A New Definition of Dewar-Type Resonance Energies

Jun-ichi Aihara

Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan. *Received June 13, 1975*

Abstract: In order to analytically estimate the HMO resonance energy for a conjugated compound, a reference polynomial, i.e., a characteristic polynomial for the reference structure, is constructed by graph-theoretically excluding from the coefficients of the HMO characteristic polynomial all contributions from cyclic components in the π system. The resonance energy is then defined as the difference between the total π energy calculated from the HMO characteristic polynomial for the original compound and that calculated from the corresponding reference polynomial. The method can be applied to conjugated hydrocarbons, heterocycles, and even ionic species. The obtained resonance energies are in excellent agreement with those of Hess and Schaad, and are evidently of Dewar type. The uniqueness of these resonance energies, derived without ambiguities or arbitrary parametrization, is characteristic of this approach.

Resonance energy and aromaticity are key concepts in the theory of conjugated hydrocarbons and heterocycles. So far, molecular orbital theories have provided much of the information concerning aromatic stability.[1] Especially, the total π energy of a conjugated hydrocarbon with n double bonds has often been compared with that of n ethylene molecules. Delocalization energy, which is defined as the difference between these two π energies, has been considered as a measure of aromaticity.[1a] The published experimental resonance energies are all related to such HMO delocalization energies.[1a] However, the lack of correlation between delocalization energies for conjugated hydrocarbons and their chemical behavior definitely shows that the delocalization energies are disqualified from predicting their aromaticities.[2]

In 1965, an epoch-making theory of aromaticity was proposed by Dewar and Gleicher,[3] and was later developed by Dewar's group.[4,5] The important point in their theory is that the reference energy, relative to which aromatic stabilization is calculated, was dramatically redefined. Using a Pariser–Parr–Pople (PPP) method, they found that the energy of any acyclic polyene is an additive function of individual bond energy terms. With the same bond energies, they estimated a reference energy for a cyclic conjugated system. Their reference energy hence represents the energy which the compound would possess if it were absolutely olefinic in nature. It is noteworthy that a considerable double bond character was attached to the formal single bonds in the reference structure for the conjugated system. The results were that acyclic polyenes were defined as nonaromatic with zero resonance energies, whereas cyclic compounds were found to have a wide and continuous variation in resonance energies, from positive (aromatic) to negative (antiaromatic). These resonance energies were termed Dewar-type resonance energies or Dewar resonance energies for short.[6] Dewar resonance energies can be considered as the best aromaticity values available, and they correlate very well with experimental stabilities.[4-6]

In 1971, Hess and Schaad obtained analogous resonance energies on the basis of the simple HMO method.[2,7-13] They classified π bonds in acyclic polyenes into eight different types (five types of carbon–carbon double bonds and three types of carbon–carbon single bonds, depending upon the number of attached hydrogens) and assigned a particular π-bond energy to each π-bond type.[7] They showed that the π energy of any acyclic polyene can be expressed with these π-bond energies. With the same π-bond energies, they estimated the reference energies for cyclic conjugated systems, and obtained resonance energies which nicely parallel the PPP results.

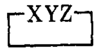
Recently, we developed a similar theory of aromaticity[14,15] according to the same principle as Dewar's[3-5] within the HMO model. In contrast to the method of Hess and Schaad, we adopted the π energy of an infinitely large monocyclic system as a nonaromatic basis to estimate the reference energy for a monocyclic compound of finite size. As will be seen later, the obtained resonance energies are in close and consistent parallel with those of Hess and Schaad.[7,10-13]

Attempts have also been made to correlate Dewar-type resonance energies with particular structural features of unsaturated compounds. Herndon demonstrated that a parametrized structure-resonance theory which uses only Kekulé structures nicely duplicates Dewar-type resonance energies for a series of benzenoid and nonbenzenoid hydrocarbons.[16,17] It has been emphasized that the algebraic structure count (ASC) and not the number of Kekulé structures plays an important role in stabilizing the conjugated hydrocarbon.[18] For benzenoid hydrocarbons, ASC agrees with the number of Kekulé structures. Quite recently, Herndon et al. found that, for these compounds, the resonance energy is simply proportional to the logarithm of ASC.[19] Other topological methods for estimating the total π energy might also be useful for predicting the stability of the conjugated system.[20,21]

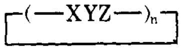
In this context, we examine graph-theoretically the HMO characteristic polynomials for the conjugated systems in detail, and present a new definition of Dewar-type resonance energies for conjugated hydrocarbons and heterocycles. We assume the HMO theory throughout this article. All energies are given in units of β.

Method A-I for Evaluating Resonance Energies

To begin with, we describe briefly our previous method for evaluating resonance energies of monocyclic conjugated systems.[15] Consider a hypothetical monocyclic periodic conjugated system with n unit structures. A general formula for such a conjugated system is illustrated as I, in which the unit structure (XYZ) in brackets is so chosen that the entire system with n = 1 becomes the compound under consideration, II.

