AROMATICITY AND DIATROPICITY

Jun-ichi Aihara

Department of Chemistry, Faculty of Science
Shizuoka University, Oya, Shizuoka 422, Japan

Abstract — Aromaticity can be interpreted as extra
stabilization of a cyclic unsaturated molecule arising from
cyclic conjugation of π-electrons. The extra stabilization
energy is estimated relative to the π-electron energy of a
hypothetical reference molecule formed by the "localized"
π bonds. It is termed the resonance energy due to
aromaticity. Our graph theory of aromaticity defines this
type of resonance energy exactly. Diamagnetic
susceptibility due to ring currents can be formulated in
the same graph-theoretical terms. This formula reveals
that aromatic stabilization and diamagnetic susceptibility
exaltation arise from the same cyclic interactions of π
electrons. For conjugated systems, both monocyclic and
polycyclic, the susceptibility due to a ring current
induced in any of the π-electron rings is roughly
proportional to the contribution of the ring to the
resonance energy, multiplied by a factor proportional to
the ring area squared.

INTRODUCTION

Originally, the term "aromatic" was associated with a fragrant odor of a
structurally diverse group of compounds (1). This attribute was then
replaced by the tendency to undergo substitution reactions (2). The aromatic
compounds were naturally restricted to the cyclic unsaturated systems with
this tendency in common (3). Later, the idea of special stability came to
play a significant role (1). Benzene is very stable; there appeared to be no
reason why three double bonds in the classical Kekulé structure should not
readily undergo addition reactions. In fact, this compound has much larger
heat of formation than some reference compounds imagined so far (2,4).
Aromaticity is now often identified with this property of lower molecular
energy (2,4,5).

Attempts to describe how stable a given aromatic compound is in terms of
molecular orbital (MO) calculations have been centered on the concept of
resonance energy. Delocalization energy is a kind of resonance energy,
defined in valence bond theory (6). It is given as the calculated additional
bonding energy which results from delocalization of π electrons, originally
constrained to isolated double bonds in a Kekulé structure. However, almost
all compounds, even ones which are very unstable, were found to have large
delocalization energy. Furthermore, the calculated delocalization energies
were not in the experimental order of stability (7).

Dewar et al. were the first to overcome these faults (8). They found that
the calculated atomization energies of acyclic polyenes can be expressed as
sums of bond energies, implying that the bonds in such compounds are
localized; the corresponding "polyene" C-C and C=C bond energies differ from
those expected for "pure single" and "pure double" carbon-carbon bonds,
respectively. This result leads to the definition of so-called Dewar
resonance energy (8,9) as the difference in energy between a given aromatic
compound and a corresponding "localized" structure (e.g., benzene and 1,3,5-
cyclohexatriene); the energy of the latter structure was estimated as a sum
of "polyene" bond energies. There was a good correlation between Dewar

resonance energy and experimental stability for many compounds (8-10). Hess and Schaad showed that Dewar resonance energy can also be defined in terms of Hückel molecular orbital (HMO) theory (7,11,12). The success of definition of Dewar resonance energy rests primarily on the apparent additivity of bond energies in acyclic polyenes.

The next step forward was to formulate Dewar resonance energy without using empirical "polyene" bond energies, namely, to construct a non-parametric theory of aromaticity. Analytic aspects of aromaticity do not emerge from sophisticated MO theory, because the detailed complexity of the calculations hides them. However, they had a lucky chance of emerging from treatments which focused on molecular topology. For polycyclic hydrocarbons, Dewar resonance energy correlates well with particular structural features of the molecule (2,13). The HMO theory of conjugated systems can be reduced to a graph-theoretical formalism (14,15). This formalism was found to allow an exact mathematical definition of the π-electron energy of a "localized" reference structure. We then managed to construct a graph theory of aromaticity on this basis (16,17). The London theory of diamagnetism due to ring currents (18,19) was incorporated in this theoretical framework (20-22). It was made clear that diatropic compounds, i.e., compounds with diamagnetic ring currents, often have strong conjugative stabilization. In this paper, a general survey of this theory of aromaticity is made in conjunction with diatropicity.

STABILITY OF BUTALENE

As an illustration of the theory, let us consider aromatic character of butalene. Its conjugated system K is shown in Fig. 1. The Hückel secular
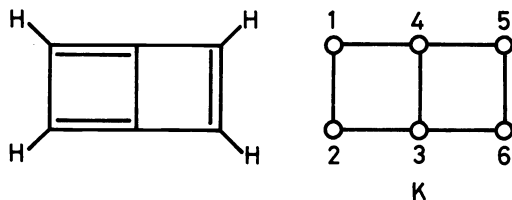

Fig. 1. Butalene and its conjugated system K.

determinant can be set up in the usual way (23), and it can be expanded to give a polynomial in $(\alpha-\epsilon)$ as follows:

$$D_K(\epsilon) = \begin{vmatrix} \alpha-\epsilon & \beta_{12} & 0 & \beta_{14} & 0 & 0 \\ \beta_{21} & \alpha-\epsilon & \beta_{23} & 0 & 0 & 0 \\ 0 & \beta_{32} & \alpha-\epsilon & \beta_{34} & 0 & \beta_{36} \\ \beta_{41} & 0 & \beta_{43} & \alpha-\epsilon & \beta_{45} & 0 \\ 0 & 0 & 0 & \beta_{54} & \alpha-\epsilon & \beta_{56} \\ 0 & 0 & \beta_{63} & 0 & \beta_{65} & \alpha-\epsilon \end{vmatrix}$$

