parr reference but with a single-bond length of 1.48 Å which was felt to be more appropriate for an sp^2-sp^2 single bond than the 1.54 Å used by Mulliken and Parr. The second, called semiempirical and used in Figure 6, was a modification of the first.

They compared these six sets of computed resonance energies for the annulenes "with experimental evidence which indicates that none of the $4n$-membered polyenes are aromatic, and that the ($4n$ + 2)-membered polyenes are aromatic only if n is less than 6 or 7". None of the results with the Mulliken−Parr-like reference was satisfactory. The semiempirical reference used with the Hückel calculations also failed but gave reasonable results with the SPO and slightly better results with the PPP calculations. These last are shown for the annulenes in Figure 9, where it is seen that all $4n$ compounds are predicted to be antiaromatic and all ($4n$ + 2) compounds to be aromatic. It is a little surprising that the aromaticity of benzene is greater than the antiaromaticity of cyclobutadiene and that antiaromaticity, after decreasing from cyclobutadiene to cyclooctatetraene, then increases slightly for the larger $4n$ cycles, but it could not be said with any certainty that these features of the Chung−Dewar results are incorrect.

Chung and Dewar also applied their semiempirical reference to other compounds. Results with the PPP method for those of the 11 in Figure 6 that they treated are shown in column 2 of that figure. These are less satisfactory than their annulene calculations by the same method in Figure 9. Benzene is less aromatic than naphthalene, and pentalene and fulvalene are more aromatic than fulvene. This is scarcely an improvement on the Hückel order in the first column.
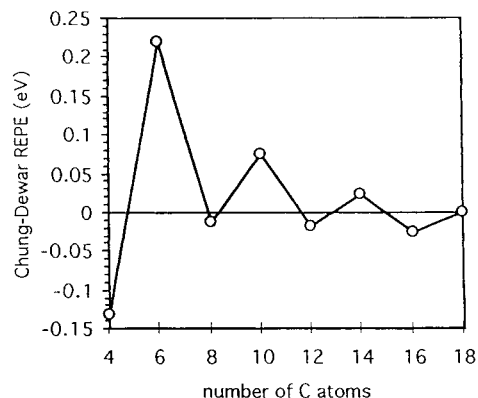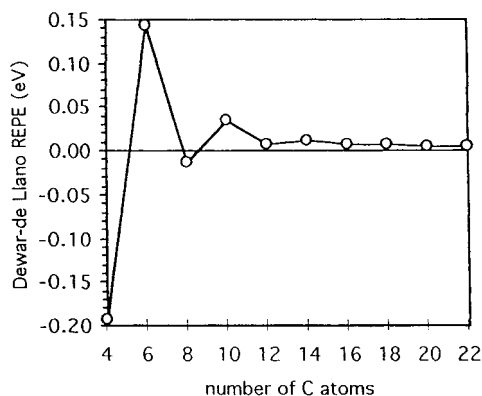
Figure 10. Resonance energies per π electron in units of electronvolts for the conjugated monocyclic hydrocarbons using the Dewar–de Llano reference structure with two bond types and the Pariser–Parr–Pople computational method.

5. Dewar–de Llano Reference Structure

Important earlier work by Dewar and Schmeising[75,76] and by Dewar and Gleicher[77,78] in which the π energy of linear polyenes was examined in closer detail, again with the PPP computational method, lead to the Dewar–de Llano (or simply Dewar as it is often called) reference structure. These papers showed that the apparent resonance energy found earlier for open-chain polyenes was caused by the use of an inappropriate sp^3-sp^3 single bond length of 1.54 Å in these compounds instead of an sp^2-sp^2 length of 1.46 Å. With this correction, calculated atomization energies of these polyenes could be written accurately as

$$\Delta H_a = n'E' + n''E'' + n_{CH}E_{CH} \qquad (10)$$

where n' and n'' are respectively the numbers of formally single and formally double C–C bonds in the polyene, $E' = 4.3499$ eV and $E'' = 5.5378$ eV are their energies, and n_{CH} and $E_{CH} = 4.4378$ eV are defined similarly for the C–H bonds. The C–C single bonds in these systems include significant π character, and E' includes these contributions.