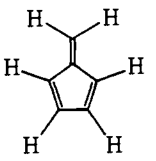


I

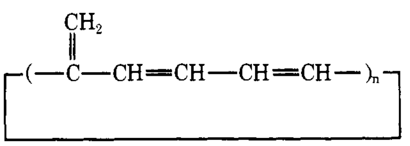


II

For example, to estimate the resonance energy of fulvene (III), one begins by imagining the periodic system IV. The



III

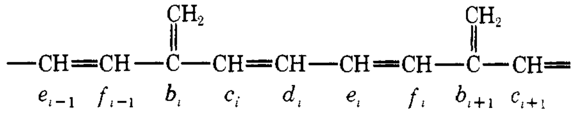


IV

π energy of this hypothetical compound can be determined after solving the following HMO secular equations:[7]

$$
\begin{aligned}
-a_iX + b_i &= 0\\
-b_iX + f_{i-1} + a_i + c_i &= 0\\
-c_iX + b_i + d_i &= 0\\
-d_iX + c_i + e_i &= 0\\
-e_iX + d_i + f_i &= 0\\
-f_iX + e_i + b_{i+1} &= 0\\
i = 1, 2, \ldots, n-1, n &
\end{aligned}
\tag{1}
$$

where a_i, b_i, c_i, d_i, e_i, and f_i are the Hückel coefficients of the atomic orbitals on the carbon atoms arranged in this manner:



The signs of these coefficients are determined so as to accord with the graph-theoretical definitions,[22] which will be referred to later.

These equations must be solved together with boundary conditions:[7]

$$a_{n+1} = a_1;\ b_{n+1} = b_1;\ c_{n+1} = c_1;\ d_{n+1} = d_1;\ e_{n+1} = e_1;\ \text{and}\ f_{n+1} = f_1 \tag{2}$$

The function

$$b_i = \sin i\Lambda \tag{3}$$

automatically satisfies eq 2 if

$$\Lambda = \Lambda_{nm} = 2m\pi/n \tag{4}$$

$$m = 0, 1, \ldots, n-1$$

The elimination of a_i, c_i, d_i, e_i, f_i, and f_{i-1} in eq 1, followed by substitution of eq 3 and 4, gives n algebraic equations of degree six:

$$P_{nm}(X) = X^6 - 6X^4 + 8X^2 - 2\cos\Lambda_{nm}X - 1 = 0 \tag{5}$$

In general, HMO secular equations for a monocyclic periodic system with n unit structures (I) can be reduced to n algebraic equations of the same degree as the number of atoms ($N = 2j$) in every unit structure:

$$P_{nm}(X) = \sum_{k=0}^{N} A_k(\cos\Lambda_{nm})X^{N-k} = 0 \tag{6}$$

where the coefficients $A_k(\cos\Lambda_{nm})$ are the linear functions of $\cos\Lambda_{nm}$.

The roots of $P_{nm}(X) = 0$ correspond to N of the π-orbital energies for the type-I system with n unit structures. They are arranged in a decreasing order:

$$
\begin{aligned}
X = X_1(\cos\Lambda_{nm}) \geq X_2(\cos\Lambda_{nm}) \geq \ldots \geq X_j(\cos\Lambda_{nm})\\
\geq X_{j+1}(\cos\Lambda_{nm}) \geq \ldots \geq X_{N-1}(\cos\Lambda_{nm})\\
\geq X_N(\cos\Lambda_{nm})
\end{aligned}
\tag{7}
$$

Among them, the larger j roots give the π energies of the occupied π orbitals in the type-I system. Accordingly, the total π energy of the type-I system is obtained by summing the larger j roots for every Λ_{nm} over all m values.

The unit π energy which represents the π energy assigned to every unit structure can be obtained by dividing the total π energy of the system by the number of unit structures (n). It is a function of the number of unit structures in the system, because the π energy might be influenced by the aromatic character for smaller systems. When n is large enough, the type-I system can, however, be considered as a nonaromatic species. The unit π energy of any infinitely large type-I compound should hence be free from aromaticity. The unit π energy for such an infinitely large type-I compound (E_{U}) is generally expressed as follows:[23]

$$
\begin{aligned}
E_{\mathrm{U}} &= \lim_{n\to\infty} \frac{2}{n} \sum_{m=0}^{n-1} \{X_1(\cos\Lambda_{nm}) + \ldots + X_j(\cos\Lambda_{nm})\}\\
&= 2\int_0^1 \{X_1(\cos 2\pi x) + \ldots + X_j(\cos 2\pi x)\}\,\mathrm{d}x
\end{aligned}
\tag{8}
$$

According to Dewar's finding that the π energy of a nonaromatic species is additively estimated,[3] a monocyclic type-I system of any size should have the same unit π energy as that of the corresponding infinitely large type-I system if it were not resonance stabilized. This implies that E_{U} can be used as a reference energy in estimating the aromaticity of the simplest type-I compound, i.e., the one with $n = 1$ (II).