$$\begin{aligned} &= (\alpha-\epsilon)^6 - (\beta_{14}\beta_{41} + \beta_{12}\beta_{21} + \beta_{23}\beta_{32} + \beta_{34}\beta_{43} + \beta_{45}\beta_{54} + \beta_{56}\beta_{65} \\ &\quad + \beta_{36}\beta_{63})(\alpha-\epsilon)^4 + (\beta_{14}\beta_{41}\beta_{23}\beta_{32} + \beta_{14}\beta_{41}\beta_{56}\beta_{65} + \beta_{14}\beta_{41}\beta_{36}\beta_{63} \\ &\quad + \beta_{12}\beta_{21}\beta_{34}\beta_{43} + \beta_{12}\beta_{21}\beta_{45}\beta_{54} + \beta_{12}\beta_{21}\beta_{56}\beta_{65} + \beta_{12}\beta_{21}\beta_{36}\beta_{63} \\ &\quad + \beta_{23}\beta_{32}\beta_{45}\beta_{54} + \beta_{23}\beta_{32}\beta_{56}\beta_{65} + \beta_{34}\beta_{43}\beta_{56}\beta_{65} + \beta_{45}\beta_{54}\beta_{36}\beta_{63} \\ &\quad - \beta_{41}\beta_{12}\beta_{23}\beta_{34} - \beta_{43}\beta_{32}\beta_{21}\beta_{14} - \beta_{34}\beta_{45}\beta_{56}\beta_{63} - \beta_{36}\beta_{65}\beta_{54}\beta_{43})(\alpha-\epsilon)^2 \\ &\quad - (\beta_{14}\beta_{41}\beta_{23}\beta_{32}\beta_{56}\beta_{65} + \beta_{12}\beta_{21}\beta_{34}\beta_{43}\beta_{56}\beta_{65} + \beta_{12}\beta_{21}\beta_{45}\beta_{54}\beta_{36}\beta_{63} \\ &\quad - \beta_{41}\beta_{12}\beta_{23}\beta_{34}\beta_{56}\beta_{65} - \beta_{43}\beta_{32}\beta_{21}\beta_{14}\beta_{56}\beta_{65} - \beta_{12}\beta_{21}\beta_{34}\beta_{45}\beta_{56}\beta_{63} \\ &\quad - \beta_{12}\beta_{21}\beta_{36}\beta_{65}\beta_{54}\beta_{43} + \beta_{41}\beta_{12}\beta_{23}\beta_{36}\beta_{65}\beta_{54} + \beta_{45}\beta_{56}\beta_{63}\beta_{32}\beta_{21}\beta_{14}). \quad (1) \end{aligned}$$

Here, ε is an energy variable; β_{ij} is a resonance integral between bonded carbon atoms i and j; for simplicity, all carbon atoms are assumed to have a constant value for the Coulomb integral α, but this is not a necessary condition for the present theory.

As we may see from eq. (1), all coefficients of the polynomial are expressible in terms of closed cyclic products of resonance integrals (24-27). The simplest closed cyclic product is just of the type $\beta_{ij}\beta_{ji}$, which corresponds to the π bond between carbon atoms i and j. Such a bond-type product of resonance integrals represents an interchange of π electrons between the two carbon atoms. This will be called a bond interaction. Seven bond interactions appear in eq. (1), since there are seven π bonds in K. As shown in Fig. 2, they are:

$$B_1 = \beta_{14}\beta_{41}, \quad B_2 = \beta_{12}\beta_{21}, \quad B_3 = \beta_{23}\beta_{32}, \quad B_4 = \beta_{34}\beta_{43},$$
$$B_5 = \beta_{45}\beta_{54}, \quad B_6 = \beta_{56}\beta_{65}, \quad \text{and} \quad B_7 = \beta_{36}\beta_{63}.$$
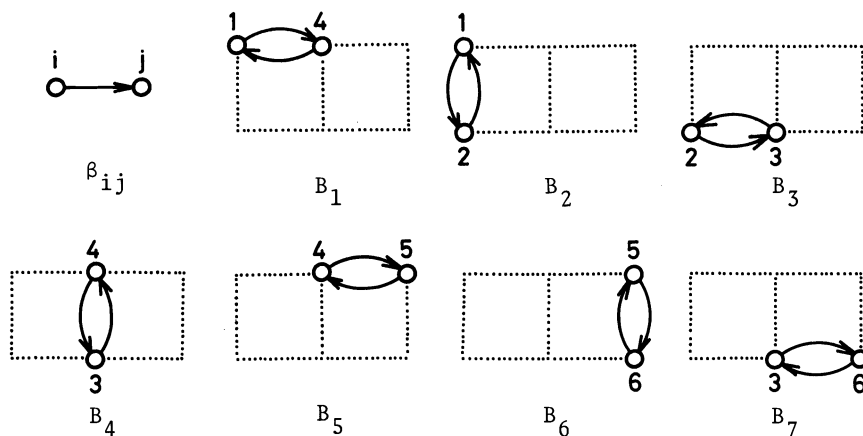

Fig. 2. Bond interactions in K.

In addition to these bond interactions, there are another type of interactions. They are expressed as closed cyclic products of more than two resonance integrals. These products appear in pairs like $\beta_{ij}\beta_{jk}\cdots\beta_{pq}\beta_{qi}$ and $\beta_{iq}\beta_{qp}\cdots\beta_{kj}\beta_{ji}$. Pairing products are equal in magnitude, because $\beta_{ij}=\beta_{ji}$; these are products of resonance integrals around the same π-electron ring.

Such a ring-type product of resonance integrals represents a clockwise (C^+) or counterclockwise (C^-) displacement of all π electrons located around the ring concerned. Therefore, this will be called a ring interaction. Three pairs of ring interactions appear in eq. (1), corresponding to three possible ways of choosing one π-electron ring from K. As shown in Fig. 3, they are:

$$C_1 = \beta_{14}\beta_{43}\beta_{32}\beta_{21}(=C_1^+) = \beta_{12}\beta_{23}\beta_{34}\beta_{41}(=C_1^-),$$
$$C_2 = \beta_{34}\beta_{45}\beta_{56}\beta_{63}(=C_2^+) = \beta_{36}\beta_{65}\beta_{54}\beta_{43}(=C_2^-), \quad \text{and}$$
$$C_3 = \beta_{14}\beta_{45}\beta_{56}\beta_{63}\beta_{32}\beta_{21}(=C_3^+) = \beta_{12}\beta_{23}\beta_{36}\beta_{65}\beta_{54}\beta_{41}(=C_3^-).$$

These ring interactions are underlined in eq. (1).

Let $X=(\varepsilon-\alpha)/\beta$, where β is a standard value of the resonance integral for carbon-carbon π bonds, and the polynomial in eq. (1) is reduced to a much simpler form:

$$P_K(X) = X^6 - (B_1+B_2+B_3+B_4+B_5+B_6+B_7)\beta^{-2}X^4 + (B_1B_3+B_1B_6+B_1B_7+B_2B_4$$
$$+B_2B_5+B_2B_6+B_2B_7+B_3B_5+B_3B_6+B_4B_6+B_5B_7-2C_1-2C_2)\beta^{-4}X^2 - (B_1B_3B_6$$
$$+B_2B_4B_6+B_2B_5B_7-2C_1B_6-2B_2C_2+2C_3)\beta^{-6}. \tag{2}$$

This type of polynomials in a dimensionless form are called characteristic polynomials (28).

