# Resonance Theory. V. Resonance Energies of Benzenoid and Nonbenzenoid $\pi$ Systems

**William C. Herndon* and M. Lawrence Ellzey, Jr.**

*Contribution from the Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968.* *Received April 27, 1974*

**Abstract:** Structure-resonance theory for $\pi$-molecular systems based solely on covalent Kekulé structures is justified phenomenologically and by reference to recent theoretical work. The idea of antiaromaticity is shown to be a logical extension of the theory, and a concept of a local ring aromaticity or antiaromaticity is quantitatively defined. Estimates of resonance stabilization energies are substantially lower than predictions based on Hückel MO theory. The resonance theory results agree with those from SCF–LCAO–MO calculations.

The recognition of extremely simple algorisms for counting Kekulé structures[1] and their permutations induced us to test a semiempirical quantum theory with a basis of Kekulé structure functions.[2] The mathematical equivalencies[3–5] between Hückel molecular orbital (HMO) and valence bond (VB) theories for the benzenoid class of hydrocarbons led us to expect a correspondence of our results to previously known HMO quantities. The results[2] were surprising in that it was found that calculated resonance energies, RE, for an extensive series did not correlate well with HMO delocalization energies (correlation coefficient, 0.493 for resonance energy per electron, REPE). Instead there was a congruity with resonance energy values obtained from SCF–LCAO–MO calculations[6] (correlation coefficient, REPE, 0.991).

The approach that we use is essentially a quantification of the structural resonance theory traditionally applied to structure–reactivity problems in organic chemistry.[7] In this paper we try to provide some justification for our procedures which will be described in more detail than in the previous communication.[2] Calculations of resonance energies of several classes of aromatic compounds will then be presented, and comparisons with previous MO results and experimental properties will be delineated. We emphasize throughout that our computational procedure is so easily carried out and leads to such sensible results that it should be the method of choice for calculating resonance energies. Applications to the estimation of heats of formation[8] and carcinogenic activities[9] of benzenoid hydrocarbons have already given good results, and a description of bond-order relationships will appear in a following article.[10]

## Resonance Theory

The formulism of the method is that of VB theory.[11] For a $\pi$-electronic system each energy eigenfunction is written as given in eq 1. The $\psi(u)$ are structure functions, the $c_i$ are coefficients, the index $u$ indicates the type of electron distribution associated with the function, and the subscript $i$ numbers the function. After selecting functions, the coefficients and eigenvalues can be evaluated by solving eq 2, where $\mathbf{H}$ is the Hamiltonian matrix and $\mathbf{S}$ is the overlap matrix. A conventional approximation is to assume zero overlap of the wave functions so that off-diagonal elements in the matrix involve Hamiltonian integrals only. A significant simplification in obtaining a ground-state eigenvalue is also provided if one assumes a wave function consisting of equal contributions from the class of functions corresponding to Kekulé structures. Then the eigenvalue or resonance energy is calculated from

$$\Psi = \sum_i c_i(u)\psi_i(u) \qquad (1)$$

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0 \qquad (2)$$

$$E = (2/\mathrm{K.S.})(\Sigma H_{ij}) \qquad (3)$$

The matrix elements $H_{ij}$ between the structure functions can be evaluated theoretically after superimposing Rumer–Pauling diagrams,[11] corresponding to the electronic arrangements of $\psi_i$ and $\psi_j$. We chose, however, to determine these integrals from spectroscopic data by a method described by Simpson[12] which follows the ideas of Pauling[13] and Förster.[14] Simpson postulates undefined, polyelectronic wave functions whose squares have the transformation properties of structures. The set of these structure functions forms a basis for a reducible representation of the pertinent molecular point group. Different states are represented as appropriate symmetry adapted linear combinations of structure functions, equivalent to appropriate combinations of VB structures. Particular experimentally determined term values are then taken as elements of a diagonalized square matrix, the order of

---

[1] W. C. Herndon, *Tetrahedron*, **28**, 3675 (1972); **29**, 3 (1973); *J. Chem. Educ.*, **51**, 10 (1974).

[2] W. C. Herndon, *J. Amer. Chem. Soc.*, **95**, 2404 (1973).

[3] H. C. Longuet-Higgins, *J. Chem. Phys.*, 18, 265, 275, 283 (1950); M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **214**, 482 (1952).

[4] N. S. Ham and K. Ruedenberg, *J. Chem. Phys.*, **29**, 1215 (1958); N. S. Ham, *ibid.*, **29**, 1229 (1958).

[5] (a) E. Heilbronner, *Helv. Chim. Acta*, **45**, 1722 (1962); (b) J. R. Platt in "Handbuch des Physik," Vol. XXXVII/2, S. Flügge, Ed., Springer-Verlag, Berlin, 1961, pp 187–209; (c) I. Gutman and N. Trinajstić, *Top. Cur. Chem.*, **42**, 49 (1973).

[6] M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969).

[7] G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955.

[8] W. C. Herndon, *Thermochimica Acta*, **8**, 225 (1973).

[9] W. C. Herndon, *Trans. N. Y. Acad. Sci.*, **36**, 200 (1974); *Int. J. Quantum Chem.*, in press.

[10] W. C. Herndon, *J. Amer. Chem. Soc.*, in press.

[11] L. Pauling, *J. Chem. Phys.*, 1, 280 (1933); J. H. Van Fleck and A. Sherman, *Rev. Mod. Phys.*, 7, 167 (1935).

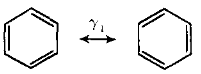
[12] W. T. Simpson, *J. Amer. Chem. Soc.*, **75**, 597 (1953); W. T. Simpson and C. W. Looney, *ibid.*, **76**, 6285 (1954); C. W. Looney and W. T. Simpson, *ibid.*, **76**, 6293 (1954); W. T. Simpson, *ibid.*, **78**, 3585 (1956).

[13] L. Pauling, *Proc. Nat. Acad. Sci. U. S.*, **25**, 577 (1939).

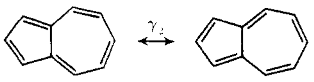
[14] Th. Förster, *Z. Phys. Chem., Abt. B*, **41**, 287 (1938).

which must correspond to the number of basis structures. The diagonal matrix is orthogonally transformed to nondiagonal form, where base vectors in the transformed system are interpreted to represent isoenergetic structures. The application of this approach in classifying and understanding the spectra of aromatic dyes was discussed in detail.[12] Apropos of the present work, it was found that first electronic transitions of benzene ($^1A_{1g} \rightarrow {}^1B_{2u}$, 4.89 eV), naphthalene ($^1A_g \rightarrow {}^1B_{3u}$, 3.97 eV), and azulene ($^1A_1 \rightarrow {}^1B_2$, 1.79 eV) were assigned consistently with correct polarization when bases of Kekulé structures were used.

The off-diagonal elements of the transformed matrix are the $H_{ij}$ that can be substituted in eq 3 to give the ground-state resonance energy. Examination of all Kekulé structures for benzene and for azulene indicates that in effect the $H_{ij}$ are integrals that result in permutations of pairs of $\pi$ electrons over the $\sigma$ bond framework of an aromatic molecule. Three pairs of electrons in a single ring are permuted by $\gamma_1$, and five pairs of electrons in two annelated rings are permuted by $\gamma_2$. The ratio of $\gamma_2$ to $\gamma_1$ is given by the ratio of the electronic transitions given above for benzene and azulene, $\gamma_2/\gamma_1 = 0.37$. This result is in close agreement with a value of 0.36 which is obtained from VB superposition diagrams with values of Coulomb and exchange integrals calculated by Coulson and Dixon.[15] Also, anticipating later results, the best correlative value of the ratio of $\gamma_2/\gamma_1$ is 0.40 ($\gamma_1 = 0.841$ eV) by comparison with a large number of SCF–LCAO–MO[6,16] calculations of resonance energies. The SCF method, which we will call the Dewar–de Llano method,[6] is a variable bond-length semiempirical approach parameterized with experimental thermodynamic values, and it provides very accurate estimates of heats of formation and very reasonable values for resonance energies.



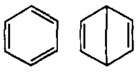
1



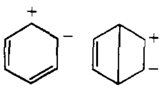
2

The resonance theory results for benzenoid hydrocarbons[2] show that it is not necessary to include the effect of integrals that result in permutations of larger than five pairs of electrons in order to obtain resonance energies consonant with the previous theoretical work. However, two- and four-electron pair permutations are demonstrated to have a considerable effect in assigning resonance energies, but a discussion of their relative values will be deferred to a later section following the detailed outline of the computational procedures.

Pragmatically, one seems justified in using the small limited set of Kekulé structures as basis functions for a calculation of resonance energy. One notes that many practitioners of VB theory have not apologized for choosing a small set of "reasonable" structures from among all possible canonical structures and ionic forms that could be drawn.[17] However, there are two reasons why more justification may be necessary for the compounds discussed in the present paper. First, an exceedingly large number of canonical nonionic structures can be written for even relatively small $\pi$-molecular systems (anthracene, 429 structures; benzanthracene, 4862; dibenzanthracene, 58,786). Several workers have shown that for most aromatic molecules the total weight of long-bond structures dominates over the total weight of Kekulé structures.[18] Coulson has emphatically stated that it is not appropriate to use the VB resonance method when there are more than about ten atoms in the $\pi$ system.[19] Second, a large body of theoretical evidence is accumulating on the importance of including ionic structures in VB calculations.[20] A recent *ab initio* VB calculation on benzene[21] indicated that covalent Kekulé and Dewar structures **3** are relatively unimportant in the ground-state wave function as compared to singly polar structures **4**. The number of these polar forms is also much larger than the number of nonionic structures.