Then, the Dewar-type resonance energy for the simplest type-I compound is given as the difference between the total HMO π energy of the compound and the unit π energy of the corresponding infinitely large periodic species. As stated in previous papers,[14,15] this method for estimating resonance energies is very successful in predicting the aromaticities of monocyclic compounds such as annulenes, radialenes, heteroannulenes, and fulvenes. This method is hereafter referred to as method A-I. The original method of Hess and Schaad is abbreviated to method HS.

Method A-II for Evaluating Resonance Energies

Next, we define a reference polynomial $R(X)$ for a monocyclic conjugated system of type II as

$$R(X) = \sum_{k=0}^{N} B_kX^{N-k} \tag{9}$$

where the coefficients B_k are determined from the coefficients of $P_{nm}(X)$ for the corresponding type-I system in the manner:

$$B_k = \lim_{n\to\infty} \frac{1}{n} \sum_{m=0}^{n-1} A_k(\cos\Lambda_{nm}) = \int_0^1 A_k(\cos 2\pi x)\,\mathrm{d}x \tag{10}$$

In order to obtain the coefficients of $R(X)$, we have only to replace every cosine in the coefficients $A_k(\cos\Lambda_{nm})$ by its average value, i.e., zero, because the latter coefficients are the linear functions of $\cos\Lambda_{nm}$, and because the common argument of the cosine varies from 0 to 2π. For example, the reference polynomial for fulvene, readily derived from eq 5, is given by eq 11.

$$R(X) = X^6 - 6X^4 + 8X^2 - 1 \tag{11}$$

In 1972, Trinajstić et al. established the graph-theoretical method for determining the coefficients of the HMO characteristic polynomial for a conjugated hydrocarbon.[22] The HMO characteristic polynomial $P(X)$ for a conjugated hydrocarbon is written in a general form as

$$P(X) = \sum_{k=0}^{N} C_kX^{N-k} \tag{12}$$

$$(C_0 = 1)$$

and each coefficient C_k can be obtained graph-theoretically as a function of the number of disjoint bonds and/or cyclic components of the molecular graph. The method has been described in detail previously.[22] One can also obtain the same polynomial by the expansion of eq 13,

$$P(X) = \prod_{i=1}^{N} (X - X_i) \tag{13}$$

where the X_i are the HMO eigenvalues for the π system under consideration. Either method gives the HMO characteristic polynomial for fulvene as

$$P(X) = X^6 - 6X^4 + 8X^2 - 2X - 1 \tag{14}$$

As may be noted by comparing eq 5, 11, and 14, these three kinds of polynomials resemble each other, in that they have many common coefficients. In fact, the $P(X)$-type polynomial for a given hydrocarbon can readily be derived by replacing the factors of 2 cos Λ_{nm} by 2 in the coefficients of $P_{nm}(X)$ for the corresponding type-I system. It is especially noteworthy that the coefficients of the reference polynomial $R(X)$ are determined graph-theoretically by ignoring enumeration of the cyclic components of the molecular graph. Therefore, $R(X)$ for a conjugated hydrocarbon is defined as

$$R(X) = \sum_{k=0}^{j} (-1)^k p(2k) X^{N-2k} \tag{15}$$

where $p(2k)$ is the number of ways in which k bonds are so chosen from the π system of the hydrocarbon that no two of them are connected to each other,[24] and j is half the number of carbon atoms. By definition, $p(0)$ is equal to unity. The summation of $p(2k)$ over all k values gives Hosoya's topological index.[24] Such a reference polynomial is always an even function of X for even-membered conjugated hydrocarbons, so that, if X_i is a root of $R(X) = 0$, $-X_i$ is also a root.

Now, let us examine the physical meaning of the reference polynomial. In method A-I, every root of $P_{nm}(X) = 0$ for a periodic type-I system is expressed as a function of cos Λ_{nm}. By analogy with solid state theory,[25] when n is large enough, the kth roots $X_k(\cos \Lambda_{nm})$ for all m values are considered to form the kth energy band as a whole. Conversely, the kth energy band in the type-I system is said to accommodate densely n π levels specified by the number m.

From another viewpoint, each energy level in a given compound II is considered to split into n levels in the corresponding type-I system with n unit structures. Therefore, the reference energy adopted in method A-I is nothing else but the sum of the averaged band energies over all occupied energy bands. The averaged band energies may be termed the π-orbital energies of the reference structure.