The equation $P_K(X)=0$ can be solved, and the six roots determined. The jth largest root X_j is related to the jth π-electron MO energy of butalene. Its
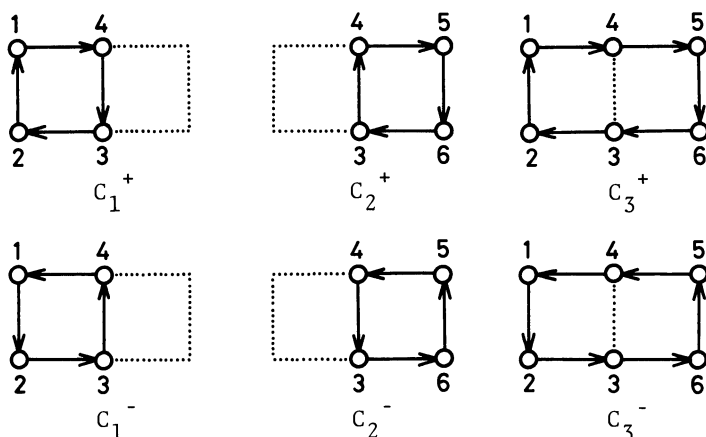

Fig. 3. Ring interactions in K.

magnitude depends upon all coefficients of $P_K(X)$, each coefficient being expressed in terms of bond and/or ring interactions. If any of these interactions change in magnitude, the six roots will also change to a varying extent. Here, we assume that all bond interactions are constant, but that all pairs of ring interactions can be treated as independent parameters. Then, X_j can be expressed hypothetically as a function of three pairs of ring interactions, i.e.,

$$X_j=X_j(C_1,C_2,C_3). \tag{3}$$

This is not the result of logical reasoning, since all the ring interactions are not independent of each other; they are not independent of the bond interactions, either. Then, if C_1's take their respective values in real butalene, the jth π-electron MO energy will be expressed in the form:

$$\varepsilon_j=\alpha+X_j(C_1,C_2,C_3)\beta, \tag{4}$$

since $X_j=(\varepsilon_j-\alpha)/\beta$.

For acyclic polyenes, no ring interactions appear in the coefficients of the characteristic polynomial, since there are no π-electron rings. In this view, the non-existence of ring interactions may be essential to the "localized" nature of π bonds in these compounds. Conversely, it is highly probable that ring interactions bring about delocalization of π bonds in cyclic conjugated systems. Since both aromatic and antiaromatic molecules always have cyclic conjugated systems (8,29), aromaticity and antiaromaticity might be attributed to the ring interactions.

This way of chemical thinking leads to the central postulate, that is, if all ring interactions happen to vanish in a cyclic conjugated system, all the π bonds would be localized as in acyclic polyenes. This postulate asserts that, if there were no ring interactions in butalene, the jth π-electron MO energy would change to:

$$\varepsilon_j{}^0=\alpha+X_j(0,0,0)\beta. \tag{5}$$

In practice, the value for $X_j(0,0,0)$ is given as the jth zero of the following polynomial, obtained by setting all C_i's in the coefficients of $P_K(X)$ equal to zero:

$$R_K(X) = X^6 - (B_1 + B_2 + B_3 + B_4 + B_5 + B_6 + B_7)\beta^{-2}X^4 + (B_1B_3 + B_1B_6 + B_1B_7 + B_2B_4$$
$$+ B_2B_5 + B_2B_6 + B_2B_7 + B_3B_5 + B_3B_6 + B_4B_6 + B_5B_7)\beta^{-4}X^2 - (B_1B_3B_6$$
$$+ B_2B_4B_6 + B_2B_5B_7)\beta^{-6}. \tag{6}$$

In other words, $X_j(0,0,0)$ is the jth root of the equation $R_K(X) = 0$. $R_K(X)$ is termed a reference polynomial for the conjugated system K (16,30), which may be interpreted as a characteristic polynomial for the reference structure with "localized" π bonds.

Next, let us calculate explicitly the π-electron MO energies of butalene and its reference structure. For simplicity, we assume that there is no bond alternation in K, so that all resonance integrals can be set equal to β. In this case, $B_i = \beta^2$ for all π bonds, and $C_i = \beta^m$, where m is the number of carbon atoms constituting the ring. A characteristic polynomial for butalene becomes:

$$P_K(X) = X^6 - 7X^4 + 7X^2 - 1. \tag{7}$$

The π-electron MO energies obtained from this polynomial are shown in Fig. 4. Six π electrons are put into the first three MO's, giving a total π-electron energy of $6\alpha + 7.657\beta$ for butalene. A reference polynomial for this compound becomes:

$$R_K(X) = X^6 - 7X^4 + 11X^2 - 3. \tag{8}$$

The resulting π-electron MO energies are compared in Fig. 4. Six roots are again placed in the first three MO's, giving a total π-electron energy of $6\alpha + 8.261\beta$ for the butalene reference structure. The resonance energy is
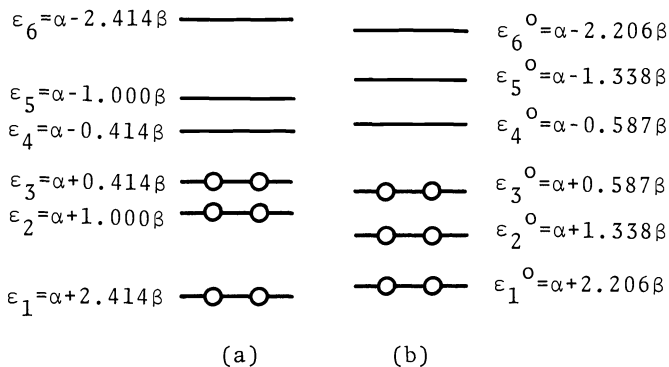

Fig. 4. π-Electron MO energies of butalene (a) and
its "localized" reference structure (b).

defined as the difference between these two total π-electron energies. Here and hereafter the term "resonance energy" is used in Dewar's sense (8,11). It is $-0.604\underline{\beta}$ for butalene, where $\underline{\beta}$ is an absolute value of β. A large negative value of the resonance energy indicates that butalene might be much more unstable than common acyclic polyenes with no ring interactions. In fact, this compound is very unstable, and cannot be isolated from the frozen matrix (31). As far as butalene is concerned, agreement between theory and stability thus appears acceptable (32).