3



4

The difficulties outlined in the previous paragraph should not be ignored, but they are not really consequential in the context of the present calculations. It is important to remember that the theory used here is a parameterized theory that uses VB structures only as representations of squares of undefined, many-electron wave functions. The assumption is that the transformation properties of the underlying wave functions are the same as those of the structure representations. Simpson points out[12] that for benzene the sum of the unknown wave function must transform like $A_{1g}$, and the difference like $B_{2u}$, and he states that attempts to draw such entities will result in drawings which closely resemble Kekulé structures. Quantitative realizations of these "drawings" are found in recent calculations by Paldus, Cizek, and Sengupta.[22] Their separated-pair localized geminal calculations using a Pariser–Parr–Pople-type Hamiltonian gave very good ground- and first excited-state energies, and the wave functions used are exact analogs of Kekulé structures.

Several years ago Dewar and Schmeising[23] suggested that the individual Kekulé structures have a more profound significance than is usually ascribed to the canonical structures of VB theory. The views of Simpson[12] and the calculations cited above[22] show how this apparent anomaly can be resolved. Our own results indicate that, with empirical parameterization of matrix elements, the use of Kekulé structures alone yields resonance energies of SCF–LCAO–MO quality.

---

[15] C. A. Coulson and W. T. Dixon, *Tetrahedron*, 17, 215 (1962).

[16] C. J. Gleicher, D. N. Newkirk, and J. C. Arnold, *J. Amer. Chem. Soc.*, **95**, 2526 (1973).

[17] Examples: H. M. McConnell and H. H. Dearman, *J. Chem. Phys.*, **28**, 51 (1958); J. C. Schug, T. H. Brown, and M. Karplus, *ibid.*, **35**, 1873 (1961); W. J. Van der Hart, J. J. C. Mulder, and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **94**, 5724 (1972).

[18] A. Pullman, *Ann. Chim. (Paris)*, 2, 5 (1947); C. Daudel and R. Daudel, *J. Chem. Phys.*, **16**, 639 (1948).

[19] C. A. Coulson, *Proc. Roy. Soc., Ser. A*, 207, 91 (1951); C. A. Coulson in "Physical Chemistry, An Advanced Treatise," Vol. 5, Academic Press, New York, N. Y., 1970, p 379.

[20] A. L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937); D. P. Craig, *Proc. Roy. Soc., Ser. A*, **200**, 401 (1950); R. S. Berry, *J. Chem. Phys.*, **30**, 936 (1959); J. C. Schug, *ibid.*, **42**, 2547 (1965); M. Craig and R. S. Berry, *J. Amer. Chem. Soc.*, **89**, 2801 (1967).

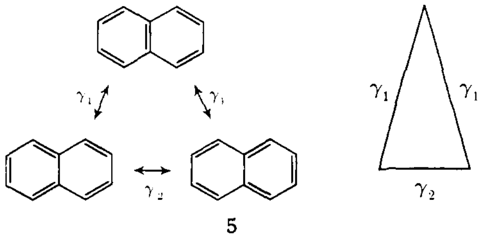
[21] J. M. Norbeck and G. A. Gallup, *J. Amer. Chem. Soc.*, **95**, 4661 (1973).

[22] J. Paldus, J. Cizek, and S. Sengupta, *J. Chem. Phys.*, **55**, 2452 (1971); S. Sengupta, J. Paldus, and J. Cizek, *Int. J. Quantum Chem., Symp.*, **No. 6**, 153 (1972).

[23] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 11, 96 (1960).

## Computational Method

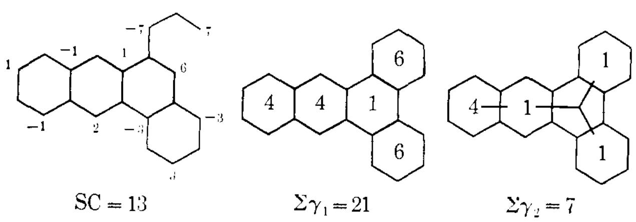
The exclusive use of Kekulé structures for benzenoid compounds in a structure-resonance theory is justified in the previous section. To implement the theory one needs to enumerate the number of Kekulé structures and the numbers of matrix elements that convert one structure into another. We will refer to these matrix elements ($\gamma_1$ and $\gamma_2$) as permutation integrals or resonance integrals, and they are pictorially defined in **1** and **2**. Of course one can simply draw all structures and count all required permutations. To do this we find it convenient to construct a graph, vertices of which represent Kekulé structures, and edges of which are weighted by the values of the permutation integrals. The triangular graph shown for naphthalene in **5** is a graph of this type, and it bears a superficial resemblance to the HMO graph of the cyclopropenyl system. One can imagine eigenfunctions of the graph in **5**, each eigenfunction corresponding to a particular eigenstate. The graph eigenfunctions transform according to the irreducible representations of state symmetry species. The ground-state graph eigenfunction for naphthalene ($A_g$) therefore has no nodes and a good approximation to its resonance energy is given by eq 3.[24] Using $\gamma_1$ = 0.841 eV and $\gamma_2/\gamma_1$ = 0.400 the resonance energy is $(2/3)(2\gamma_1 + \gamma_2) = 1.600\gamma_1$ (1.346 eV), which is close to the value of 1.323 eV computed by Dewar and de Llano.[6] The average deviation of the resonance method results from the LCAO–SCF–MO values is ±0.037 eV for all of the benzenoid molecules that we have examined.



**5**

For larger benzenoid molecules, the writing of resonance structures can become tedious. It is easier to use the graph-theoretical concept of the "structure count" (SC) described in recent papers.[1] The SC method requires one to delete a vertex from the graph of the aromatic molecule and then to write the nonarbitrary vertex coefficients (smallest coefficient unity) that sum to zero around every vertex in the residual graph. Most readers will recognize these coefficients as the unnormalized coefficients of a nonbonding molecular orbital for the odd residual system.[25] The sum of the absolute value of the coefficients adjacent to the deleted vertex is the SC, *i.e.*, the number of Kekulé structures that can be drawn for the original molecule. Then the number of $\gamma_1$ permutations for each ring in the molecule is the SC for the residual molecule with that particular ring excised from the structure. Similarly, $\gamma_2$'s are enumerated by deleting adjacent rings two at a time and summing the SC's for the residual systems.

The whole procedure is economically carried out on three drawings of the molecular graph as illustrated in **6** for dibenz[*a*,*c*]anthracene. The resonance energy of dibenz[*a*,*c*]anthracene is therefore $(2/13)(21\gamma_1 + 7\gamma_2) = 3.662\gamma_1$ (3.079 eV). The SCF result[6] is 3.058 eV.

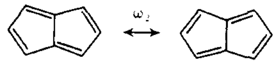


**6**

## Antiaromaticity

Many of the molecular structures that we wish to examine in this paper can be at least partially represented by Kekulé structures that are related by permutations of even numbers of pairs of electrons. Cyclobutadiene (**7**) and pentalene (**8**) are two structures of this kind, and larger molecules may incorporate either one of these structures or both types as part of the molecular framework. The permutation integrals characteristic of resonance between the structures in **7** and **8** will be called $\omega_1$ and $\omega_2$, respectively.

**7**



**8**

The properties of these molecules show that they have fundamentally different characters from the benzenoid hydrocarbons. There is no doubt that benzenoid hydrocarbons are resonance stabilized, where we accept the common definition that a compound is resonance stabilized if cyclic delocalization of $\pi$ electrons stabilizes it relative to an open-chain model compound.[26] Benzenoid compounds also would be classified as aromatic compounds by any of the several criteria that have been suggested to define aromaticity.[27] In contrast, the cyclobutadiene structure has been suggested to be an "antiaromatic" structure,[28] with $\pi$-electron energy higher than that of two isolated or linearly conjugated double bonds. The idea is an outgrowth of the long-recognized $4n + 2$ ($n$ = integer) Hückel rule for aromaticity used to explain the relative stability of the aromatic sextet.[29]

MO calculations confirm the idea of antiaromaticity for cyclobutadiene.[30–32] The Dewar–de Llano method[6] gives a destabilization of −0.78 eV attributable to cyclic delocalization of $\pi$ electrons in cyclobutadiene.[32] Interestingly, this destabilizing energy is obtained after distortion of the square-planar molecule to an extreme rectangular form with essentially alternating double and single bonds. This shows that it is not possible to

---

(24) W. C. Herndon and E. Silber, *J. Chem. Educ.*, **48**, 502 (1971).

(25) General procedures to obtain nonbonding orbital coefficients are described in ref 1 and in T. Zivković, *Croat. Chem. Acta*, **44**, 351 (1972).

(26) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 692 (1965).

(27) For recent reviews see (a) A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968); (b) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, 1969; (c) "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," E. D. Bergmann and B. Pullman, Ed., Israel Academy of Sciences and Humanities, Jerusalem, 1971; (d) I. Agranat, *MTP Int. Rev. Sci. Org. Chem., Ser. One*, **3**, 139 (1973).

(28) R. Breslow, *Accounts Chem. Res.*, **6**, 393 (1973).

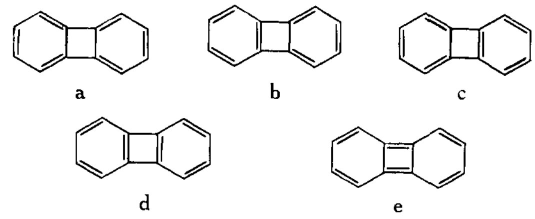
(29) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 10.

(30) N. L. Allinger and J. C. Thai, *Theor. Chim. Acta*, **12**, 29 (1968).