Dewar and de Llano then used the additivity of eq 10 to define a polyene-like reference structure for computing the resonance energy of any conjugated hydrocarbon. For example, in the case of benzene, the reference is "cyclohexatriene" whose heat of atomization is given by eq 10 so that

$$RE(benzene) = \Delta H_a(benzene) - \Delta H_a(reference) =$$
$$\Delta H_a(benzene) - [3E' - 3E'' - 6E_{CH}] \quad (11)$$

It follows from eq 10 and a generalization of eq 11 that all open-chain polyenes are essentially nonaromatic.

This reference structure gives the annulene aromaticities in Figure 10. These are perhaps slightly worse than the results in Figure 9 since only cyclobutadiene and cyclooctatetraene are computed to be antiaromatic. The order of the 11 compounds in column three of Figure 6 is fairly good. Benzene is now at the top of the list, cyclobutadiene is antiaromatic, and butadiene is nonaromatic. However, three

compounds appear misplaced: benzocyclobutadiene should be antiaromatic rather than more aromatic than azulene, fulvalene should be antiaromatic rather than weakly aromatic, and pentalene should be antiaromatic rather than nonaromatic.

6. Hess–Schaad Reference Structure

It was not clear to us whether the improvement found by Dewar and de Llano (column 3 of Figure 6) over the original Hückel results (column 1 of Figure 6) was caused by their change in reference structure from isolated double bonds of eq 9 to a polyene-like structure satisfying eq 10 or to the change from the simple Hückel to the somewhat more rigorous PPP calculation method. We therefore tried combining the Hückel computation and the Dewar reference.[56] Since only π electrons are considered, the term for C–H bond energies in eq 10 is now dropped, leaving only two bond-energy terms to fit to the energies of the conjugated acyclics. We could not get a satisfactory fit for the acyclics with only two bond types, and even the simple acyclic, 3-methylene-1,4-pentadiene deviated so far from additivity that it was predicted to be more antiaromatic than pentalene.[79]

Accordingly, we classified the carbon–carbon bonds as single or double and by the number of hydrogen atoms attached to the two carbon atoms of the bond. Thus, E_{ij} is the bond-energy term for a carbon–carbon bond of order i ($i = 1$ or 2) with j H atoms attached. In the case of two H atoms on a double bond, a prime was used to distinguish the case of both hydrogen atoms on one carbon from the case of one on each. This classification gives eight distinct carbon–carbon bond types for conjugated hydrocarbons. However, a compound cannot be constructed with arbitrary numbers of these bond types. Let n_{ij} be the number of bonds with bond-energy term E_{ij} in some given compound. The n_{ij} can be shown to be connected by the two linear relations[56]

$$n_{11} + 2n_{12} = n_{21} + 2n_{22} + n_{23}$$

$$2(n_{10} + n_{11} + n_{12}) = 4n_{20} + 3n_{21} + 2n_{22} +$$
$$2n_{22'} + n_{23} \quad (12)$$

The two bond-energy terms E_{23} and $E_{22'}$ were arbitrarily set to 2β and the remaining six fit by least squares to the Hückel π energies of 40 acyclic polyenes[56] to give a standard deviation of 0.0016β and a maximum error of 0.004β per π electron. These eight Hückel π-bond-energy terms are shown in Table 1. With these, the Hückel π energy of 3-methylene-1,4-pentadiene differs from the additive energy ($2E_{23}$ + $E_{22'}$ + $2E_{11}$) by only 0.004β per π electron rather than by -0.024β with two bond-energy terms. It is certainly no surprise that eight bond-energy terms fit the actual acyclic energies much better than two. The question is whether the use of these eight to define a reference will predict reasonable aromaticities. Define then the resonance energy of compound X by

$$RE(X) = E_\pi(X) - E_{ref}(X) = E_\pi(X) - \sum_{ij} n_{ij}E_{ij} \quad (13)$$

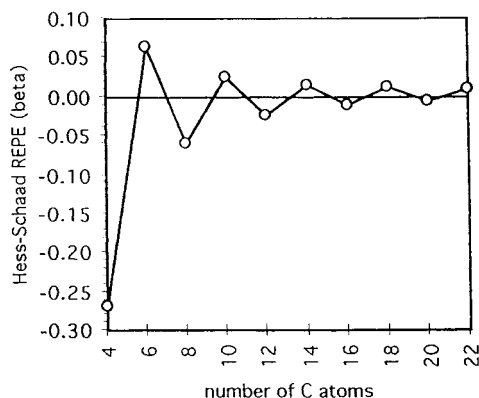**Figure 11.** Resonance energies per π electron in units of β for the conjugated monocyclic hydrocarbons using the Dewar–de Llano reference structure with eight bond types and the Hückel computational method.