GENERAL DEFINITION OF RESONANCE ENERGY

The above definition of resonance energy can be extended easily to include all cyclic conjugated hydrocarbons (16,30). Let a given hydrocarbon contain N carbon atoms and u π bonds in the conjugated system G. Different bond

interactions are defined for all these π bonds. If v pairs of closed cyclic products of more than two resonance integrals can be chosen from G, v pairs of ring interactions are defined by them. This means that there are v ways of choosing an annulene-like π-electron ring from G. Expansion of the secular determinant yields a characteristic polynomial of the same type as eq. (2), and this is denoted by $P_G(X)$. Coefficients of $P_G(X)$ can be expressed in terms of u bond and v pairs of ring interactions and β.

Our formalism requires that all bond interactions be constants, but that all pairs of ring interactions can be treated as independent parameters; we assume that each pair of ring interactions can take any value independently of other interactions in the same conjugated system. This is a trick to tackle the problem of aromaticity. Suppose C_i denotes a pair of ring interactions in the ith π-electron ring, and N roots of the equation $P_G(X)=0$ can be expressed formally as functions of v pairs of ring interactions, i.e.,

$$X_j = X_j(C_1, C_2, \ldots, C_{v-1}, C_v), \tag{9}$$

where X_j's are numbered in decreasing order. When C_i's really take their respective values in G, the jth π-electron MO energy is given by:

$$\epsilon_j = \alpha + X_j(C_1, C_2, \ldots, C_{v-1}, C_v)\beta. \tag{10}$$

The total π-electron energy for G is then:

$$E_\pi = \sum_{j=1}^{N} g_j \epsilon_j, \tag{11}$$

where g_j is the number of π electrons in the jth π-electron MO.

On the other hand, the π-electron MO energies of the "localized" reference structure are given formally by:

$$\epsilon_j^0 = \alpha + X_j(0, 0, \ldots, 0, 0)\beta. \tag{12}$$

These MO energies are numbered anew in increasing order. The reference polynomial $R_G(X)$ is obtained by assuming all C_i's in the coefficients of $P_G(X)$ to vanish. In practice, the values for $X_j(0,0,\ldots,0,0)$ are the roots of the equation $R_G(X)=0$. These roots are always real numbers (27,33). The total π-electron energy for this reference structure is:

$$E_\pi^0 = \sum_{j=1}^{N} g_j^0 \epsilon_j^0. \tag{13}$$

Here, g_j^0 is the number of π electrons in the jth π-electron MO, which must be chosen so as to minimize E_π^0 (34). We are finally led to the resonance energy defined by:

$$RE = -(E_\pi - E_\pi^0). \tag{14}$$

This resonance energy represents the contribution of all ring interactions to the total π-electron energy; it is an extra stabilization energy of G to be expected in comparison with a "localized" reference structure, defined by eq. (12). Both eqs. (11) and (13) apply not only to neutral conjugated systems but also to ionic ones (16,30,35-37).

For conjugated hydrocarbons with no alternation of π-bond lengths, all resonance integrals can be set equal to β. In this case, a reference polynomial greatly simplifies to (14-16):

$$R_G(X) = X^N + \sum_{j=1}^{[N/2]} (-1)^j p(j) X^{N-2j}. \qquad (15)$$

Here, $[N/2]$ is a maximum integer not larger than $N/2$, and $p(j)$ the number of ways of choosing j disjoint π bond from G. This formula is of general use for simplifying the computational procedure. It is noteworthy that eq. (15) also gives a definition of a characteristic polynomial for acyclic polyenes (14). This indicates that a characteristic polynomial for an acyclic polyene is exactly the same as its reference polynomial. Therefore, the resonance energy vanishes for such a system. Thus, our theory satisfies Dewar's requirement that acyclic polyenes be nonaromatic with no resonance energy (8). Furthermore, the reference polynomial defined by eq. (15) is either an even or odd function of X, depending upon the number of conjugated carbon atoms. Consequently, the energy levels are symmetrically disposed about $X=0$; when X_j is a root of the equation $R_G(X)=0$, $-X_j$ is also a root. In this view, the reference structure defined for any conjugated hydrocarbon can be regarded as a kind of alternant hydrocarbon (38). A characteristic polynomial can be readily obtained, if necessary, by expanding:

$$P_G(X) = \prod_{j=1}^{N} [X - X_j(C_1, C_2, \ldots, C_{v-1}, C_v)], \qquad (16)$$

in which X_j's are given by solving the secular equation for G.

One of the best ways of testing the validity of our theory is to compare the calculated resonance energies with those of Hess and Schaad (11), both based on the simple HMO model. The latter ones have been accepted as being of Dewar type, since the energies of the "localized" reference structures were estimated with empirically chosen "polyene" π-bond energies. In fact, our resonance energies (16,35) correlated very well with those of Hess and Schaad (11), with a correlation coefficient of 0.967 for 40 typical hydrocarbons (TABLE 1). Such an excellent correlation (39) unanimously justifies the expectation that our resonance energies would be of Dewar type. We can now say that the reference polynomial, as defined by eq. (15), really represents a "localized" structure with polyene-like π bonds; bond interactions are the only source of "localized" π-bond energies in acyclic polyenes and in the reference structures of cyclic conjugated systems alike. Mathematically, this comes from the fact that $R_G(X)$ for cyclic conjugated systems is defined in the same manner as $P_G(X)$ for acyclic polyenes with "localized" π bonds.

Therefore, the resonance energy defined by eq. (14) can naturally be associated with aromaticity or antiaromaticity, depending upon the sign.

In general, an aromatic compound is characterized by the appreciable positive resonance energy, and an antiaromatic compound by the appreciable negative resonance energy (8-13). However, if two compounds have resonance energies comparable in magnitude, that of smaller size will be more stable (11,12). Thus, when compounds of different size are compared, the percent resonance energy (%RE) , rather than the overall resonance energy, is particularly suitable (40,41). The %RE is defined as 100 times the resonance energy, divided by the energy of the reference structure. As shown in TABLE 1, the %RE value is quite consistent with experimental stability for a variety of compounds. Compounds with %RE>0.50 are generally stable, and most compounds with %RE<-0.50 are extremely unstable (41). Resonance energy per π bond also serves as a practical measure of stability (42). As for annulenes, those with (4n+2) π electrons are predicted to be aromatic, and those with 4n π electrons to be antiaromatic. These predictions are in complete agreement with Hückel's (4n+2) rule (43-45). When n is large enough, the two series of annulenes are essentially nonaromatic, having negligible %RE's. Radialenes are all predicted to be nonaromatic. These compounds have been regarded as representative cyclic polyenes (8,44,45).