(31) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

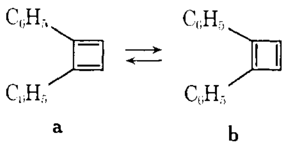
(32) M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *J. Amer. Chem. Soc.*, **93**, 3437 (1971).

avoid this consequence of antiaromaticity by distortion to a formally localized structure. In the context of the structure-resonance theory, this could mean that one cannot avoid introducing $\omega_1$ and $\omega_2$ terms by judiciously selecting a subset of Kekulé structures to represent a particular molecule. In the past, selection of particular Kekulé structures has not been considered to be undesirable. For example, the structure of biphenylene has several times been postulated to be characterized by a single resonance structure **9a** or the set of three structures with structures **9d** and **9e** excluded.[33-35]

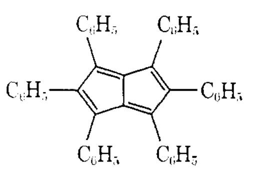


9

Another well-known peculiarity of $4n$ $\pi$-electron systems is their susceptibility to pseudo-Jahn–Teller distortions from high symmetries to lower symmetries of the nuclear framework.[36] Both recent VB[15,37,38] and MO[32,38-41] calculations agree that the effect should manifest itself in cyclobutadiene and pentalene, with cyclobutadiene having a rectangular ($D_{2h}$) singlet state and pentalene having alternating bonds and $C_{2h}$ symmetry. Bond fixation in **7** and **8** is also supported by experimental facts. For example, 1,2-diphenylcyclobutadiene is known to react with weak dienophiles to yield a single Diels–Alder adduct (from **10a**) and with more reactive dienophiles to give two adducts characteristic of both **10a** and **10b**, indicating that the cyclobutadiene exists as an equilibrating mixture of the two highly reactive and unstable, singlet isomers.[42] Pentalene is not known, but the phenyl-substituted derivative **11** has been synthesized,[43] and it is also unstable and reactive. Two other aspects of molecular structure consistent with destabilization and distortion of $4n$ $\pi$-electron systems are the nonplanar alternating structure of cyclooctatetraene[44] and the alternation of bond lengths in [16]annulene from X-ray data.[45]

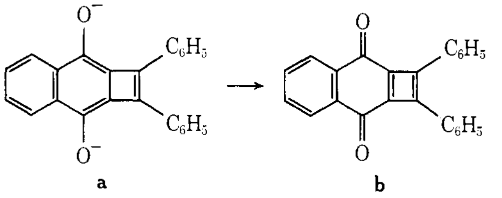


10

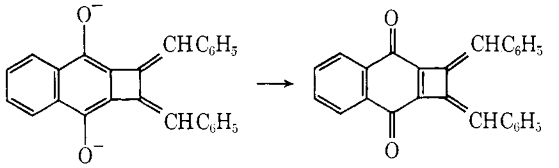


11

Lastly, Breslow has described the results of some very elegant thermodynamic experiments designed to delimit the magnitude of antiaromaticity.[28,46] From the observed oxidation potentials of **12a** (−1.15 eV) and **13a** (−1.67 eV), he argued that cyclobutadiene conjugation is in fact destabilizing by at least 0.52 eV. However, since some of the cyclobutadiene destabilization of **12b** is present in **12a** before oxidation, the actual magnitude of the effect is somewhat larger, comparing very well with the SCF–MO estimation of 0.78 eV quoted earlier.[32]



12



13

Now it is established that calculated and experimental properties give a pattern of bond distortions and antiaromaticity for some simple $4n$ $\pi$-electron systems. We also have some feeling for the magnitudes of the effects. How are these to be related to the resonance theory based on Kekulé structures? Perhaps more important, how do we reconcile the established destabilizing effects with the fact that Hamiltonian elements ($\gamma_1$, $\gamma_2$, $\omega_1$, $\omega_2$ in the resonance theory) always enter the solutions of secular determinants as squared terms, so that any assignment of sign effects is lost in the solution for the eigenvalue? This factor led to an early empirical VB prediction of very large, stabilizing resonance energy for cyclobutadiene.[47]

A way out of this dilemma is based on the following *ad hoc* argument. For either cyclobutadiene or pentalene many valence bond studies have shown that the ground states of these two systems are nontotally symmetric species,[15,37,48-51] $^1B_{2g}$ for cyclobutadiene and $^1B_{1g}$ for pentalene. These species would then be classified by Craig's rules[52] as pseudoaromatic compounds.

---

(33) W. Baker, J. F. W. McOmie, D. R. Preston, and V. Rogers, *J. Chem. Soc.*, 414 (1960).

(34) T. C. W. Mak and J. Trotter, *J. Chem. Soc.*, 1 (1962).

(35) J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, 20, 87 (1966).

(36) For a review see L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, Chapter 8.

(37) P. C. den Boer, D. H. W. den Boer, C. A. Coulson, and T. H. Goodwin, *Tetrahedron*, 19, 2163 (1963).

(38) W. J. Hunt, P. J. Hay, and W. A. Goddard, III, *J. Chem. Phys.*, 57, 738 (1972).

(39) G. Binsch in ref 27c, pp 25–32.

(40) H. Kuroda, T. Ohta, and T. L. Kunii, ref 27c, pp 236–255.

(41) T. Nakajima, *Pure Appl. Chem.*, 28, 219 (1971).

(42) P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969); P. Reeves, T. Devon, and R. Pettit, *ibid.*, 91, 5890 (1969).

(43) E. Le Goff, *J. Amer. Chem. Soc.*, **84**, 3975 (1962).

(44) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Amer. Chem. Soc.*, **86**, 3576 (1964).

(45) S. M. Johnson and I. C. Paul, *J. Amer. Chem. Soc.*, **90**, 6555 (1968).

(46) R. Breslow, R. Grubbs, and S. Murahushi, *J. Amer. Chem. Soc.*, **92**, 4139 (1970).

(47) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(48) D. P. Craig, *J. Chem. Phys.*, **49**, 143 (1952); *J. Chem. Soc.*, 3175 (1951); *Discuss. Faraday Soc.*, **9**, 5 (1950); *Proc. Roy. Soc., Ser. A*, **202**, 498 (1950).

(49) R. McWeeny, *Proc. Roy. Soc., Ser. A*, **223**, 63, 306 (1964); **227**, 288 (1955).

(50) S. Takekiyo, *Bull. Chem. Soc. Jap.*, **34**, 1686 (1961); **35**, 355, 463 (1962).

(51) D. P. Craig and A. Maccoll, *J. Chem. Soc.*, 964 (1949).

(52) D. P. Craig in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, pp 16–19.

If the ground states of cyclobutadiene and pentalene are to be represented by graphs involving only Kekulė structures as described earlier in this paper for benzenoid compounds, the correct graph eigenfunctions for the ground states must transform according to $B_{2g}$ and $B_{1g}$, respectively. *The graphical eigenfunctions for the ground states of* **7** *and* **8** *each therefore have a single node and should be described as the negative combination of the two structure functions representing each compound.* In each ground state the two structures have opposite signs or parities in accordance with an old idea of Dewar and Longuet-Higgins[3] regarding a parity assignment for VB structures. The node in the graph implies that any resonance between the two structures will destabilize the system leading to a higher energy than that possessed by a model noncyclic system. The resonance energy can still be approximated with eq 3 by simply affixing matrix elements between structures of opposite parity with a negative sign.

We then generalize the conclusion italicized above and assume that the same effect will be obtained in larger molecules. The net result is that destabilizing-energy terms will arise from such interactions simultaneously with stabilizing permutations leading to a diminution in the overall resonance energy of the $\pi$ system under consideration. This means, for example, that all five structures **9a–e** contribute to the resonance hybrid of biphenylene, but the four structures **9a–d** enter in a positive way, and **9e** enters as a structure function with a negative sign. The interactions of **9e** with the other structures give negative resonance energies, and the permutations among **9a–d** give positive resonance energies. Overall, biphenylene would be predicted to have a reduced resonance energy because of the incorporation of **9e**.

Several years ago, Platt[53] suggested that resonance theorists should add as one of their basic postulates a rule that Kekulė structures of opposite sign give destabilizing rather than stabilizing resonance interactions. He then stated that such a resonance theory would be in rigorous agreement with molecular orbital results and in better experimental agreement with chemical results. The work described already provides some degree of justification for these ideas. However, as will be seen, the main justification is that the approach seems to work and it leads to agreeable results.

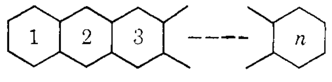
In actual calculations, we decided to use the average of the experimental[28,46] and the LCAO–SCF theoretical[32] value for the magnitude of the $\omega_1$ permutation integral. This value is 0.650 eV, equivalent to our estimation of the antiaromaticity of cyclobutadiene. There does not seem to be a straightforward experimental method to estimate the ratio of $\omega_2$ to $\omega_1$ so we used Rumer–Pauling diagrams for this purpose, finding coincidentally $\omega_2/\omega_1$ close to 0.4, the same as the ratio $\gamma_2/\gamma_1$. Structure parities (signs) are obtained as outlined by Dewar and Longuet-Higgins[3] or by using the structure-count and corrected-structure-count concepts described by Herndon in recent publications.[1]

## Comparisons of Resonance Energies

**A. Benzenoid Systems.** For our purpose we limit the term benzenoid to carbocyclic compounds containing only six-membered rings and at the most one odd-membered ring. The three previous most useful methods for calculating the extent of resonance stabilization of $\pi$ systems are the HMO method, the reference structure modified HMO procedure of Hess and Schaad (HS–HMO),[54] and SCF–MO methods typified by the work of Dewar and coworkers[6,26] and of Lo and Whitehead.[55] The HS–HMO method requires one to combine an HMO calculation with an empirical calculation for the energy of the reference structure. The reference structure energy is found by summation of eight parameters defined for particular kinds of structural features found in $\pi$-molecular systems. The parameters were determined after assuming that HMO $\pi$ energies are strictly additive for acyclic polyene molecules.[54] The SCF–MO resonance energies are also referred to polyene structures, but only two parameters are used in the reference structure calculation.[6] The results of our resonance theory calculations are also referred to a single localized structure, whose energy it is not necessary to calculate as it constitutes one of the defined isoenergetic basis functions to which resonance energies are compared.