On the other hand, we have averaged the coefficients of $P_{\rm nm}(X)$ of the infinitely large type-I system to obtain the coefficients of $R(X)$ for the corresponding type-II system. For the following reason, this might be considered as a kind of random phase approximation,[26] applied to the linear periodic lattice. It is interpreted as the expectation that the averaged band energies might be represented fairly well by the roots of $R(X) = 0$, because the Λ_{nm} dependence of the π energies of all levels in every band might tend to cancel. We expect that the averaged band energies derived from $P_{nm}(X) = 0$ are close to the roots of the same equation, the coefficients of which are instead averaged, namely,

$$\overline{X_k(\cos \Lambda_{nm})} \approx X_k(\overline{\cos \Lambda_{nm}}) \tag{16}$$

where the bar is indicative of the arithmetic average. As long as this holds fairly well, the roots of $R(X) = 0$ can also be regarded as the π-orbital energies of the reference structure. The reference polynomial itself can hence be assumed to be a characteristic polynomial for the aromaticity-free reference structure.

This assumption leads to a new definition of Dewar-type resonance energies for monocyclic conjugated systems. The new reference energy is obtained by filling the π orbitals of the reference structure with the same number of π electrons as that of the actual molecular system, and then summing the π energies of all the occupied π orbitals. According to this definition, the resonance energy of a monocyclic conjugated system is calculated as the difference between the total HMO π energy of the system and the reference energy derived from $R(X) = 0$ of the same system. This method for evaluating the resonance energies is referred to as method A-II.

It is self-evident that the reference polynomial for any acyclic polyene is identical with the HMO characteristic polynomial for it, because both polynomials are exactly defined by eq 15. Accordingly, the resonance energy for the acyclic polyene completely vanishes, in accord with Dewar's finding that the acyclic polyene is nonaromatic.[3,4]

Resonance Energies of Monocyclic Hydrocarbons

In order to see the reasonableness of method A-II, it is most instructive to compare the resonance energies calculated by this method (A-II resonance energies) with those calculated by methods HS and A-I (HS resonance energies and A-I resonance energies). The resonance energies for monocyclic hydrocarbons, obtained by these three methods, are listed in Table I.

As is easily seen from Table I, the hydrocarbons predicted to be aromatic by methods HS and A-I are predicted to be aromatic by method A-II. Conversely, those predicted to be antiaromatic by them are predicted to be similarly antiaromatic by method A-II. Although the calculated resonance energies depend slightly upon the method adopted, we might safely say that the A-II resonance energies are in close parallel with the HS and A-I resonance energies. We note that, since methods HS and A-I are based on the additivity of π-bond energies in nonaromatic species, the obtained resonance energies are obviously of Dewar type. From the above comparative study, method A-II can also be considered to give Dewar-type resonance energies, at least, for monocyclic conjugated hydrocarbons. Interestingly, the sign of the A-II resonance energy exactly agrees with that of the A-I resonance energy for every hydrocarbon investigated, even though the absolute value of the resonance energy might often be very small.

As for annulenes, those with $(4n + 2)$ π electrons are predicted to be aromatic, and those with $4n$ π electrons are predicted to be antiaromatic. This is in exact accord with Hückel's $(4n + 2)$ rule of aromaticity.[27] Radialenes, fulvenes, and xylylenes are all predicted to be substantially nonaromatic. The antiaromatic character of dimethylenecyclobutene[28] was reproduced by method A-II. As stated by Hess and Schaad,[28] the relative experimental stability of dimethylenecyclobutene and the extreme instability of xylylenes[29] must be ascribed to some effects other than their degrees of aromaticity.

Resonance Energies of Heterocyclic Compounds

In evaluating the resonance energies for monocyclic hydrocarbons, we could safely neglect the effect of bond alternation on the π system, and all the resonance integrals were assumed to have a constant value. However, there are many π systems in which the effect of bond alternation cannot be neglected. In principle, method A-II, as well as method A-I, can be applied to these systems with little difficulty. First, we consider the aromaticity of monocyclic systems containing one or more heteroatoms, in which the resonance inte-

Table I. Resonance Energies in Units of β of Monocyclic Conjugated Hydrocarbons

Compd	Total π energy	Resonance energy		
		Method HS	Method A-I	Method A-II
Cyclobutadiene	4.000	−1.07[a]	−1.093	−1.226
Benzene	8.000	0.39[a]	0.361	0.273
Styrene	10.424	0.371	0.327	0.249
Cyclooctatetraene	9.657	−0.48[a]	−0.529	−0.595
[10]Annulene	12.944	0.26[a]	0.212	0.159
[12]Annulene	14.928	−0.29[a]	−0.351	−0.394
[14]Annulene	17.976	0.23[a]	0.151	0.113
[3]Radialene	7.301	−0.01[a]	0.005	0.009
[4]Radialene	9.657	−0.08[a]	−0.071	−0.072
[5]Radialene	12.160	−0.02[a]	0.000	0.000
[6]Radialene	14.601	−0.01[a]	0.009	0.009
Triafulvene	4.962	0.020	0.031	0.063
Fulvene	7.466	−0.01[a]	0.010	0.020
Heptafulvene	9.994	−0.02[a]	0.005	0.009
Dimethylenecyclobutene	7.208	−0.17[a]	−0.159	−0.163
o-Xylylene	9.954	0.040[b]	0.060	0.059
p-Xylylene	9.925	0.044[b]	0.062	0.061

[a] Reference 7. [b] Reference 29.