So far, the theory has been described in terms of the simple HMO model. This model is best applicable to alternant hydrocarbons, but is less applicable to nonalternant ones with uneven charge distributions (46,47). For example, calicene and sesquifulvalene have been predicted to have very large resonance energies (11,16,30), although chemically they behave like polyenes (48). The ω-technique calculations (46,47) greatly ameliorate this situation (41). As

TABLE 1. Resonance energies of 40 cyclic conjugated hydrocarbons.

| Species | Resonance energy (β) | | | %RE[b] |
| | Hess-Schaad[a] | Present theory | | |
		Simple HMO	ω-Technique	
Cyclobutadiene	-1.072	-1.226	-1.226	-23.46
Benzene	0.392	0.273	0.273	3.53
Cyclooctatetraene	-0.487	-0.595	-0.595	-5.80
[10]Annulene	0.265	0.159	0.159	1.25
[12]Annulene	-0.287	-0.394	-0.394	-2.57
[14]Annulene	0.225	0.113	0.113	0.63
[3]Radialene	-0.007	0.009	-0.005	-0.06
[4]Radialene	-0.086	-0.072	-0.072	-0.73
[5]Radialene	-0.019	0.000	0.000	0.00
[6]Radialene	-0.014	0.009	0.009	0.06
Triafulvene	0.020	0.063	-0.145	-2.96
Fulvene	-0.012	0.020	-0.082	-1.10
Heptafulvene	-0.020	0.009	-0.052	-0.52
Dimethylenecyclobutene	-0.170	-0.163	-0.163	-2.21
o-Xylylene	0.040	0.059	0.059	0.60
p-Xylylene	0.044	0.061	0.061	0.62
Triafulvalene	-0.592	-0.461	-0.607	-7.66
Calicene	0.347	0.433	0.038	0.36
Triaheptafulvalene	-0.215	-0.210	-0.370	-2.83
Fulvalene	-0.329	-0.299	-0.367	-2.81
Sesquifulvalene	0.267	0.272	0.023	0.15
Heptafulvalene	-0.195	-0.218	-0.261	-1.43
Butalene	-0.402	-0.604	-0.604	-7.31
Pentalene	-0.141	-0.215	-0.411	-3.85
Naphthalene	0.552	0.389	0.389	2.92
Heptalene	-0.050	-0.141	-0.252	-1.60
Octalene	-0.100	-0.259	-0.259	-1.41
Benzocyclobutadiene	-0.214	-0.393	-0.393	-3.65
Bicyclo[6.2.0]decapentaene				
	-0.289	-0.461	-0.461	-3.46
Benzocyclooctatetraene	0.054	-0.106	-0.106	-0.67
Azulene	0.231	0.151	0.055	0.42
Cyclopent[cd]azulene	0.220	0.101	-0.030	-0.18
Acenaphthylene	0.473	0.354	0.319	1.96
Aceheptylene	0.229	0.106	0.014	0.07
Pleiadiene	0.463	0.339	0.317	1.69
s-Indacene	0.110	0.055	-0.056	-0.35
as-Indacene	-0.249	-0.306	-	<-1.92
Biphenylene	0.331	0.123	0.123	0.75
Anthracene	0.659	0.475	0.475	2.52
Phenanthrene	0.766	0.546	0.546	2.89

[a]Reference 11. [b]Derived from ω-technique resonance energy.

we have seen, the reference structure of any conjugated hydrocarbon is mathematically identical with an alternant hydrocarbon (16), for which charge density is unity on each carbon atom (49). Therefore, even if the ω-technique is employed, the energy of the reference structure remains unchanged. Then, the resonance energies of nonalternant hydrocarbons can be refined simply by applying the ω-technique to the real system alone. Resonance energies of alternant hydrocarbons are not modified by this technique. A comparison of the resonance energies derived from the simple HMO and ω-technique calculations is made in TABLE 1; a standard value of $\omega=1.4$ was used for the latter calculations (41,50). In the case of ionic conjugated systems, the "localized" reference structure is also reorganized by application of the ω-technique.

We have not referred to radicals containing unpaired π electrons. Chemically, they show no aromatic behavior, being very reactive and polymerizing easily (51). For these systems, the reference structure must be very unstable, since it must still retain radical character. The resonance

energy is calculated relative to the energy of such an unstable reference
structure, so it can hardly be related to the apparent instability (34). It
is obvious that this kind of instability has a different origin from
antiaromaticity.

RING CURRENTS AND AROMATICITY

In general, diamagnetic susceptibility of an organic molecule is an additive
function of its constituents (52). However, benzene and other cyclic
conjugated systems possess rather larger susceptibilities than expected from
a comparison with the values of alkenes (53). It has been accepted that the
exaltation of diamagnetic susceptibility is not only a manifestation of the
existence of fully delocalized π electrons but also an excellent criterion
of aromaticity (54). It is now known that the induced ring currents are
responsible for this magnetic exaltation (18,19). The present theory is
useful for clarifying the physical ground for the relationship between
resonance energy due to aromaticity and susceptibility due to ring currents
(20,21,26,45).

Suppose an external magnetic field of strength H is applied perpendicularly
to the planar conjugated system G, and the field-dependent characteristic
polynomial is given formally by replacing every ring interaction C_i in the
coefficients of $P_G(X)$ for the field-free system by (20,21,26):

$$C_i(H) = C_i(0)\cos(\Theta_i H)$$

$$= C_i(0)(1 - \frac{1}{2}\Theta_i^2 H^2 + \ldots). \qquad (18)$$

Here, $C_i(0)$ represents C_i in eq. (9), being equal to the value for the field-
free system; $\Theta_i = eS_i/c\hbar$, in which S_i is the area of the ith π-electron ring,
and e, c, and $\hbar$ are the constants with these symbols. Bond interactions are
not influenced by the field. Therefore, by substitution eq. (18) in eq. (9),
the field-dependent π-electron MO energies are written as:

$$\varepsilon_j(H) = \alpha + X_j[C_1(H), C_2(H), \ldots, C_{v-1}(H), C_v(H)]\beta. \qquad (19)$$

The field-dependent total π-electron energy $E_\pi(H)$ is then given by summing
$\varepsilon_j(H)$ over all the π electrons. Coefficients of the reference polynomial do
not contain ring interactions, so the "localized" reference structure is
independent of the external magnetic field (26,45). Thus, the "localized"
reference structure again resembles an acyclic polyene, this time in that
the field has no effect.