Resonance energies calculated by all four approaches are listed in Table I. One can see that the resonance theory and Dewar–de Llano LCAO–SCF results correlate closely. One can also note a general parallelism to the HS–HMO values, although the correlation is not as exact. Previous discussions have pointed out the failure of simple HMO theory to correctly indicate stability and reactivity in the benzenoid hydrocarbons.[6,16,26,54,55] The similarities between the results of the SCF and the HS–HMO method have been emphasized,[16,54] and the use of HS–HMO results partially defended on that basis. However, we will focus attention on the dissimilarities of the various methods for predicting resonance energies. In particular, we will show that the HS–HMO method leads to very different conclusions regarding the stabilities of larger benzenoid hydrocarbons than does our structure-resonance theory. Consequently, the SCF and the HS–HMO methods must also differ in this respect.

First, consider the $\pi$ energies of the polyacenes with $n$ rings as shown in **14**. Using known trigonometric relationships for HMO eigenvalues,[56,57] general approximate formulas can be derived for the HMO and HS–HMO resonance energies of large members of the series. It is also possible to obtain a rather simple, exact general expression for all polyacenes using resonance theory. These formulas are given in Table II. According to both Hückel methods, the $\pi$ energies and resonance energies increase in a linear manner with increasing number of rings, although the total resonance energy is much lower by the HS–HMO procedure. The resonance theory result is quite different in that a



**14**

---

(53) Reference 5b, pp 202–203.

(54) B. A. Hess, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **93**, 305, 2413 (1971); *J. Org. Chem.*, 37, 4179 (1972).

(55) D. H. Lo and M. A. Whitehead, *Can. J. Chem.*, **46**, 2027, 2041 (1968).

(56) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of $\pi$-Electron Calculations," Pergamon Press, Elmsford, N. Y., 1965.

(57) W. England and K. Reudenberg, *J. Amer. Chem. Soc.*, **95**, 8769 (1973).

Table I. Resonance Energies of Benzenoid Hydrocarbons

| Compd | HMO, $\beta^a$ | HS–HMO, $\beta^b$ | SCF–MO, eV$^c$ | Resonance theory, eV$^f$ |
|---|---|---|---|---|
| Benzene | 2.00 | 0.39 | 0.87 | 0.84 |
| Naphthalene | 3.68 | 0.55 | 1.32 | 1.35 |
| Anthracene | 5.31 | 0.66 | 1.60 | 1.60 |
| Phenanthrene | 5.45 | 0.77 | 1.93 | 1.95 |
| Pyrene | 6.51 | 0.82 | 2.10 | 2.13 |
| Benzo[*c*]phenanthrene | 7.19 | 0.95 | 2.48 | 2.52 |
| Benz[*a*]anthracene | 7.10 | 0.90 | 2.29 | 2.31 |
| Chrysene | 7.19 | 0.95 | 2.48 | 2.52 |
| Triphenylene | 7.27 | 1.01 | 2.65 | 2.65 |
| Perylene | 8.25 | 0.96 | 2.61 | 2.69 |
| Naphthacene | 6.93 | 0.76 | 1.82 | 1.75 |
| Pentacene | 8.54 | 0.84 | 2.00 | 1.85 |
| Dibenz[*a*,*c*]anthracene | 8.94 | | 3.06 | 3.08 |
| Dibenz[*a*,*h*]anthracene | 8.88 | 1.12 | 2.95 | 2.97 |
| Dibenz[*a*,*j*]anthracene | 8.88 | 1.12 | 2.95 | 2.97 |
| Benzo[*a*]pyrene | 8.22 | 0.98 | 2.58 | 2.58 |
| Benzo[*d*]pyrene | 8.34 | 1.06 | 2.85 | 2.87 |
| Benzo[1,12]perylene | 9.43 | 1.12 | 3.13 | 3.15 |
| Coronene | 10.57 | 1.27 | 3.52 | 3.50 |
| Benzo[1,14]bisanthene | | | 3.86 | 3.90 |
| Ovalene | 14.50 | 1.54 | 4.54 | 4.44 |
| Zethrene | 9.80 | 0.98 | 2.69 | 2.69 |
| Quaterrylene | | | 5.31 | 5.38 |
| Anthanthrene | 9.25 | 0.99 | 2.63$^d$ | 2.62 |
| Naphtho[2,3-*b*]pyrene | | | 2.78$^d$ | 2.76 |
| Dibenzo[*a*,*e*]pyrene | 10.06 | 1.26 | 3.31$^d$ | 3.31 |
| Dibenzo[*a*,*h*]pyrene | 9.93 | 1.13 | 2.93$^d$ | 2.90 |
| Dibenzo[*a*,*i*]pyrene | 9.95 | 1.15 | 3.01$^d$ | 3.05 |
| Dibenzo[*a*,1]pyrene | | | 3.25$^d$ | 3.24 |
| Phenanthra[2,3-*b*]pyrene | | | 3.59$^d$ | 3.51 |
| Biphenyl | 4.38 | 0.72 | 1.70 | 1.68 |
| Styrene | 2.42 | 0.37 | 0.86 | 0.84 |
| Stilbene | 4.88 | 0.71 | 1.71 | 1.68 |
| Fluoranthene | 6.50 | 0.77 | 2.14 | 2.19 |
| 1,2-Naphthalenequinodimethide | 4.80 | 0.34 | 0.99$^e$ | 0.84 |
| 2,3-Naphthalenequinodimethide | 4.80 | 0.34 | 0.93$^e$ | 0.84 |

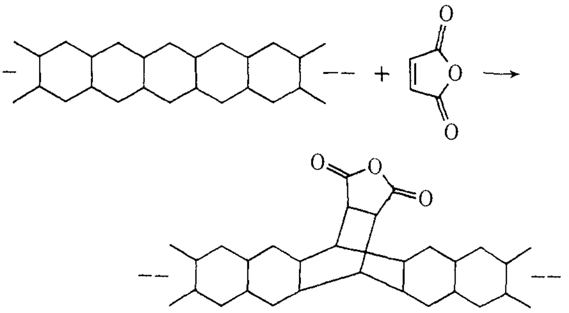
[a] A. Streitwieser, Jr., J. I. Brauman, and C. A. Coulson, "Supplemental Tables of Molecular Orbital Calculations with a Dictionary of $\pi$-Electron Calculations," Pergamon Press, Oxford, 1965. [b] Reference 54. [c] Reference 6, excepting superscripted values. [d] This work. [e] Reference 16. [f] $\gamma_1$ = 0.841 eV; $\gamma_2$ = 0.336 eV.

Table II. $\pi$ Energies of Polyacenes

| Method | Resonance energy | Lim($n \rightarrow \infty$) | REPE |
|---|---|---|---|
| HMO ($\beta$) | $0.479 + 1.613n$ | $\infty$ | 0.403 |
| HS-HMO ($\beta$) | $0.396 + 0.088n$ | $\infty$ | 0.022 |
| Resonance theory ($\gamma_1$) | $2(1.40n - 0.40)/(n + 1)$ | 2.80 | 0.0 |

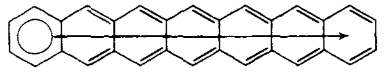
limit in the resonance energy of 2.80 $\gamma_1$ is approached for large numbers of rings. The resonance energy of benzene is 1.00 $\gamma_1$ so this upper limit of polyacene resonance energies is a little less than that of three isolated benzene rings.

The HS-HMO REPE for large polyacenes is 0.022 $\beta$, comparable to the REPE of azulene (0.023 $\beta$) and biphenylene (0.027 $\beta$).[29] Polyacenes would therefore be classified as aromatic in nature by the HS method. The resonance theory REPE would be zero in the limit of large *n*, which would classify large polyacenes as nonaromatic with predicted reactivity comparable to acyclic polyolefins. In fact, in addition reactions like the Diels–Alder reaction with maleic anhydride, a gain in resonance energy of 2.80 $\gamma_1$ would be expected on creation of two large, separate polyacene systems as shown in eq 4. Perhaps this explains the enormous reactivity of compounds with over six linear annelated rings. Such compounds react instantaneously with maleic anhydride and are difficult to prepare in a pure state.[58] The changes in resonance energy predicted by the HS–HMO method for reactions of this type are much smaller quantities ranging from +0.122 $\beta$ for anthracene to +0.308 $\beta$ for all large polyacenes. The very large reactivity difference between anthracene and the larger polyacenes is not correlated well by these latter values.

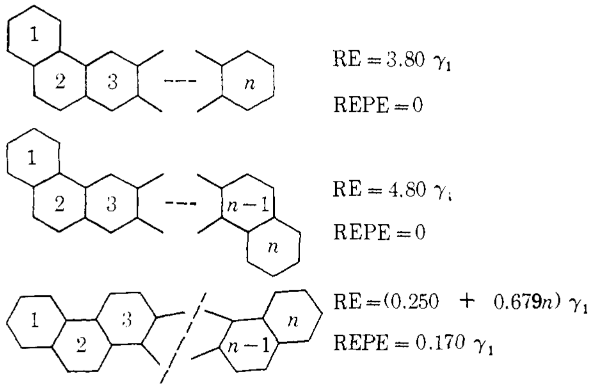


(4)

Clar has proposed a qualitative nonmathematical theory for aromatic systems that seems to be in harmony with many experimental facts, summarized in a recently published book.[59] He represents the linear polyacenes as $\pi$ systems that share a single aromatic sextet regardless of the size of the molecule, as illustrated in **15** for heptacene. According to Clar, the benzenoid character of a polyacene is due to a single mobile sextet of electrons which becomes diluted upon linear annelation, the higher polyacenes finally losing all aromatic character and becoming cyclic polyenes.[59] The resonance theory quantitative results are in better agreement with this qualitative picture than are the HS–HMO results. The confluence of the Clar arguments, the SCF–LCAO–MO calculations, and the resonance theory procedures seems to us to provide mutual support for arguing the essential correctness of the three approaches.