Table II. Heteroatom Parameters Adopted in This Work

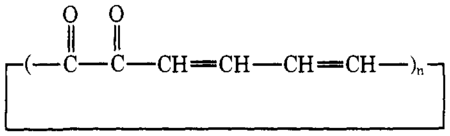
X	h_X	$k_{C\text{-}X}$
Ether oxygen (Ö)[a]	2.00	0.34
Ketone oxygen (Ȯ)[b]	0.22	0.99
Amine nitrogen (N̈)[a]	1.50	0.90
Imine nitrogen (N)[c]	0.38	0.70
Thioether sulfur (S)[d]	1.00	0.68

[a] Reference 10. [b] Reference 11. [c] Reference 13. [d] Reference 12.

grals for the carbon–heteroatom bonds must be changed from that for carbon–carbon bonds (β).

When HMO calculations are performed on these compounds, appropriate corrections must be made to the Coulomb integral for each heteroatom and to the resonance integral for each carbon–heteroatom bond. A considerable amount of effort has been devoted to estimating these heteroatom parameters.[1a] Among them, Hess et al. evaluated the heteroatom parameters for the amine nitrogen,[10] the imine nitrogen,[13] the ether oxygen,[10] the ketone oxygen,[11] and the thioether sulfur,[12] strictly on the basis of an experimental ground-state property, the heats of atomization. In the following calculations, we adopted these values, as they can be expected to be most suited to the estimation of another ground-state property, resonance energies. They are listed in Table II.

In order to estimate the resonance energies for heteroatom-containing monocyclic systems, the reference polynomials must be determined for them. Although we cannot apply eq 15 to the heterocycle, the reference polynomial can be obtained by deriving first $P_{nm}(X)$ for the corresponding type-I system, and then replacing the cosines in the coefficients by zero. For example, the reduced secular equation



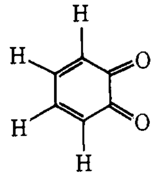
$$\left(-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-CH{=}CH-CH{=}CH-\right)_n$$

V

for the system V is derived as

$$\begin{aligned}P_{nm}(X) = {} & X^8 - 2h_{\dot{O}}X^7 \\ & - (6 + 2k_{C\text{-}\dot{O}}^2 - h_{\dot{O}}^2)X^6 + (12h_{\dot{O}} + 2h_{\dot{O}}k_{C\text{-}\dot{O}}^2)X^5 \\ & + (9 + 8k_{C\text{-}\dot{O}}^2 + k_{C\text{-}\dot{O}}^4 - 6h_{\dot{O}}^2)X^4 \\ & - (18h_{\dot{O}} + 8h_{\dot{O}}k_{C\text{-}\dot{O}}^2)X^3 \\ & - (2 + 6k_{C\text{-}\dot{O}}^2 + 3k_{C\text{-}\dot{O}}^4 - 9h_{\dot{O}}^2 + 2\cos\Lambda_{nm})X^2 \\ & + (4h_{\dot{O}} + 6h_{\dot{O}}k_{C\text{-}\dot{O}}^2 + 4h_{\dot{O}}\cos\Lambda_{nm})X \\ & - (k_{C\text{-}\dot{O}}^4 - 2h_{\dot{O}}^2 - 2h_{\dot{O}}^2\cos\Lambda_{nm}) = 0 \qquad (17)\end{aligned}$$

From these equations, the reference polynomial for *o*-benzoquinone (VI) is straightforwardly given as



VI

$$\begin{aligned}R(X) = {} & X^8 - 2h_{\dot{O}}X^7 \\ & - (6 + 2k_{C\text{-}\dot{O}}^2 - h_{\dot{O}}^2)X^6 + (12h_{\dot{O}} + 2h_{\dot{O}}k_{C\text{-}\dot{O}}^2)X^5 \\ & + (9 + 8k_{C\text{-}\dot{O}}^2 + k_{C\text{-}\dot{O}}^4 - 6h_{\dot{O}}^2)X^4 \\ & - (18h_{\dot{O}} + 8h_{\dot{O}}k_{C\text{-}\dot{O}}^2)X^3 \\ & - (2 + 6k_{C\text{-}\dot{O}}^2 + 3k_{C\text{-}\dot{O}}^4 - 9h_{\dot{O}}^2)X^2 \\ & + (4h_{\dot{O}} + 6h_{\dot{O}}k_{C\text{-}\dot{O}}^2)X - (k_{C\text{-}\dot{O}}^4 - 2h_{\dot{O}}^2) = 0 \qquad (18)\end{aligned}$$