Diamagnetic susceptibility due to ring currents, χ_π, is defined as the
second derivative of $E_\pi(H)$ with respect to H (19,20,26). Hence, $E_\pi(H)$ can be
expanded in powers of H:

$$E_\pi(H) = E_\pi(0) + \frac{1}{2}\chi_\pi H^2 + \ldots, \qquad (20)$$

where $E_\pi(0)$ is identical with E_π in eq. (11). Since an aromatic system does
not have a permanent magnetic moment, the term proportional to H vanishes.

We can now prove that the diamagnetic susceptibility due to ring currents
really reflects aromaticity. As shown in eq. (18), the magnetic field H
affects exclusively the ring interactions. Since H can be treated as a small
perturbation, every ring interaction $C_i(H)$ is a monotonically decreasing
function of H. Therefore, the role of the field is to diminish the
conrtibution of all ring interactions to the coefficients of the
characteristic polynomial, i.e., to change the field-free conjugated system
into a variant with smaller ring interactions (26). In this way, the applied
field commonly destabilizes an aromatic system, and stabilizes an
antiaromatic system. The absolute value of the resonance energy
correspondingly decreases in the field, since the energy of the reference
structure remains unchanged. According to eq. (20), the decrement of

resonance energy due to the field is proportional to the susceptibility due to ring currents, χ_π. Therefore, the sign of resonance energy commonly disagrees with that of χ_π. This is the primary reason why the exaltation of diamagnetic susceptibility is a valid criterion for the determination of aromaticity (54). As we will see, however, this criterion is not an exact one (20).

The above magnetic behavior of aromatic compounds can be visualized explicitly in the case of comparatively simple conjugated hydrocarbons. For monocyclic and bicyclic hydrocarbons, the reference polynomial is given as (14,15):

$$R_G(X) = P_G(X) + 2 \sum_{i=1}^{v} P_{G-r_i}(X), \qquad (21)$$

where $G-r_i$ is a subsystem of a conjugated system G, obtained by deleting from G the ith π-electron ring (r_i) and all π bonds adjacent to it; $P_{G-r_i}(X)$ can be obtained by means of eq. (16). If $G-r_i=0$, $P_{G-r_i}(X)=1$ by definition. As for subsystems of the butalene conjugated system, see Fig. 5, where G=K. The
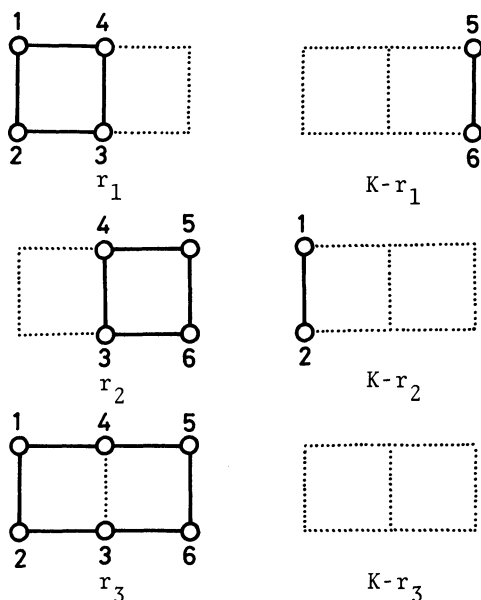

Fig. 5. Subsystems of the butalene conjugated system K.

jth largest root of the equation $P_G(X)=0$ is hereafter denoted by X_j, and the corresponding root of the equation $R_G(X)=0$ abbreviated to $X_j^{\,o}$. By application of Newton's method to the equation $R_G(X)=0$, where $R_G(X)$ is given in the form of eq. (21), we obtain the roots in the form (22):

$$X_j^{\,o} \simeq X_j - 2 \sum_{i=1}^{v} \frac{P_{G-r_i}(X_j)}{P_G'(X_j)}, \qquad (22)$$

where $P_G'(X)$ is the first derivative of $P_G(X)$ with respect to X. Then, the resonance energy is expressed approximately as:

$$RE = \underline{\beta} \sum_{j=1}^{N} g_j (X_j - X_j^{\,o}) \simeq 2\underline{\beta} \sum_{j=1}^{N} \sum_{i=1}^{v} \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)}, \qquad (23)$$

This approximate resonance energy is an additive function of the constituent π-electron rings, so it can be divided among the rings, namely:

$$RE^{(i)} = 2\underline{\beta} \sum_{j=1}^{N} \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)},\tag{24}$$

Ring resonance energies thus calculated for butalene are listed in TABLE 2.

TABLE 2. Ring resonance energies and ring susceptibilities of butalene

r_i	$RE^{(i)}(\underline{\beta})$	$\chi^{(i)}(\underline{\beta})^a$
r_1	-0.707	$0.707\Theta_1^2$
r_2	-0.707	$0.707\Theta_2^2$
r_3	0.561	$-0.561\Theta_3^2$
Total	-0.853	$-0.830\Theta_1^2$

^{a} $\Theta_1 = \Theta_2 = \Theta_3/2$.

These expressions can also be applied to pericondensed tricyclic hydrocarbons, such as acenaphthylene, aceheptylene, pleiadiene, and cyclopent[cd]azulene (22,55).

For any conjugated hydrocarbon, diamagnetic susceptibility due to ring currents can be expressed in the analytical form (20):

$$\chi_\pi = -2\underline{\beta} \sum_{j=1}^{N} \sum_{i=1}^{v} \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)} \Theta_i^2.\tag{25}$$

This is a graph-theoretical version of the London theory of diamagnetism (19). The susceptibility is now an additive function of the π-electron rings, so it can be divided among the rings:

$$\chi^{(i)} = -2\Theta_i^2 \underline{\beta} \sum_{j=1}^{N} \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)}.\tag{26}$$

This quantity is called the ring susceptibility. Comparing eqs. (24) and (26), we see that the ith ring resonance energy is evidently related to the ith ring susceptibility; the two expressions differ only by the factor $-\Theta_i^2$.

This relationship shows that the sign of the ring susceptibility is opposite to that of the ring resonance energy (22). Since (4n+2)-membered rings commonly have positive resonance energies (20,35), they must have negative ring susceptibilities. Conversely, 4n-membered rings commonly have negative ring resonance energies (20,35), so they must have positive ring susceptibilities. For ring susceptibilities of butalene, see again TABLE 2.