**15**

General formulas can also be derived for the limiting resonance energy of other types of benzenoid aromatics. These are given in **16** for series related to benzanthracene



**16**

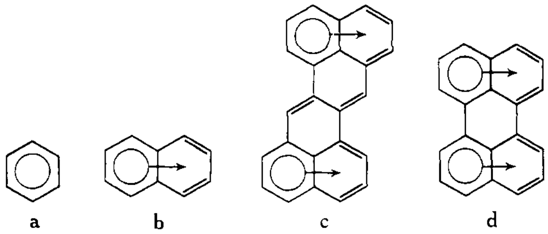
---

(58) E. Clar, "Polycyclic Hydrocarbons," Vol. I, Academic Press, New York, N. Y., 1964, Chapters 24–27.

(59) E. Clar, "The Aromatic Sextet," Wiley, London, 1972.

cene, dibenzanthracene, and chrysene. The HS–HMO and resonance theories are only in agreement for the third type of compound in **16**. In this case, both methods predict a resonance energy per ring of approximately 70% of that for an isolated benzene ring. For the other two compound types, the HS–HMO method predicts a linearly increasing energy with increasing size.

Another interesting concept is the characterization of the aromaticity of individual rings within a polycyclic benzenoid hydrocarbon. The accumulated evidence for such localized aromatic regions has been convincingly summarized by Clar.[59] In his descriptive pictures of aromatic compounds, one finds fully benzenoid rings, rings that may share a migrating sextet of electrons, rings with fixed double bonds, or even completely empty rings. In **17**, structures are depicted in which each of these kinds of structural features may be identified in turn. The resonance theory and Dewar–deLlano calculations are in good agreement with the qualitative ideas expressed by these pictures. Both zethrene (**17c**) and perylene (**17d**) are calculated to have exactly twice the resonance energy of naphthalene (see Table I), implying a completely localized diene system in **17c** and an empty central ring in **17d**. The HS–HMO method predicts an extra resonance energy for these two molecules of about 50% of the resonance energy of benzene.



17

There have been recent attempts to formulate mathematical indexes that would quantify Clar's intuitive ideas.[60–62] The most straightforward analysis is by Randić[62] who derives an index based on the HMO bond orders of the six bonds in a benzenoidal ring, eq 5.

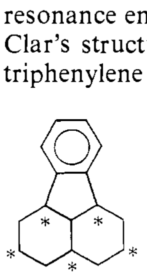
$$R = (\sqrt{2}/6)\sum_{u,v}^{R}(1 + p_{uv})^{1/2} \tag{5}$$

This equation is derived[63] by projecting the set of HMO eigenfunctions onto selected combinations of localized functions that correspond to the particular Clar-type structure being considered. The characterization of the local aromaticity by this index is in accordance with a postulate of Kemula and Krygowski[64] that a compound is more aromatic if the average bond order is larger. The $R$ index ranges from 0.3726 in benzene to values approaching 0.3500 for "empty" rings such as the central ring in perylene. No ring is more aromatic than that of benzene, and in general the $R$ values parallel the Clar representations of structures.[62]

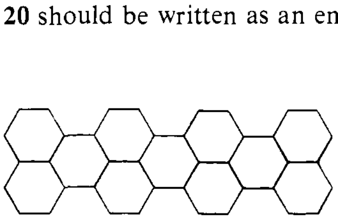
It is much easier to calculate a numerical local aromaticity index based on our structure-resonance theory. The resonance energy due to each ring can be separately determined, and the ratio of the ring resonance energy to that of benzene (1000 $\gamma_1$) is a unitless index of aromaticity. The resonance theory $R$ index is, of course, a function of the ratio of $\gamma_2$ to $\gamma_1$, but the $R$ index of a ring in, for example, naphthalene, will never be unity unless the value of $\gamma_2$ is equal to that of $\gamma_1$. The $R$ indexes from resonance theory and Randić's[62] values are listed in Table III for a few selected molecules. For the most part, the values are roughly parallel, but a plot of the two $R$ indexes *vs.* one another shows a great deal of scatter, the average deviation of $R$ (Randić) from $R$ (Herndon-Ellzey) being about 20% of the total range of $R$.

Whether or not the discrepancies are important must await detailed testing of these local aromaticity indexes against particular experimental properties. It is of obvious future interest to compare $R$ with nmr chemical shifts, coupling constants, diamagnetic susceptibility exaltation values, and specific kinds of chemical reactivities. The fact that $R$ (Randić) barely distinguishes between terminal rings in polyacenes and polyphenes may be important in this regard. The reversal of relative $R$ values for the linear polyacenes should also be noted. The range of the resonance theory $R$, from unity to zero, is inherently satisfying, and its ease of calculation may be enough reason to dictate its use in defining local aromaticity.

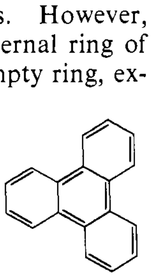
Clar's postulate of "empty" rings,[59] as in ring B of perylene, is confirmed by the $R$-index calculations. Ring B makes no contribution of resonance energy to perylene, the total energy being the sum for that of two naphthalene systems. Whenever a molecule can be divided into two or more even subsystems for which Kekulé structures are possible, and if the subsystems are joined at points that belong to only one set of alternant positions in either or both subsystems, then the resonance energy of the molecule is the sum of the resonance energies of the separate subsystems.[1] So, for example, the internal rings of fluoranthene (**18**) and quarterrylene (**19**) do not contribute to the resonance energy of either molecule, the latter system having the resonance energy of four naphthalene units. However, Clar's structure also indicates that the internal ring of triphenylene **20** should be written as an empty ring, excluding one of the nine Kekulé structures (shown in **20**) from contributing to the resonance hybrid.[59] Resonance theory does not agree with this interpretation since the $R$ value of the central ring is 0.356. As pointed out before, in general, all Kekulé structures contribute to the resonance hybrid.



18



19



20

In discussing the $R$ index as defined in this section, one should perhaps speak of a benzene index rather than an aromaticity index. Then this allows one to define further local indexes based on other structural

---

(60) O. Polansky and G. Derflinger, *Int. J. Quantum Chem.*, 1, 379 (1967).

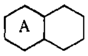
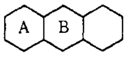
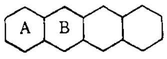
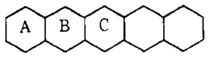
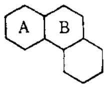
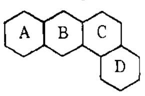
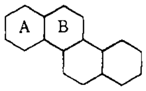
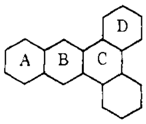
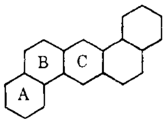
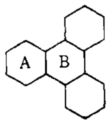
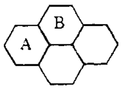
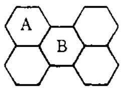
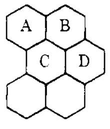
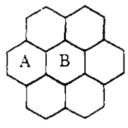
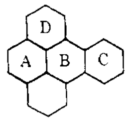
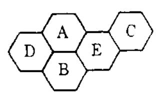
(61) J. Kruszewski, *Soc. Sci. Lodz., Acta Chim.*, 16, 77 (1971).

(62) M. Randić, *Tetrahedron*, in press.

(63) A. Graovac, I. Gutman, M. Randić, and N. Trinajstić, *J. Amer. Chem. Soc.*, **95**, 6267 (1973).

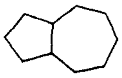
(64) W. Kemula and T. M. Krygowski, *Tetrahedron Lett.*, 5135 (1968).

Table III. Ring Aromaticity Indices

| Compound | Ring | $R$ (this work) | $R$ (Randić[62]) |
|---|---|---|---|
|  | A | 1.000 | 0.3727 |
|  | A | 0.800 | 0.3667 |
|  | A | 0.600 | 0.3655 |
| | B | 0.700 | 0.3612 |
|  | A | 0.480 | 0.3651 |
| | B | 0.560 | 0.3601 |
|  | A | 0.400 | 0.3650 |
| | B | 0.467 | 0.3599 |
| | C | 0.467 | 0.3591 |
|  | A | 0.880 | 0.3678 |
| | B | 0.560 | 0.3600 |
|  | A | 0.686 | 0.3659 |
| | B | 0.743 | 0.3621 |
| | C | 0.400 | 0.3587 |
| | D | 0.914 | 0.3680 |
|  | A | 0.85 | 0.3675 |
| | B | 0.55 | 0.3613 |
|  | A | 0.738 | 0.3661 |
| | B | 0.769 | 0.3629 |
| | C | 0.246 | 0.3516 |
| | D | 0.954 | 0.3688 |
|  | A | 0.900 | 0.3679 |
| | B | 0.467 | 0.3591 |
| | C | 0.800 | 0.3622 |
|  | A | 0.933 | 0.3686 |
| | B | 0.356 | 0.3530 |
|  | A | 0.800 | 0.3647 |
| | B | 0.467 | 0.3607 |
|  | A | 0.800 | 0.3649 |
| | B | 0.0 | 0.3524 |
|  | A | 0.829 | 0.3653 |
| | B | 0.571 | 0.3611 |
| | C | 0.229 | 0.3546 |
| | D | 0.714 | 0.3621 |
|  | A | 0.640 | 0.3617 |
| | B | 0.320 | 0.3561 |
|  | A | 0.509 | 0.3606 |
| | B | 0.291 | 0.3536 |
| | C | 0.945 | 0.3687 |
| | D | 0.836 | 0.3655 |
|  | A | 0.577 | 0.3618 |
| | B | 0.311 | 0.3619 |
| | C | 0.756 | 0.3668 |
| | D | 0.800 | 0.3645 |
| | E | 0.622 | 0.3584 |

features, such as azulene, pentalene, or cyclobutadiene moieties. Later, we will show how this concept can be used in determining the local antiaromatic character of four-membered rings in polycyclic unsaturated systems.