where the sum in eq 13 goes over all ij defined in Table 1. For example, in the case of benzene

$$E_{ref}(benzene) = 3E_{22} + 3E_{12} = 3(2.0699 +$$
$$0.4660)\beta = 7.6077\beta \quad (14)$$

$$RE(benzene) = E_{ref}(benzene) -$$
$$E_{Hückel}(benzene) = (8.0000 - 7.6077)\beta = 0.3923\beta \quad (15)$$

so that $REPE(benzene) = RE/6 = 0.0654\beta$.

REPEs for the annulenes using the Hess–Schaad reference structure are in Figure 11. These of course are for the planar annulenes with all C–C bonds of equal length. Nevertheless, Figure 11 does appear to predict with reasonable accuracy what is known about the actual systems.

Column 4 of Figure 6 shows the predicted order of aromaticity of our set of 11 compounds using the simple Hückel energy calculation but with the Hess–Schaad reference structure. Thus, the only difference between the results in column 1 and column 4 is the choice of reference structure. This difference has a large consequence, and it seems to us that while the computed order of aromaticity in column 1 is poor, the order in column 4 is quite satisfactory. Benzene is at the top followed by naphthalene. Calicene and azulene are predicted to be more weakly aromatic, followed by the nonaromatics, butadiene, fulvene, and heptalene. The antiaromatics pentalene, benzocyclobutadiene, and fulvalene follow with cyclobutadiene, the most antiaromatic, at the bottom.

7. Graph-Theoretical Reference Structure

In 1950 Coulson[80] showed how the first few high-order coefficients of the Hückel secular equation of a conjugated hydrocarbon could be obtained by an examination of the structural formula of the molecule itself.

It then turned out that the mathematical theory of "graphs", which during those years received considerable attention, has a direct connection to the Hückel theory of aromaticity and in particular to Coulson's way of writing down individual coefficients of the secular equation. A graph in this sense consists of a set of points together with a set of edges

Scheme 2
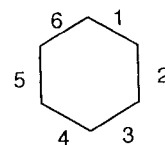
connecting specified pairs of points. If one deletes the lines distinguishing double from single bonds in, for example, the structural formulas of the 11 compounds in Figure 6, what remains is a graph for each compound, a hexagon for benzene and a square for cyclobutadiene, etc. In these graphs, the vertexes represent carbon atoms and an edge between two vertexes indicates a π bond between the two corresponding carbon atoms. Such graphs are just what is needed to write down the secular determinant for these molecules in the Hückel theory.

In 1964 Sachs[81] published a study of the adjacency matrix of graphs (i.e., of the Hückel matrixes of conjugated molecules) which allows correction, simplification, and generalization of Coulson's work, though Sachs himself was not interested in molecular calculations and made no mention of this connection.

To see how Sachs' method works, let us take the example of benzene and write down its structural formula (= molecular graph) in the way just discussed.

The bonds in Scheme 2 are numbered for convenience below. To get the secular equation in the usual way, write down the secular determinant and expand to get the polynomial equation for $x = (\alpha - E)/\beta$, where E is one of the orbital energies of benzene and α and β are, respectively, Coulomb and resonance energies of carbon $2p\pi$ orbitals

$$P(x) = \sum_{i=0}^{n} a_i x^{n-i} = x^6 - 6x^4 + 9x^2 - 4 =$$
$$(x - 2)(x + 2)(x - 1)^2(x + 1)^2 \quad (16)$$

where n is the number of conjugated atoms in the molecule.