However, the sign of the overall resonance energy does not always differ from that of the overall susceptibility (22). This can be seen by substituting eq. (24) in eq. (25):

$$\chi_\pi = -\sum_{i=1}^{v} RE^{(i)} \Theta_i^2.\tag{27}$$

Each of the weighting factors $-\Theta_i^2$ is proportional to the corresponding ring area squared. Therefore, larger rings contribute much more to the susceptibility than to the resonance energy. As a result, the sign of the overall susceptibility is sometimes determined by one or some large rings with small ring resonance energies. If these ring resonance energies are

different in sign from the overall resonance energy, the sign of the overall susceptibility will be the same as that of the overall resonance energy. Thus, it is sometimes dangerous to regard the diamagnetic exaltation as an indication of aromaticity. Butalene is one of such exceptions. When there are degenerate orbitals in G, eqs. (22)-(26) need some modification, but eq. (27) still holds (20,22).

An NMR criterion of aromaticity has been used widely, according to which diamagnetic ring currents indicate aromaticity while paramagnetic ring currents indicate antiaromaticity (56). We can show why compounds with diamagnetic ring currents also have strong conjugative stabilization. The current induced in the ith π-electron ring is given as the first derivative of the ith ring susceptibility with respect to the ring area (57). Therefore, the sign of the ring current, i.e., the direction of the current, is opposite to the sign of the ring resonance energy. In brief, diatropicity indicates aromaticity of the ring concerned. This provides a theoretical justification for the utility of proton chemical shifts as a conventional measure of aromaticity (56).

CONCLUDING REMARKS

It was in 1965 that Dewar et al. first published the idea of a "localized" reference structure for conjugated hydrocarbons (8). Their reference structure was a patchwork of empirically chosen "polyene" bonds. Our theory, for the first time, was able to define the "localized" reference structure of exactly the same geometry as a real conjugated system. Its mathematical framework is very similar in many respects to that of an acyclic polyene. Three advantages of the theory are that the resonance energy defined in it can be linked to the diamagnetic susceptibility exaltation (i.e., χ_π), that no fitting of parameters is needed in applications to hydrocarbons, and that molecular ions can be examined in addition to neutral species (58).

In this paper, conjugated hydrocarbons alone were used to illustrate the theory. The theory is of course applicable to all kinds of compounds, including heterocycles (16,30,59) and three-dimensional conjugated systems (40,60), although some knowledge of simple graph theory (25,61) is needed to obtain the reference polynomials. Even if so, the physical meaning of the resonance energy remains the same. Aromatic transition states in the pericyclic reactions can also be characterized in terms of the present theory (62). In conclusion, aromaticity is best described as being due to delocalization of bonding π electrons, brought about by ring interactions; the ring interactions are always the only source of aromatic stabilization and diamagnetic exaltation.

REFERENCES

1. J.P. Snyder, Nonbenzenoid Aromatics, Edited by J.P. Snyder, Academic Press, New York (1969), Vol. I, Chapter 1.
2. F.A. Carey and R. Sundberg, Advanced Organic Chemistry, Plenum Press, New York (1977), Part A, Chapter 9.
3. There are, however, many exceptions to this reactivity-based criterion of aromaticity. See, e.g., D. Lloyd and D.R. Marshall, Angew. Chem., Int. Ed. Engl. 11, 404 (1972).
4. P.J. Garratt, Comprehensive Organic Chemistry, Edited by Sir D. Barton and W.D. Ollis, Pergamon Press, Oxford (1979), Vol. 1, Chapter 2.4.
5. M.J. Cook, A.R. Katritzky, and P. Linda, Adv. Heterocycl. Chem. 17, 255 (1974).
6. A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists, Wiley, New York (1961), Chapter 9.
7. L.J. Schaad and B.A. Hess, Jr., J. Am. Chem. Soc. 94, 3068 (1972); J. Chem. Educ. 51, 641 (1974).
8. M.J.S. Dewar and G.J. Gleicher, J. Am. Chem. Soc. 87, 685, 692 (1965); M.J.S. Dewar and C. de Llano, Ibid. 91, 789 (1969); M.J.S. Dewar, Molecular Orbital Theory of Organic Chemistry, McGraw-Hill, New York (1969), Chapter 5.
9. N.C. Baird, Can. J. Chem. 47, 3535 (1969); J. Chem. Educ. 48, 509 (1971).
10. M.J.S. Dewar, A.J. Harget, and N. Trinajstić, J. Am. Chem. Soc. 91, 6321 (1969); M.J.S. Dewar and N. Trinajstić, Tetrahedron, 26, 4269 (1970); M.J.S. Dewar, A.J. Harget, N. Trinajstić, and S.D. Worley, Ibid. 26, 4505 (1970).