**B. Azuleno Compounds.** The resonance energy of azulene (**21**) has empirically been estimated to be 49–



21

60% of the naphthalene value from thermochemical data.[65–67] The diamagnetic susceptibility exaltation values of azulene and naphthalene are practically identical which might infer identical aromaticities.[68] Theoretically, the HMO delocalization energies are azulene, 3.363 $\beta$, and naphthalene, 3.683 $\beta$, whereas the Hess and Shaad method gives 0.23 $\beta$ and 0.55 $\beta$ resonance energies, respectively.[54] Dewar and de Llano estimate the resonance energy of azulene as 0.169 eV, 13% of naphthalene's attributed value of 1.323 eV,[6] and resonance theory gives 0.400 $\gamma_1$ for azulene, 1.600 $\gamma_1$ for naphthalene, *i.e.*, 0.336 and 1.346 eV, respectively. The difference between the calculated SCF and resonance theory resonance energies of azulene is four times the average deviation for the benzenoid compounds in Table I. For this reason and for use as a calibration, we repeated the Dewar–de Llano azulene calculation and found a resonance energy of 0.257 eV. This is in better agreement with resonance theory and with the result of 0.232 eV calculated with the Dewar–de Llano technique by Dasgupta and Dasgupta.[69]

We cannot account for the differences of the three SCF results. The important point remains that the SCF and the resonance theory calculations give very similar results, a significantly low resonance energy for azulene. It is also noteworthy that the azulene resonance energy is empirically calculated to be 0.404 eV on the basis of the latest thermochemical data,[70,71] and on the assumptions that the naphthalene SCF resonance energy value is correct, and that strain energy contributions of the five- and seven-membered rings are 0.26 eV each.[72]

One expects from the foregoing discussion that the resonance energies of azuleno systems, calculated by resonance theory, will be quite low in comparison to isomeric benzenoid systems. However, the possibility that fused azuleno units could produce stable, aromatic nonalternant hydrocarbons has been raised as a result of HS–HMO calculations. Of the three series of compounds represented by **22–24**, **23** and **24** are suggested to be stable aromatic "azulenoid" systems with REPE's close to that of azulene.[54] The REPE of **22** is found to decrease steadily as the number $n$ of azulene units increases, and this is confirmed by the resonance theory approach. The general formula for the resonance energy is $\mathrm{RE}(\mathbf{22}) = 2(n\gamma_2)/(n + 1)$ with a limit of $2\gamma_2$ = 0.673 eV for large $n$. This means that, even for very large molecules of this type, the total resonance energy is

(65) Reference 7, pp 98–100.

(66) R. B. Turner, W. R. Meador, W. V. E. Doering, L. H. Know, J. R. Mayer, and D. W. Wiley, *J. Amer. Chem. Soc.*, **79**, 4127 (1957).

(67) E. Heilbronner in ref 52, pp 210–218.

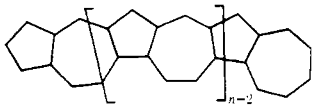
(68) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity in "Nonbenzenoid Aromatics," Vol. II, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1971, Chapter 3.

(69) A. Dasgupta and N. K. Dasgupta, *Tetrahedron*, **28**, 3587 (1972).

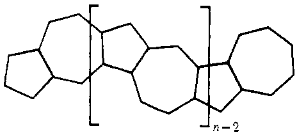
(70) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, pp 170–171.

(71) E. Morawetz, *J. Chem. Thermodyn.*, **4**, 455 (1972).

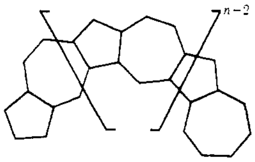
(72) N. C. Baird, *Can. J. Chem.*, **47**, 3535 (1969).



22



23



24

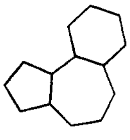
less than that of a single benzene molecule, and the REPE approaches zero. The characterization of these molecules as polyolefinic would seem to be accurate, and they are close analogs to the linear polyacenes.

The resonance theory description of series **24** is in qualitative agreement with the HS–HMO treatment also. These compounds are analogs of the chrysene series of benzenoid compounds. The limiting REPE is 0.0286 $\gamma_1$ comparable to azulene with REPE = 0.040 $\gamma_1$. These compounds have 17% of the resonance energy of the corresponding isomeric benzenoid compounds whereas the HS–HMO method predicts 38%. The series of compounds depicted in **23** is found by resonance theory to have the same energy as **22**, a limiting value of 0.8 $\gamma_1$ and a limiting REPE of zero. Series **23** therefore does not represent a stable aromatic series as inferred by Hess and Shaad.[54]

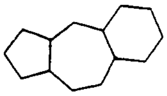
It is simple to deduce the qualitative structure pattern that will give rise to the two different kinds of azuleno compounds. If one can draw a single Kekulé structure with a formal double bond at every annelation point of the azulene moieties, the compound will be aromatic with low resonance energy and a constant REPE. All isomeric azulenoids of this type have the same resonance energy, that of **24**. Compounds in which only one annelation point has a formal double bond correspond to compounds like **22** and **23** and have a limiting resonance energy of 0.80 $\gamma_1$. Other intermediate series can also be identified.

Although the resonance energies of annelated azuleno compounds are low, it is possible that these compounds may still be unreactive in many reactions that unstable aromatic compounds usually undergo. Part of the driving force for the cycloaddition reaction of a linear polyacene with dienophiles must be the production of more stable aromatic systems (*cf.* eq 4). For tetracene the gain in resonance energy is calculated to be 0.52 $\gamma_1$ and for hexacene 1.21 $\gamma_1$. For the same reactions in the analogous azuleno compounds, the changes in resonance energy would be a loss of 0.13 $\gamma_1$ and a gain of 0.20 $\gamma_1$, respectively. The same considerations apply to addition reactions of double bonds like those found at the angular positions in phenanthrene derivatives.

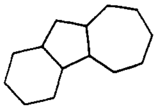
Table IV contains resonance energies calculated by the methods under discussion for compounds **21–34**. These molecules meet the criteria of having Kekulé structures whose permutations are all defined in terms of the parameters $\gamma_1$, $\gamma_2$, and permutation integrals for larger than five pairs of electrons, which are set equal to zero. The resonance-theory energies were determined by drawing all Kekulé structures and counting permutations. The Dewar–de Llano results were calculated by the published procedures,[6] and the HS–HMO values were taken from the papers of Hess and Schaad.[54]



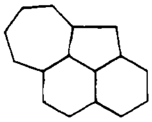
25



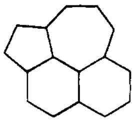
26



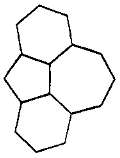
27



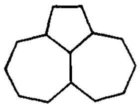
28



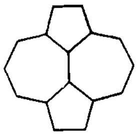
29



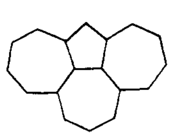
30



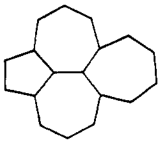
31



32



33



34

Again, the resonance theory results and the LCAO–SCF calculations give remarkably consistent results. The average difference in calculated resonance energies is ±0.056 eV, a little more than 1 kcal and slightly larger than the variation found for benzenoid hydrocarbons. Also, some interesting differences between the resonance theory results and those from the HS–HMO approach are again evident. One general trend is that the HS–HMO method predicts the benzo and naphtho-annelated azulene compounds to be resonance stabilized to about two-thirds the value of isomeric benzenoid compounds. Compare, for example, the HS–HMO resonance energy of anthracene (0.66 $\beta$) with that of compounds **25–27** (0.43 to 0.41 $\beta$). The resonance theory resonance energy 0.933 $\gamma_1$ is about half that of anthracene, 1.900 $\gamma_1$. A comparison of resonance energies of pyrene (0.816 $\beta$, HS–HMO; 2.533 $\gamma_1$, resonance theory) with that for compounds **28** and **29** gives qualitatively the same result.

Simple alkyl derivatives or the parent compounds have been synthesized for all compounds in Table III except **22**, **23**, **30**, and **34**.[73–81] The calculated resonance theory energies are in good agreement with this fact. In particular, the nonexistence of **30** after several synthetic attempts and the facile syntheses of **31–33** are well correlated. Compound **30** with no resonance energy should be described as a large polyene, and the reactive nature of such compounds would make it very difficult to isolate. It should also be noted that **30** has been calculated to possess a triplet ground state.[82] In

(73) D. M. Reid, W. H. Stafford, and J. P. Ward, *J. Chem. Soc.*, 1193 (1955).

(74) P. D. Gardner, C. E. Wulfman, and C. L. Osborn, *J. Amer. Chem. Soc.*, **80**, 143 (1958).

(75) K. Hafner and J. Schneider, *Justus Liebigs Ann. Chem.*, **624**, 37 (1959).

(76) K. Hafner, R. Fleischer, and K. Fritz, *Angew. Chem., Int. Ed. Engl.*, **4**, 69 (1965).

(77) K. Hafner, G. Hafner-Schneider, and F. Bauer, *Angew. Chem., Int. Ed. Engl.*, **7**, 808 (1968).

(78) K. Hafner, *Pure Appl. Chem.*, **28**, 153 (1971).

(79) A. G. Anderson, Jr., A. A. MacDonald, and A. F. Montana, *J. Amer. Chem. Soc.*, **90**, 2993 (1968).

(80) B. M. Trost, G. M. Bright, C. Frihart, and D. Britelli, *J. Amer. Chem. Soc.*, **93**, 736 (1971).