Sachs' formula for the coefficients a_i is

$$a_i = \sum_{s_i} (-1)^{c_i}(2)^{r_i} \quad (17)$$

The sum in eq 17 goes over all Sachs graphs with i vertexes. A Sachs graph S_i of the molecular graph is a subgraph with i vertexes of that molecular graph containing only disjoint (i.e., nontouching) bonds and/or rings. The constant c_i is the number of components (i.e., disjoint parts) in S_i, and r_i is the number of rings it contains. The coefficient a_o always equals 1.

Consider applying eq 17 to the case of benzene. Benzene contains no Sachs graphs with an odd number of vertexes so $a_i = 0$ for all odd i. To get a_2, construct all Sachs graphs with 2 atoms. These are simply the bonds 1–6. Each has 1 component and 0 rings. There are six of these; therefore

$$a_2 = 6 \times (-1)^1(2)^0 = -6 \quad (18)$$

The nine pairs of disjoint bonds (1,3), (1,4), ..., (4,6)

form the Sachs graphs with four atoms. Each has two components and no rings to give

$$a_4 = 9 \times (-1)^2 (2)^0 = +9 \qquad (19)$$

There are three Sachs graphs with six atoms. They are the two sets of three bonds (1,3,5) and (2,4,6) each with three components and no rings and also the molecular graph itself with one component and one ring. Therefore

$$a_6 = 2 \times (-1)^3 (2)^0 + 1 \times (-1)^1 (2)^1 = -4 \quad (20)$$

These coefficients, of course, agree with those in eq 16.

Mallion, Schwenk and Trinajstić[82] have shown how Sachs' result can be extended to include the important case of heteroatoms. However, the important point for us is not that Sachs' result provides an alternative way to compute the coefficients of the secular polynomial, but that it also suggests a new way to define the reference structure or more precisely a new way to define the secular equation of the reference polynomial, as shown by Aihara[83] and by Gutman, Milun, and Trinajstić.[84] Suppose benzene had been an acyclic compound, then none of the coefficients of the secular equation as given by eqs 18–20 would have contributions from rings. These authors therefore define the secular equation of the reference structure of a molecule to be simply the secular equation of that molecule but with all contributions of rings deleted. In the case of benzene, only the coefficient a_6 contains a ring contribution, the second term in eq 20. The secular equation for benzene and its reference structure are therefore identical, except that $a_6 = -4$ for benzene and -2 for its reference structure. The secular equation for the benzene reference structure has roots $x = \pm 2^{1/2}\beta$ and $\pm(2 \pm 3^{1/2})\beta$. Doubly filling the three lowest energy levels of the reference structure gives 7.727β as the energy of the benzene reference structure and $(8 - 7.727)\beta/6 = 0.046\beta$ as the resonance energy per π electron for benzene computed using the graph-theoretical reference structure, as in column five of Figure 6. Columns 4 and 5 in Figure 6 differ only in the transposition of the three neighboring pairs: calicene and naphthalene, fulvene and butadiene, fulvalene and benzocyclobutadiene.

Similarly, Figures 11 and 12 show that the Hess–Schaad and graph-theoretical reference structures give very similar predictions of aromaticity for the annulenes. Without a more precise experimental definition that is generally accepted, we cannot say which of these two reference structures is better. Both appear to give at least roughly correct predictions of aromaticity.