11. B.A. Hess, Jr., and L.J. Schaad, J. Am. Chem. Soc. 93, 305, 2413 (1971);
    J. Org. Chem. 36, 3418 (1971).
12. B.A. Hess, Jr., L.J. Schaad, and C.W. Holyoke, Jr., Tetrahedron 28, 3657,
    5299 (1972); Ibid. 31, 295 (1975); B.A. Hess, Jr., and L.J. Schaad,
    J. Am. Chem. Soc. 95, 3907 (1973).
13. W.C. Herndon, J. Am. Chem. Soc. 95, 2404 (1973); W.C. Herndon and M.L.
    Ellzey, Jr., Ibid. 96, 6631 (1974); M. Randić, Chem. Phys. Lett. 38, 68
    (1976); J. Am. Chem. Soc. 99, 444 (1977); R. Swinborne-Sheldrake, W.C.
    Herndon, and I. Gutman, Tetrahedron Lett. 755 (1975); W.C. Herndon, J.
    Org. Chem. 40, 3583 (1975).
14. H. Hosoya, Theor. Chim. Acta 25, 215 (1972); H. Hosoya, K. Hosoi, and I.
    Gutman, Ibid. 38, 37 (1975).
15. H. Sachs, Publ. Math. (Debrecen) 11, 119 (1964); A. Graovac, I. Gutman,
    N. Trinajstić, and T. Živković, Theor. Chim. Acta 26, 67 (1972); I.
    Gutman and N. Trinajstić, Top. Curr. Chem. 42, 49 (1973); D.H. Rouvrey,
    Chemical Applications of Graph Theory, Edited by A.T. Balaban, Academic
    Press, London (1976), Chapter 7.
16. J. Aihara, J. Am. Chem. Soc. 98, 2750 (1976); Kagaku No Ryoiki, 30, 379
    (1976).
17. J. Aihara, J. Org. Chem. 41, 2488 (1976); Kagaku No Ryoiki, 30, 812
    (1976).
18. L. Pauling, J. Chem. Phys. 4, 673 (1936).
19. F. London, J. Phys. Radium 8, 397 (1937).
20. J. Aihara, J. Am. Chem. Soc. 101, 5913 (1979); Bull. Chem. Soc. Jpn. 54,
    1245 (1981).
21. R.C. Haddon, J. Am. Chem. Soc. 101, 1722 (1979); J. Aihara, Bull. Chem.
    Soc. Jpn. 53, 1163 (1980).
22. J. Aihara, J. Am. Chem. Soc. in press.
23. See, e.g., Reference 6, Chapter 2.
24. J.A. Pople, Mol. Phys. 1, 175 (1958).
25. J. Aihara, J. Am. Chem. Soc. 98, 6840 (1976).
26. J. Aihara, J. Am. Chem. Soc. 101, 558 (1979).
27. J. Aihara, Bull. Chem. Soc. Jpn. 52, 1529 (1979).
28. If each element of the secular determinant is divided by β, it will
    become $k_{ij} = \beta_{ij}/\beta$ or X. A characteristic polynomial is obtained by
    expanding this determinant. All the coefficients will be expressed in
    terms of closed cyclic products of k_{ij}'s.
29. See, e.g., J.A. Elvidge and L.M. Jackman, J. Chem. Soc. 859 (1961).
30. I. Gutman, M. Milun, N. Trinajstić, J. Am. Chem. Soc. 99, 1692 (1977).
    They independently published essentially the same definition of resonance
    energy. They used the term "acyclic polynomial" instead of a reference
    polynomial.
31. R. Breslow, J. Napierski, and T.C. Clarke, J. Am. Chem. Soc. 97, 6275
    (1975).
32. By the way, delocalization energy of butalene is 1.657β. This large
    positive value should be interpreted simply as a conjugation energy
    arising from the interaction of three double bonds originally isolated in
    the classical Kekulé structure.
33. O.J. Heilmann and E.H. Lieb, Commun. Math. Phys. 25, 190 (1972); C.D.
    Godsil and I. Gutman, Z. Naturforsch. A 34, 776 (1979).
34. J. Aihara, Chem. Phys. Lett. 73, 404 (1980).
35. J. Aihara, J. Am. Chem. Soc. 99, 2048 (1977).
36. J. Aihara, Bull. Chem. Soc. Jpn. 51, 3540 (1978).
37. P. Ilić and N. Trinajstić, J. Org. Chem. 45, 1738 (1980).
38. C.A. Coulson and G.S. Rushbrooke, Proc. Cambridge Phil. Soc. 36, 193
    (1940).
39. A correlation coefficient of 0.993 was obtained for the two sets of
    resonance energies of 48 benzenoid hydrocarbons (35).
40. J. Aihara, Bull. Chem. Soc. Jpn. 52, 2202 (1979).
41. J. Aihara, Bull. Chem. Soc. Jpn. 53, 2689 (1980).
42. J. Aihara, Bull. Chem. Soc. Jpn. 50, 3057 (1977).
43. E. Hückel, Z. Phys. 70, 204 (1931); Ibid. 76, 628 (1932); J. Aihara,
    Bull. Chem. Soc. Jpn. 49, 1427 (1976).
44. J. Aihara, Bull. Chem. Soc. Jpn. 48, 517 (1975).
45. J. Aihara, Bull. Chem. Soc. Jpn. 53, 1751 (1980).
46. G.W. Wheland and D.E. Mann, J. Chem. Phys. 17, 264 (1949).
47. Reference 6, Chapter 4.
48. H. Prinzbach, Pure Appl. Chem. 28, 281 (1971).
49. I. Gutman, Bull. Soc. Chim. Beograd 43, 191 (1978).
50. Zimmerman recommended the $\omega = 0.8$ value [H.E. Zimmerman, Quantum Mechanics
    for Organic Chemists, Academic Press, New York (1975), Chapter 4]. The
    following resonance energies are obtained with this value:

[3]radialene, -0.002; [5]radialene, -0.000; triafulvene, -0.091; fulvene, -0.057; heptafulvene, -0.038; triafulvalene, -0.553; calicene, 0.180; triaheptafulvalene, -0.325; fulvalene, -0.347; sesquifulvalene, 0.113; heptafulvalene, -0.249; pentalene, -0.358; heptalene, -0.226; azulene, 0.083; cyclopent[cd]azulene, 0.012; acenaphthylene, 0.328; aceheptylene, 0.041; pleiadiene, 0.324; s-indacene, -0.030; as-indacene, not obtained. All these resonance energies are given in units of $\underline{\beta}$.

51. See, e.g., Reference 6, Chapter 13.
52. See, e.g., P.W. Selwood, <u>Magnetochemistry</u>, 2nd Ed., Interscience, New York (1956), Chapter 6.
53. See, e.g., Reference 52, Chapter 7.
54. H.J. Dauben, Jr., J.D. Wilson, and J.L. Laity, <u>Nonbenzenoid Aromatics</u>, Edited by J.P. Snyder, Academic Press, New York (1971), Vol. II, Chapter 3.
55. For conjugated hydrocarbons, other than monocyclic, bicyclic, and pericondensed tricyclic ones, some correction terms must be added to eqs. (21)-(24) and (27). However, a gross aromatic behavior of the compounds can still be conjectured from the uncorrected expressions.
56. R.C. Haddon, V.R. Haddon, and L.M. Jackman, <u>Top. Curr. Chem.</u> <u>16</u>, 103 (1971); F. Sondheimer, <u>Acc. Chem. Res.</u> <u>5</u>, 81 (1972).
57. See, e.g., L. Salem, <u>The Molecular Orbital Theory of Conjugated Systems</u>, W.A. Benjamin, New York (1966), Chapter 4.
58. See, e.g., W.C. Herndon and C. Párkányi, <u>Tetrahedron</u> <u>34</u>, 3419 (1978).
59. A. Sabljić and N. Trinajstić, <u>J. Mol. Struct.</u> <u>49</u>, 415 (1978); W.C. Herndon, <u>Tetrahedron Lett.</u>, 3283 (1979); J. Aihara, <u>J. Am. Chem. Soc.</u> <u>103</u>, 1633 (1981).
60. J. Aihara, <u>Bull. Chem. Soc. Jpn.</u> <u>51</u>, 1541 (1978); <u>J. Am. Chem. Soc.</u> <u>100</u>, 3339 (1978).
61. A. Graovac, O.E. Polansky, N. Trinajstić, and N. Tyutyulkov, <u>Z. Naturforsch.</u> A <u>30</u>, 1696 (1975).
62. J. Aihara, <u>Bull. Chem. Soc. Jpn.</u> <u>51</u>, 1788 (1978).