(81) R. Munday and I. O. Sutherland, *J. Chem. Soc. C*, 1427 (1969).

(82) P. Baumgartner, E. Weltin, C. Wagniere, and E. Heilbronner, *Helv. Chim. Acta*, **48**, 751 (1965).

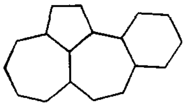
Table IV. Resonance Energies of Azulene Derivatives$^a$

| Compd | HMO, $\beta$ | HS-HMO, $\beta$ | SCF-MO, eV | Resonance theory, eV |
|---|---|---|---|---|
| **21** | 3.36 | 0.23 | 0.26 | 0.34 |
| **22** | 6.52 | 0.31 | 0.39 | 0.45 |
| **23** | 6.58 | 0.38 | 0.40 | 0.45 |
| **25** | 5.11 | 0.43 | 0.84 | 0.78 |
| **26** | 5.08 | 0.43 | 0.82 | 0.78 |
| **27** | 5.10 | 0.41 | 0.85 | 0.78 |
| **28** | 6.21 | 0.51 | 1.15 | 1.18 |
| **29** | 6.22 | 0.52 | 1.15 | 1.18 |
| **30** | 5.99 | 0.29 | −0.08 | 0.0 |
| **31** | 4.91 | 0.23 | 0.52 | 0.45 |
| **32** | 6.05 | 0.35 | 0.69 | 0.67 |
| **33** | 6.40 | 0.17 | 0.42 | 0.51 |
| **34** | 6.30 | 0.06 | 0.25 | 0.34 |

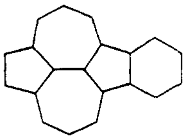
$^a$ See Table I for references.

contrast to the above correlations, the HS-HMO predicts a larger resonance energy for the nonisolable **30** than for the known compounds **31** and **33**.

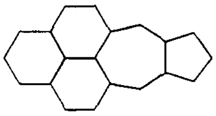
Some other polycyclic $\pi$ systems containing azulene residues are shown in **35–40**, with **35**, **36**, **37**, and **39** being known compounds.[78,83–86] It is generally true that benzoannelation stabilizes a compound in comparison to the nonannelated derivative; compare **35**[78] and **36**[83] relative to **31** and **32**, respectively. However, even in dibenzo compounds like **39**[86] and **40**, the RE is always much less than that of two isolated benzene ring or the isomeric benzenoid hydrocarbons. It is interesting that the predicted less stable dibenzoazulene **39** has been synthesized,[86] but the more stable isomer **40** is unknown. Finally, some interest attaches to **37** since it is the first azuleno compound that has been demonstrated to be carcinogenic.[85] Its carcinogenic activity may be related to the relatively low K-region localization energy[9] 0.187 $\gamma_1$ to yield **38**.


35

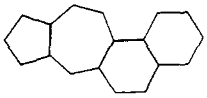
RE = 1.12$\gamma_1$


36

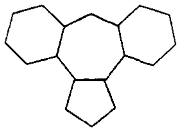
1.54$\gamma_1$


37

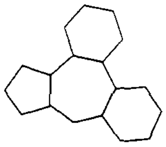
1.87$\gamma_1$


38

1.68$\gamma_1$


39

1.20$\gamma_1$


40

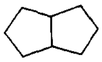
1.76$\gamma_1$

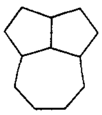
**C. Nonalternant Compounds.** In this section we consider nonalternant molecules other than those which contain azuleno moieties as the only nonalternant component. In many cases, we will need to make use of the resonance-theory concepts induced in the previous section on antiaromaticity, including the use of integrals $\omega_1$ and $\omega_2$ and the restriction of stabilizing resonance to interactions between structures of equal parity. Because of financial requirements, our Dewar-de Llano SCF calculations are limited to the examples of known systems and a few other key compounds. The molecular $\pi$ systems for which we carried out both resonance theory and Dewar-de Llano calculations are depicted in **41–52**, and the calculations are summarized in Table V.

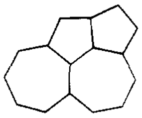
Table V. Resonance Energies of Nonalternant Compounds$^a$

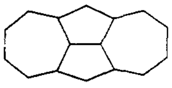
| Compd | HMO, $\beta$ | HS-HMO, $\beta$ | SCF-MO, eV | Resonance theory, eV |
|---|---|---|---|---|
| **41** | 2.46 | −0.14 | 0.01 | −0.26 |
| **42** | 4.37 | 0.22 | 0.56 | 0.62 |
| **43** | 5.95 | 0.25 | 0.61 | 0.64 |
| **44** | 6.03 | 0.33 | 0.68 | 0.80 |
| **45** | 4.62 | 0.47 | 1.34 | 1.35 |
| **46** | 5.15 | 0.46 | 1.21 | 1.35 |
| **47** | 5.43 | 0.25 | 0.84 | 1.01 |
| **48** | 6.25 | 0.55 | 1.45 | 1.01 |
| **49** | 6.19 | 0.49 | 1.27 | 1.24 |
| **50** | 6.00 | 0.31 | 0.60 | 0.58 |
| **51** | 4.30 | 0.16 | 0.44 | 0.39 |
| **52** | 3.00 | −0.62 | −0.30 | −0.52 |

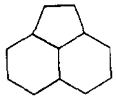
$^a$ See Table I for references.

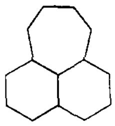

41

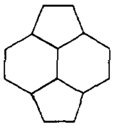

42

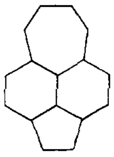

43

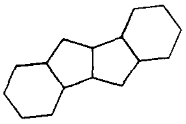

44

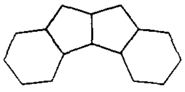

45

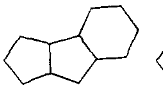

46

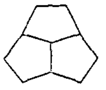

47


48


49


50


51


52

The parent compound or a substituted derivative has been synthesized corresponding to each system in Table V except for **44**, **50**, and **52**. The hexaphenyl derivative of **41**,[43] dimethyl **42**,[75] methyl **43**,[76] solutions of **47**,[80] parent **48**,[87] and triphenyl **51**[88] are single known examples. No stability barriers to the future syntheses of "cis" dibenzopentalenes **50** or dicycloheptpentalenes **44** ought to exist. All three theoretical methods agree in assigning a certain amount of resonance energies to these structures. The calculations are also in agreement regarding antiaromaticity of **52**. If one also considers that a large amount of bond-angle strain energy must be present in **52**, the possible existence of this structure is doubtful.

All of the three methods for calculating resonance energies give similar qualitative results for these compounds. Hence, no discrimination among the methods can be established from comparisons with experimental properties. However, when one considers that the resonance theory results in Table V were obtained in

---

[83] C. Jutz and E. Schweiger, *Angew. Chem., Int. Ed. Engl.*, **10**, 808 (1971).

[84] C. Jutz and R. Kirchlechner, *Angew. Chem., Int. Ed. Engl.*, **5**, 516 (1966); C. Jutz, R. Kirchlechner, and H.-J. Seidel, *Chem. Ber.*, **102**, 2301 (1969).

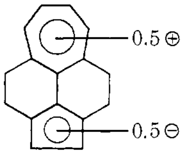
[85] N. P. Buu-Hoï, N. B. Giav, and C. Jutz, *Naturwissenschaften*, **57**, 499 (1970).

[86] W. Ried and H. J. Herrmann, *Chem. Ber.*, **107**, 152 (1974).

[87] K. Hafner and G. Schneider, *Justus Liebigs Ann. Chem.*, **672**, 194 (1964).

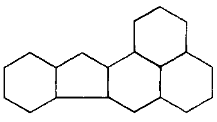
[88] E. Le Goff, *J. Amer. Chem. Soc.*, **84**, 1505 (1962).

less than an hour of hand calculation, the structure-resonance theory seems to us to be the preferred method for future applications of this type. The resonance theory calculations are tantamount to LCAO-MO-SCF calculations, and in the case of compounds **41–52** the average resonance energy difference between the two methods is 0.130 eV. This is a larger difference than in the cases of the benzenoid or azulenoid hydrocarbons but still is a satisfactory result. A large part of the discrepancy arises from acepleiadylene (**48**), 0.440 eV, where MO theories suggest a zwitterionic character as in **53**. This may be a stabilizing factor that structure-resonance theory with a basis of Kekulé structures cannot treat.



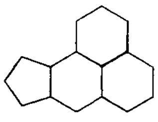
**53**

Resonance theory energies for some nonalternant compounds studied by Zahradnik and Michl[89] using the HMO method are shown in **54–58**. The HMO resonance energies per electron hardly discriminate among these compounds, ranging from 0.335 to 0.314 $\beta$ and placing the compounds in the order **54**, **55**, **57**, **58**, **56**.



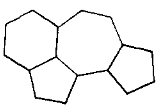
**54**

RE = 2.19$\gamma_1$



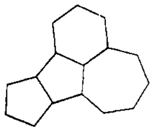
**55**

1.35$\gamma_1$



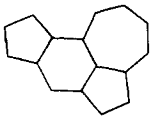
**56**

0.79$\gamma_1$



**57**

0.46$\gamma_1$

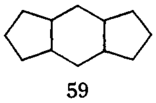


**58**

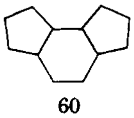
0.22$\gamma_1$

Resonance theory discriminates highly and gives **56** as significantly more stabilized than **57** or **58**. Only **54** has been synthesized,[90] although **55** and **56** ought to be capable of existence from the RE standpoint. Naively, the reason resonance predicts **56** to be the most stable of **56–58** is because both benzene ($\gamma_1$) and azulene ($\gamma_2$) type resonance integrals stabilize the resonance hybrid of three structures of the same parity. This is not possible in structures **57** and **58**.