8. Milun, Sobotka, and Trinajstić Two-Bond Reference

In section III.B.6, it was mentioned that though Dewar and co-workers[1] were able to reproduce energies of conjugated acyclic hydrocarbons computed by the Pariser–Parr–Pople method with an empirical scheme using only two bond types (single and double), we were unable to do this using Hückel calcula-
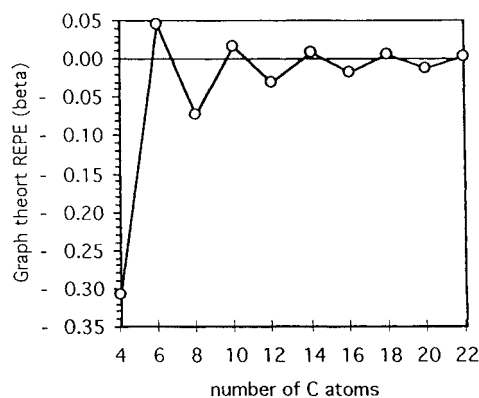
Figure 12. Resonance energies per π electron in units of β for the conjugated monocyclic hydrocarbons using the graph-theoretical reference structure and the Hückel computational method.
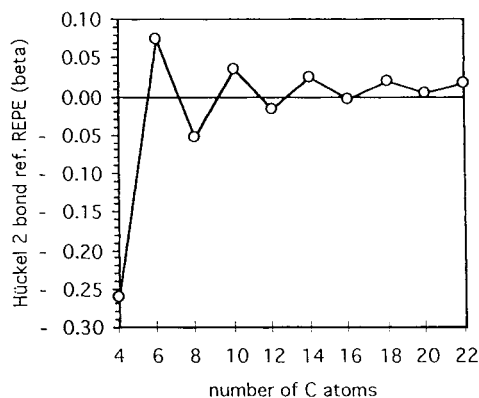
Figure 13. Resonance energies per π electron in units of β for the conjugated monocyclic hydrocarbons using the Dewar–de Llano reference structure with two bond types and the Hückel computational method.

tions.[56,79] Milun, Sobotka, and Trinajstić[59] reported results similar to ours. Their order for the 11 compounds in Figure 6 is shown in the sixth column. It is identical to our order in column four, except that heptalene is computed to be more aromatic than butadiene, but these energy differences are not large. Their annulene results in Figure 13 are also similar to ours in Figure 11, except their limiting value for large rings gives a positive rather than a zero REPE. However, not all acyclics are computed to be nonaromatic. In particular, 3-methylene-1,4-pentadiene is still found to be more antiaromatic that pentalene.

9. Other Reference Structures

Figure 6 does not exhaust all reference structures that have been suggested. Valence bond calculations are perhaps the most important of those not yet discussed, and before returning to the discussion of Goddard's ab initio valence bond results, we mention two modern semiempirical valence bond investigations and their reference structures. The first is Herndon's work[50] which uses a method based on the VB method. The second is Randić's "Method of Conjugated Circuits".[16,17] This is a semiempirical method in which structures are counted and the resonance energy estimated by these numbers. At first sight it does not appear to be a valence bond method, but it has been shown[85] that it is identical

Table 2. Applications of REPE

reference	application
87	benzenoid hydrocarbons
88	1,3-dehydrobenzene
89	nonalternant hydrocarbons
90	dimethylenecyclobutene
91	heterocycles with amine nitrogen or ether oxygen
92, 93	annulenoannulenes
94, 95	cyclobutadiene and substituted cyclobutadienes
96	heterocycles with divalent sulfur
97	heterocycles with imine nitrogen
98	porphyrins
99	correlation between PMR coupling constants and REPE in nitrogen heterocycles
100	NMR chemical shifts and REPE in tetra-*tert*-butyldehydro[*n*]annulenes
101	REPE and rate of formation of macrocyclic annulenes
102	stabilization of thiepin by substitution
103	influence of F substitution on aromaticity
104	nonalternant annulenoannulenes and corannulenes
105	ions and radicals
106	REPE and Diels–Alder reactivity
107	delocalized dicarbanions and higher delocalized carbanions
108	footballene

to the Herndon method if consistent values of the parameters are used in the two methods. It has also been found[85] that these two methods are in close agreement with the Hess–Schaad method in section III.B.6 and with the Dewar–de Llano method in section III.B.5.

In a valence bond calculation, the reference structure is a single Kekulé structure, presumably the most important in the actual mixture of such structures for the compound. This is different from the Dewar reference in that it contains any strain energy of the system, whereas Dewar's reference does not.

We found rectangular cyclobutadiene to be 85.4 kcal/mol less stable than the Dewar reference in an HF/6-31G* calculation.[86] It was estimated that 32.0 kcal/mol of this difference was caused by ring strain and −1.3 kcal/mol by interaction of nonbonded H atoms, giving rectangular cyclobutadiene as antiaromatic by 54.7 kcal/mol relative to the Dewar reference. Goddard and Voter find the square $^1B_{1g}$ cyclobutadiene to be aromatic by between 23.1 and 21.8 kcal/mol relative to a single Kekulé structure. These are very different predictions of aromaticity, but of course the reference structures are very different. It would be interesting to have more ab initio VB calculations of this kind. It *might* be that aromaticity differences with the ab initio VB method would parallel those using the Dewar reference even though aromaticities are very different. This would then agree with what was found with the semiempirical VB method, but we cannot predict how this would turn out.