The A-II resonance energies for typical heterocycles were obtained from such reference polynomials. They are listed in Table III, and are therein compared with those calculated by methods HS and A-I. The close resemblance between the A-II resonance energies and those calculated by the other two methods is also found for these heterocyclic systems, and the validity of method A-II therefore seems to be supported. This fact also strongly suggests that eq 16 widely holds very well.

The striking aspect of the resonance energies for heteroannulenes is a strong alternation between aromaticity and antiaromaticity.[15] When the heteroannulene is a $(4n + 2)$-π-electron system, it is predicted to be aromatic. When the heteroannulene is a $4n$-π-electron system, it is predicted to be antiaromatic. Such a trend in aromatic character is common to all heteroannulenes containing single heteroat-

Table III. Resonance Energies in Units of β of Monocyclic Compounds Containing Heteroatoms

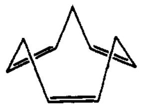
Compd	Total π energy	Resonance energy		
		Method HS	Method A-I	Method A-II
1*H*-Azirine	2.000	−0.666	−0.659	−0.725
Pyrrole	5.435	0.233	0.279	0.242
1*H*-Azepine	7.447	−0.291	−0.261	−0.288
1*H*-Azonine	10.413	0.139	0.155	0.134
Oxirene	2.000	−0.018	−0.221	−0.230
Furan	4.598	0.044	0.044	0.044
Oxepin	7.039	−0.051	−0.033	−0.034
Oxonin	9.627	0.001	0.025	0.024
Thiirene	2.000	−0.457	−0.605	−0.666
Thiophene	5.186	0.193	0.225	0.200
Thiepin	7.296	−0.232	−0.209	−0.228
Thionin	10.182	0.118	0.132	0.116
o-Benzoquinone	9.940	0.033	0.053	0.053
p-Benzoquinone	9.914	0.036	0.056	0.055
α-Pyrone	7.081	0.031	0.010	0.010
γ-Pyrone	6.999	0.042	0.010	0.010
Cyclopropenone	5.065	0.126	0.136	0.164
Cyclopentadienone	7.381	−0.094	−0.077	−0.070
Tropone	10.064	0.053	0.070	0.071
Pyridine	7.249	0.348	0.291	0.230
Phenol	8.035	0.382	0.359	0.272
Thiophenol	8.205	0.376	0.333	0.259
Aniline	8.294	0.369	0.330	0.257
Benzaldehyde	10.421	0.372	0.323	0.248

oms, and indicates that Hückel's ($4n + 2$) rule[27] can be extended to such heterocycles as heteroannulenes. Of course, their chemistry is in good agreement with these predictions.[10,12,15]

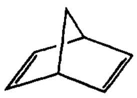
The calculated resonance energies for benzoquinones and pyrones suggest that these compounds are almost nonaromatic in accord with their chemistry.[30,31] Cyclopropenone and tropone appear to be somewhat aromatic, while cyclopentadienone is slightly antiaromatic. Pyridine and monosubstituted benzenes are supposedly as aromatic as benzene. These interpretations are quite consistent with those of Hess and Schaad.[11,13]

Resonance Energies of Homoconjugative Systems

Another typical π system in which the effect of bond alternation is of special significance is a homoconjugative system.[32] The homoconjugation among π bonds, spatially separated from each other, might give rise to substantial effects, if the π bonds are arranged in such a way that the across-space interaction between the neighbors leads to a closed loop over which the π electrons can be delocalized.

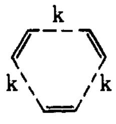


VII

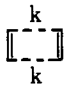


VIII

Here, we consider the aromaticity of two classical homoconjugative hydrocarbons, cyclononatriene (VII) and norbornadiene (VIII). The π frameworks of these compounds are illustrated respectively as IX and X. In these systems,



IX



X

isolated double bonds are arranged in favor of such homoconjugation.

As in the case of heterocycles, the $P_{nm}(X)$-type polynomial for the corresponding type-I system must first be determined. For example, it is determined for the type-I system corresponding to cyclononatriene as

$$P_{nm}(X) = X^6 - (3 + 3k^2)X^4 + (3 + 3k^2 + 3k^4)X^2 - (1 + k^6 + 2k^3 \cos \Lambda_{nm}) = 0 \quad (19)$$

Then the reference polynomial for cyclononatriene is

$$R(X) = X^6 - (3 + 3k^2)X^4 + (3 + 3k^2 + 3k^4)X^2 - (1 + k^6) = 0 \quad (20)$$

Here, k signifies the ratio of the resonance integral between the neighboring nonbonded sp^2-carbon atoms to that between the directly bonded sp^2-carbon atoms.