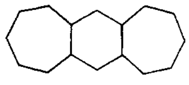
A final general conclusion about nonalternant molecules is worth mentioning. This concerns those compounds that consist of two annelated odd-membered rings as the two terminal points of an even alternant skeleton. These compounds have been called "indacene-like" hydrocarbons[91] with *s*-indacene **59** as the prototype compound. Regardless of the length of the internal alternant portion of the molecule, only two Kekulé structures are possible for any compound of this type. The parities of the structures are different when the odd-membered rings are identical, and the parities are the same when the structure incorporates a seven- and a five-membered ring. Resonance would destabilize the former group and stabilize the latter group. The relative magnitudes of the resonance integrals are such that only **62** would be predicted to be affected by resonance, being antiaromatic, RE = −0.34 eV. All other indacene-like compounds should be polyolefinic in character, which is in rough agreement with other calculations.[54,91] Compound **59** has been prepared,[92] and it is a reactive olefinic compound. The properties of a dicyano derivative of **64** may indicate some resonance stabilization.[93]



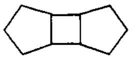
**59**



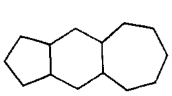
**60**



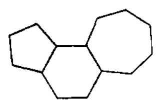
**61**



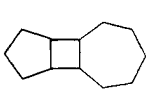
**62**



**63**

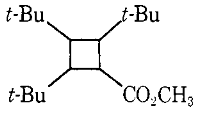


**64**

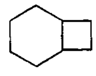


**65**

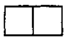
**D. Cyclobutadienes.** Substituted derivatives and the parent cyclobutadiene $\pi$ system are now well known, either as transient intermediates[42,94] or well-characterized, isolable compounds,[95] such as the tri-*tert*-butylcyclobutadienecarboxylate **66** isolated in sublimable crystalline form.[96] Benzocyclobutadienes **67** as intermediates have been extensively studied,[97] and butalene **68** is a potential target for synthesis.[98] Compounds **70** and **71** have been isolated, and **72** can be trapped but not isolated.[99] Naphtho- and anthracyclobutadienes, **73** and **74**, respectively, and biphenylene



**66**

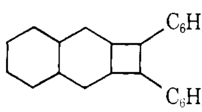


**67**

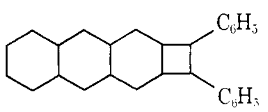


**68**

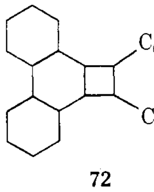
**69**



**70**



**71**



**72**

---

[89] R. Zahradnik and J. Michl, *Collect. Czech. Chem. Commun.*, **30**, 520 (1965).

[90] D. H. Reid, *Tetrahedron*, **3**, 339 (1958).

[91] R. Zahradnik, J. Michl, and J. Kopecky, *Collect. Czech. Chem. Commun.*, **31**, 640 (1966).

[92] K. Hafner, *Angew. Chem.*, **75**, 1041 (1963).

[93] H. Prinzbach and H.-W. Schneider, *Angew. Chem.*, **85**, 1112 (1973).

[94] E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, **91**, 1875 (1969).

[95] H. Kimling and A. Krebs, *Angew. Chem., Int. Ed. Engl.*, **11**, 932 (1972); R. Gompper, F. Holsboer, W. Schmidt, and G. Seybold, *J. Amer. Chem. Soc.*, **95**, 8479 (1973); G. Maier and A. Alzerreca, *Angew. Chem.*, **85**, 1056 (1973).

[96] S. Masamune, N. Nakamuro, M. Suda, and H. Ona, *J. Amer. Chem. Soc.*, **95**, 8841 (1973).

[97] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, Chapter 6.

[98] R. R. Jones and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 660 (1972); R. Breslow, J. Napierski, and A. H. Schmidt, *ibid.*, **94**, 5906 (1972).

[99] M. P. Cava and D. Mangold, *Tetrahedron Lett.*, 1751 (1964).

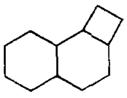
derivative **79**[100] are unknown. The remaining biphenylenes **75**–**78** have been synthesized.[101]

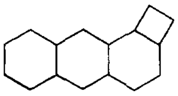
Table VI summarizes the calculations of the resonance energies of $\pi$ systems **66**–**79**. The Dewar–Gleicher calculations[102] are of the Pariser–Pople–Parr type parameterized with thermochemical data and assume a constant bond length of 1.40 Å for all bonds. It has been found that allowance for variations in the bond length (Dewar–de Llano method[6]) generally leads to lower calculated resonance energies,[16] although it is doubtful that the large differences in Table VI would be rectified completely. The important point evident from the listed data is that again the resonance theory and Dewar–de Llano methods give congruent results, and that each of the theoretical approaches yields parallel results to each of the other methods. An important difference is that the HS–HMO method predicts benzocyclobutadiene (**67**), naphtho[*a*]cyclobutadiene (**73**), and phenanthro[*l*]cyclobutadiene (**72**) to be antiaromatic. The resonance theory finds these compounds to be essentially nonaromatic, **67** and **73**, and resonance stabilized, **72**.

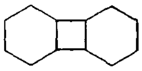
**Table VI.** Resonance Energies of Cyclobutadienes

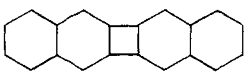
| Compd | HMO, $\beta$ | HS–HMO, $\beta$ | SCF–MO, eV[a] | Resonance theory, eV | PPP SCF–MO, eV[b] | $\Delta$RE[c] | $R$[d] |
|---|---|---|---|---|---|---|---|
| **66**[e] | 0.00 | −1.07 | −0.78 | −0.65 | | 0.65 | −0.77 |
| **67** | 2.38 | −0.21 | | −0.05 | 0.83 | 1.05 | −0.62 |
| **68** | 1.66 | −0.40 | −0.28 | −0.31 | | 0.31 | |
| **69** | 1.66 | −0.48 | −0.43 | −0.52 | | 0.52 | |
| **70**[e] | 4.20 | 0.08 | | 0.55 | 1.97 | 0.80 | −0.46 |
| **71**[e] | 5.88 | 0.24 | | 0.91 | 2.84 | 0.69 | −0.37 |
| 72[e] | 5.72 | −0.03 | | 0.60 | 2.74 | 1.35 | −0.91 |
| **73** | 4.00 | −0.15 | | 0.25 | 1.67 | 1.10 | −0.84 |
| **74** | | | | 0.47 | 2.43 | 1.13 | −0.79 |
| **75** | 4.51 | 0.33 | 1.35 | 0.88 | 2.61 | −0.04 | −0.43 |
| **76** | 7.98 | 0.66 | | 2.19 | 4.71 | 0.00 | −0.22 |
| **77** | 7.80 | 0.53 | | 1.41 | 4.40 | 0.78 | −0.69 |
| **78** | | | | 1.53 | 4.64 | 0.99 | −0.66 |
| **79** | 11.28 | 0.85 | | 2.03 | | 1.68 | −1.08 |

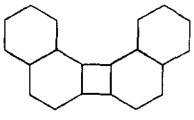
[a] Dewar–de Llano, ref 6. [b] Dewar–Gleicher, ref 102. [c] Localization energy, defined in text. [d] Resonance-theory, aromaticity ring index for the four-membered ring; see text. [e] Unsubstituted parent structure.

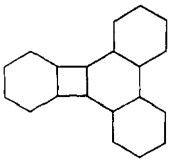

73

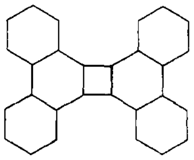

74


75


76


77


78


79

The isolabilities of compounds in Table VI are not well correlated by the resonance energies. This is to be expected, because these compounds do have a reactive four-membered ring that can be fragmented or deleted to give $\pi$ systems with much larger resonance energies. Column 7 of Table VI is the change in resonance energy ($\Delta$RE) that occurs when the most reactive double bond of the four-membered ring is removed from conjugation. The nonisolation of **67**, **72**, **73**, **74**, and **79**, the greater relative stability of **76** in comparison to **77**, and the high stability of **75** are all well understood on this basis. The aromaticity index $R$ (column 8), defined earlier in the discussion, is negative for the four-membered rings of all of these systems, and its magnitude also correlates nicely with the experimental properties of these compounds. Note that the four-membered rings of **72**, **73**, **74**, and **79** all have greater cyclobutadienoid character than does cyclobutadiene itself. This is in agreement with the qualitative deductions that higher bond orders or higher degrees of bond fixation in cyclobutadienes lead to instability.[103]

## Conclusions

The use of a structure-resonance theory based on Kekulé structures allows one to calculate resonance energies of $\pi$ systems that are in essential agreement with the results of HMO or LCAO–MO–SCF calculations, where energies are referred to a localized, single Kekulé structure defined as having no resonance energy. In some cases of very large molecules, there are differences between the HMO calculations and resonance theory results, and experimental properties are correlated better by the resonance calculations. The great advantage of resonance theory is that it requires no use of computer time, since all computations are quickly carried out by hand. There are two major disadvantages. First, a major unproven postulate regarding the introduction of a sign for Kekulé structures has been assumed. Second, some assumptions about the relative sizes of resonance integrals must be made, but since the number of parameters is less than that found in semiempirical MO theory, this latter point is less important. The justification for the sign postulate is not yet clarified.

**Acknowledgment.** The financial support of the Robert A. Welch Foundation is gratefully acknowledged.

---

(100) J. W. Barton and A. R. Grinham, *J. Chem. Soc., Perkin Trans. 1*, 634 (1972).

(101) Reference 97, Chapter 11; J. W. Barton, A. M. Rogers, and M. E. Barney, *J. Chem. Soc.*, 5537 (1965).

(102) M. J. S. Dewar and G. J. Gleicher, *Tetrahedron*, 21, 1817 (1965).

(103) Reference 97, Chapter 12.