C. Applications

We have applied the Hess–Schaad version of the Dewar reference structure to the systems listed in Table 2. Theoretical investigations of the REPE index were also published. Changes in the energy of the σ electrons in a series of compounds were found to vary linearly with though in opposite direction to π energies.[109] This provides some explanation of why π-electron-only models of conjugated systems can be as successful as they are. Reference structures were investigated,[110,111] and comparisons were made with other recent theoretical aromaticity indices.[85]

In the case of cyclobutadiene and benzene, it was shown that ab initio calculations of aromaticity using our version of the Dewar reference agreed with the simple Hückel results predicting strong aromaticity for benzene and strong antiaromaticity for cyclobutadiene.[86] These calculations were done in 1983, and since that time improvements in the Gaussian set of programs and increased speed of desktop computers would now make it possible to do ab initio calculations on many more of the compounds examined in ref 56. The problem is now how to separate the various steric energy changes in many of the conformations of many of these compounds from the resonance energy changes.

IV. Conclusions

It was never a surprise that the Hückel computational method together with the Hückel reference structure of isolated double bonds gave imperfect predictions of aromaticity as seen in column 1 of Figure 6. The computational method, after all, contained many approximations. With these obvious deficiencies in the computational method, it was natural that more investigations aimed at improving it rather than studying the reference structures used.

In fact Dewar and de Llano[1] concluded their paper that introduced the successful reference structure (column 3 of Figure 6) with "there no longer seems any point at all in carrying out calculations by less refined procedures, in particular the HMO method or variants of it". They thus appear to attribute their success to the change in computational method from HMO to Pariser–Parr–Pople rather than to their important switch in reference structure.

However, use of the HMO computational method together with a Dewar-like reference structure (column 4 of Figure 6) gives an even better result and shows that Dewar and de Llano's success was caused by their new reference structure, not by their use of the PPP instead of the HMO computational method.

The Hess–Schaad results in column 4 of Figure 6 and the graph-theoretical values of Gutman, Milun, and Trinajstić in column 5 of Figure 6 are equally satisfactory, as far as we can tell. We do not see how

to choose between the two without a rigorous and generally accepted experimental definition of degree of aromaticity. We do not expect such a definition to appear soon. Rather than worrying too much about that, we prefer to close by pointing out the considerable improvement in the prediction of aromaticity between the first two columns of Figure 6 and the last four. This is the result of Dewar's improved reference structure for the calculation of aromaticity.