As is shown in Table IV, the A-II resonance energies for the two homoconjugative hydrocarbons were calculated as a function of k. Although the HS resonance energies are lacking, the reasonableness of the A-II resonance energies is supported fairly well by comparing them with the A-I resonance energies. The absolute values of the resonance energies for the two systems are found to rapidly increase as the degree of bond alternation ($1/k$) decreases.

In order to estimate correctly the resonance energies for cyclononatriene and norbornadiene, the k values must be adjusted to the actual π systems. Fortunately, Bischof et al. determined the k values for these compounds from the photoelectron spectra:[33] cyclononatriene, 0.25; norbornadiene, 0.15.

The k value of 0.25 for cyclononatriene corresponds to the resonance energy of 0.011 according to both methods. This amount of π energy is only 3–4% of the total resonance energy of benzene ($k = 1.00$). Therefore, cyclononatriene can be regarded as a substantially nonaromatic species. This result rationalizes the absence of any indication of homoaromaticity in the molecular structure and the heat of hydrogenation[34] or in the NMR data.[35] The calculated resonance energy for this compound appears to be comparable to the experimental error of the heat of hydrogenation. For reference, the thermochemical β value was reported to be

Table IV. Resonance Energies in Units of β of Homoconjugative Hydrocarbons

k	Total π energy	Resonance energy Method A-I	Resonance energy Method A-II
A. Cyclononatriene-Type 6-π-Electron System			
0.00	6.000	0.000	0.000
0.10	6.016	0.001	0.001
0.20	6.066	0.006	0.006
0.30	6.155	0.020	0.019
0.40	6.287	0.045	0.044
0.50	6.464	0.083	0.079
0.60	6.687	0.134	0.124
0.70	6.955	0.194	0.173
0.80	7.266	0.259	0.217
0.90	7.616	0.320	0.252
1.00	8.000	0.361	0.273
B. Norbornadiene-Type 4-π-Electron System			
0.00	4.000	0.000	0.000
0.10	4.000	−0.010	−0.010
0.20	4.000	−0.040	−0.041
0.30	4.000	−0.091	−0.093
0.40	4.000	−0.162	−0.169
0.50	4.000	−0.254	−0.272
0.60	4.000	−0.369	−0.403
0.70	4.000	−0.507	−0.564
0.80	4.000	−0.671	−0.756
0.90	4.000	−0.864	−0.978
1.00	4.000	−1.093	−1.226

−32.74 kcal/mol.[2b] It is also evident that for k less than 0.3 bond alternation is too large to allow for a noticeable ring current.

In the same manner, norbornadiene with $k = 0.15$ is predicted to be negligibly antiaromatic with a resonance energy of −0.023. We note that the calculated resonance energy for a square-planar cyclobutadiene is less than −1.0. Although norbornadiene is fairly reactive,[36] it is strongly suggested that the stability of that degree is due to the introduction of marked bond alternation, which dissipates most of the great antiaromaticity inherent in the 4-π-electron system.

Resonance Energies of Carbocyclic Ions

No one has ever attempted to estimate Dewar-type resonance energies of ionic conjugated species such as annulene ions. In general these are classified as nonclassical ions.[32,37] Even though the ion is an open-chain system, the additivity of π-bond energies as formulated by Hess and Schaad[7] can no longer be applied.

However, as in the case of the neutral species, an infinitely large annulene which bears formal charges should be neither aromatic nor antiaromatic. Therefore, the unit π energy of the infinitely large charged annulene can be used for evaluating the aromatic stability of the monocyclic $C_pH_p{}^q$ series. For the estimation of the reference energy for a given $C_pH_p{}^q$. the ratio of the number of additional charges to the number of carbon atoms in the infinitely large annulene must first be adjusted to that of the ion in question (q/p). For example, the reference energy for the cycloheptatrienyl cation ($C_7H_7{}^+$) must be derived from the unit π energy of the infinitely large annulene from which a seventh part of the π electrons are removed.