V. References

(1) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.
(2) Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68.
(3) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.
(4) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.
(5) Binsch, G. *Naturwissenschaften* **1973**, *60*, 369.
(6) *Fifth International Symposium on Novel Aromatic Compounds*, University of St. Andrews, St. Andrews, Scotland, July 15−19, 1985.
(7) Zahradník, R.; Michl, J.; Pancíř, J. *Tetrahedron* **1966**, *22*, 1356.
(8) Hückel, E. *Z. Phys.* **1931**, *70*, 204.
(9) Hückel, E. *Z. Phys.* **1931**, *72*, 310.
(10) Hückel, E. *Z. Phys.* **1932**, *76*, 628.
(11) Hückel, E. *Z. Phys.* **1933**, *83*, 632.
(12) Julg, A.; François, P. *Theor. Chim. Acta* **1967**, *7*, 249.
(13) Kruszewski, J.; Krygowski, T. M. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1972**, *20*, 907.
(14) Gutman, I.; Milun, M.; Trinajstić, N. *MATCH* **1975**, *1*, 171.
(15) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.
(16) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750.
(17) Aihara, J. *J. Am. Chem. Soc.* **1977**, *99*, 2048.
(18) *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity. Proceedings of an International Symposium,* Jerusalem, March 31 to April 3, 1970; Bergmann, E. D., Pullman, A., Eds; Israel Academy of Sciences and Humanities: Jerusalem, 1971; p 33.
(19) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974; pp 102−105.
(20) Brush, S. G. *Stud. Hist. Philos. Sci.* **1999**, *30A*, 21.
(21) Brush, S. G. *Stud. Hist. Philos. Sci.* **1999**, *30A*, 236.
(22) Ihde, A. J. *The Development of Modern Chemistry*; Dover Publications: New York, 1984; p 314.
(23) Kekulé, A. *Liebigs Ann. Chem.* **1872**, *162*, 77.
(24) Schrödinger, E. *Ann. der Physik* **1926**, *79*, 361.
(25) Heitler, W.; London, F. *Z. Phys.* **1927**, *44*, 445.
(26) Coulson, C. A. *Valence*; Oxford University Press: London, 1952; p 109.
(27) Bloch, F. *Z. Phys.* **1928**, *52*, 555.
(28) Wheland, G. W. *J. Chem. Phys.* **1934**, *2*, 474.
(29) Wheland, G. W. *Proc. R. Soc. London* **1937−8**, *164*, 397.
(30) Longuet-Higgins, H. C. *Proc. Phys. Soc. London* **1948**, *60*, 270.
(31) Voter, A. F.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 2830.
(32) Balková, A.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 8972.
(33) Mo, Y.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1994**, *98*, 10048.
(34) Filatov, M.; Shaik, S. *J. Chem. Phys.* **1999**, *110*, 116.
(35) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Phys. Chem.* **1995**, *99*, 10186.
(36) Zilberg, S.; Hass, Y. *Chem.-Eur. J.* **1999**, *5*, 1755.
(37) Zilberg, S.; Hass, Y. *J. Phys. Chem.* **1998**, *102*, 10843.
(38) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Phys. Chem.* **1988**, *92*, 5086.
(39) Gallup, G. A. *J. Chem. Phys.* **1987**, *86*, 4018.
(40) Hrovat, D. A.; Borden W. T. *J. Mol. Struct. (THEOCHEM)* **1997**, *398-399*, 210.
(41) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583.
(42) Borden, W. T.; Davidson, E. R.; Hart, R. *J. Am. Chem. Soc.* **1978**, *100*, 388.
(43) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012.
(44) Masamune, S.; Souto-Bachiller, F. A.; Machiguchi, T.; Bertie, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 4889.
(45) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1978**, *100*, 4304.
(46) Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2281.
(47) Schaad, L. J.; Hess, B. A., Jr.; Ewig, C. S. *J. Org. Chem.* **1982**, *47*, 2904.
(48) Roberts, J. D.; Streitwieser, A.; Regan, C. M. *J. Am. Chem. Soc.* **1952**, *74*, 4579.
(49) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 2413.
(50) Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404.
(51) de Llano, C. R. Ph.D. Dissertation, The University of Texas, Austin, TX, 1968.
(52) Hess, B. A., Jr.; Schaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1471.

(53) Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A. Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052.
(54) Aihara, J. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3057.
(55) Ilić, P.; Jerman-Blaić-Džonova, B.; Mohar, B.; Trinajstić, N. *Croat. Chem. Acta* **1979**, *52*, 35.
(56) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305.
(57) Chung, A. L. H.; Dewar, M. J. S. *J. Chem. Phys.* **1965**, *42*, 756.
(58) Baird, N. C. *J. Chem. Educ.* **1971**, *48*, 509.
(59) Milun, M.; Sobotka, Ž.; Trinajstić, N. *J. Org. Chem.* **1972**, *37*, 139.
(60) Kende, A. S.; Izzo, P. T.; MacGregor, P. T. *J. Am. Chem. Soc.* **1966**, *88*, 3359.
(61) Kende, A. S.; Izzo, P. T.; Fulmore, W. *Tetrahedron Lett.* **1966**, 3697.
(62) von Gustorf, E. K.; Henry, M. C.; Kennedy, P. V. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 627.
(63) Al-Dulayymi, A.; Li, X.; Neuenschwander, M. *Helv. Chim. Acta* **2000**, *83*, 571.
(64) Thiec, J.; Wiemann, J. *Bull. Soc. Chim. Fr.* **1956**, 177.
(65) Dauben, H. J.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 4569.
(66) Bloch, R.; Marty, R. A.; de Mayo, P.; *J. Am. Chem. Soc.* **1971**, *93*, 3, 3071.
(67) Bally, T.; Chai, S.; Neuenschwander, M. *J. Am. Chem. Soc.* **1997**, *119*, 1869.
(68) Chapman, O. L.; Chang, C. C.; Rosenquist, N. R. *J. Am. Chem. Soc.* **1976**, *98*, 261.
(69) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614.
(70) Krantz, A.; Lin, C. Y.; Newton, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 5, 614.
(71) Mulliken, R. S.; Parr, R. G. *J. Chem. Phys.* **1951**, *19*, 1271.
(72) Breslow R.; Mohacsi, E. *J. Am. Chem. Soc.* **1963**, *85*, 431.
(73) Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.
(74) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466, 767.
(75) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166.
(76) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1960**, *11*, 96.
(77) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685.
(78) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 692.
(79) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1972**, *37*, 4179.
(80) Coulson, C. A. *Proc. Cambridge Philos. Soc.* **1950**, *46*, 202.
(81) Sachs, H. *Publ. Math. (Debrecen)* **1964**, *11*, 119
(82) Mallion, R. B.; Schwenk, A. J.; Trinajstić, N. *Croat. Chem. Acta* **1974**, *46*, 171.
(83) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750.
(84) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.
(85) Schaad, L. J.; Hess, B. A., Jr. *Pure Appl. Chem.* **1982**, *54*, 1097.
(86) Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 7500.
(87) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 2413.
(88) Hess, B. A., Jr.; Schaad, L. J. *Tetrahedron Lett.* **1971**, 17.
(89) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1971**, *36*, 3418.
(90) Hess, B. A., Jr.; Schaad, L. J. *Aust. J. Chem.* **1972**, *25*, 2231.
(91) Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron* **1972**, *28*, 3657.
(92) Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr.*Tetrahedron* **1972**, *28*, 5299.
(93) Hess, B. A., Jr.; Schaad, L. J. *Tetrahedron Lett.* **1972**, 5113.
(94) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1976**, *41*, 3508.
(95) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907.
(96) Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W. Jr. *Tetrahedron* **1975**, *31*, 295.
(97) Hess, B. A., Jr.; Schaad, L. J. *J. Theor. Biol.* **1976**, *59*, 237.
(98) Hess, B. A., Jr.; Schaad, L. J. *Tetrahedron Lett.* **1977**, 535.
(99) Hess, B. A., Jr.; Schaad, L. J.; Nakagawa, M. *J. Org. Chem.* **1977**, *42*, 2, 1669.
(100) Hess, B. A., Jr.; Schaad, L. J. *J. Chem. Soc., Chem. Commun.* **1977**, 243.
(101) Hess, B. A., Jr.; Schaad, L. J.; Reinhoudt, D. N. *Tetrahedron* **1977**, *33*, 2683.
(102) Hess, B. A., Jr.; Schaad, L. J. *Isr. J. Chem.* **1978**, *17*, 155.
(103) Hess, B. A., Jr.; Schaad, L. J.; Agranat, I. *J. Am. Chem. Soc.* **1978**, *100*, 5268.
(104) Agranat, I.; Hess, B. A., Jr.; Schaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1399.
(105) Hess, B. A., Jr.; Schaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1471.
(106) Hess, B. A., Jr.; Schaad, L. J.; Herndon, W. C.; Biermann; Schmidt, W. *Tetrahedron* **1981**, *37*, 2983.
(107) Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052.
(108) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1977**, *41*, 3902.
(109) Schaad, L. J.; Hess, B. A., Jr. L. J. *J. Am. Chem. Soc.* **1972**, *94*, 3068.
(110) Schaad, L. J.; Hess, B. A., Jr.; Nation, J. B.; Trinajstić, N.; Gutman, I. *Croat. Chem. Acta* **1980**, *52*, 233.
(111) Schaad, L. J.; Hess, B. A., Jr. *Isr. J. Chem.* **1980**, *20*, 281.