After a simple treatment of the analytical expression for the π-orbital energies of annulene,[38] the reference energy (E_{ref}) for $C_pH_p{}^q$ is given by

$$E_{\text{ref}}(C_pH_p{}^q) = \frac{4p}{\pi}\cos\left(\frac{q\pi}{2p}\right) \qquad (21)$$

Table V. Resonance Energies in Units of β of Annulene Ions

Species	Total π energy	Resonance energy Method A-I	Resonance energy Method A-II
A. 2-π-Electron Systems			
$C_3H_3{}^+$	4.000	0.692	0.536
$C_4H_4{}^{2+}$	4.000	0.399	0.305
B. 4-π-Electron Systems			
$C_3H_3{}^-$	2.000	−1.308	−1.464
C_4H_4	4.000	−1.093	−1.226
$C_5H_5{}^+$	5.236	−0.819	−0.919
$C_6H_6{}^{2+}$	6.000	−0.616	−0.692
C. 6-π-Electron Systems			
$C_4H_4{}^{2-}$	4.000	0.399	0.305
$C_5H_5{}^-$	6.472	0.418	0.317
C_6H_6	8.000	0.361	0.273
$C_7H_7{}^+$	8.988	0.299	0.225
$C_8H_8{}^{2+}$	9.657	0.246	0.186
D. 8-π-Electron Systems			
$C_6H_6{}^{2-}$	6.000	−0.616	−0.692
$C_7H_7{}^-$	8.098	−0.591	−0.665
C_8H_8	9.657	−0.529	−0.595
$C_9H_9{}^+$	10.823	−0.462	−0.520
$C_{10}H_{10}{}^{2+}$	11.708	−0.401	−0.451
E. 10-π-Electron Systems			
$C_8H_8{}^{2-}$	9.657	0.246	0.186
$C_9H_9{}^-$	11.518	0.233	0.175
$C_{10}H_{10}$	12.944	0.212	0.159
$C_{11}H_{11}{}^+$	14.053	0.190	0.143
$C_{12}H_{12}{}^{2+}$	14.928	0.170	0.128
F. 12-π-Electron Systems			
$C_{10}H_{10}{}^{2-}$	11.708	−0.401	−0.451
$C_{11}H_{11}{}^-$	13.484	−0.379	−0.426
$C_{12}H_{12}$	14.928	−0.351	−0.394
$C_{13}H_{13}{}^+$	16.110	−0.321	−0.361
$C_{14}H_{14}{}^{2+}$	17.086	−0.293	−0.329

The A-I resonance energies for annulene ions can easily be obtained with this expression.

On the other hand, we stated before that the roots of $R(X) = 0$ for a conjugated system can be interpreted as the π-orbital energies of the reference structure for it, because they represent a kind of mean band energies of the corresponding infinitely large type-I system. This interpretation tempts us to predict the aromaticity of the annulene ions with the use of method A-II.

The reference energy for a given ion is then given, as before, by filling the π orbitals of the reference structure for it with the same number of π electrons as that of the actual ion. The obtained results for a series of annulene ions are presented in Table V. Although the HS resonance energies cannot be defined for them, the general agreement between the A-II and A-I resonance energies provides further justification for method A-II and, especially, for eq 16.

It is clear from Table V that the number of π electrons is a determinant of aromaticity. All species with $(4n + 2)$ π electrons are predicted to be aromatic. All species with $4n$ π electrons are predicted to be antiaromatic. Aromaticity or antiaromaticity is found to decrease as the ring size increases. When p is even, the resonance energy of $C_pH_p{}^q$ is equal to that of $C_pH_p{}^{-q}$. The signs of the calculated resonance energies are in exact accord with available experimental evidence.[39] This approach gives the best verification of Hückel's $(4n + 2)$ rule of aromaticity[27] within the HMO theory.

In this relation, some attempts have been made to estimate the resonance energies for these cyclic ions by com-

Table VI. Resonance Energies in Units of β of Polycyclic Conjugated Hydrocarbons

Compd	Total π energy	Resonance energy	
		Method HS	Method A-II
Butalene	7.657	−0.40[a]	−0.604
Pentalene	10.456	−0.141[b]	−0.215
Naphthalene	13.683	0.55[a]	0.389
Heptalene	15.618	−0.050[b]	−0.141
Octalene	18.103	−0.10[a]	−0.259
Benzocyclobutadiene	10.381	−0.22[a]	−0.393
Azulene	13.364	0.231[b]	0.151
Triafulvalene	7.464	−0.60[a]	−0.461
Calicene	10.939	0.35[a]	0.433
Fulvalene	12.799	−0.33[a]	−0.299
Sesquifulvalene	15.931	0.27[a]	0.272
Heptafulvalene	18.005	−0.20[a]	−0.218
Diphenyl	16.383	0.72[a]	0.502
Biphenylene	16.505	0.33[a]	0.123
Stilbene	18.878	0.71[a]	0.481
1,2-Naphthalenequinododimethide	15.802	0.338[c]	0.258
2,3-Naphthalenequinododimethide	15.532	0.093[c]	0.141
Naphtho[*a*]cyclobutadiene	15.996	−0.15[a]	−0.384
Naphtho[*b*]cyclobutadiene	16.200	0.08[a]	−0.114
Acenaphthylene	16.619	0.47[a]	0.354
s-Indacene	16.231	0.110[b]	0.055
as-Indacene	15.899	−0.249[b]	−0.306
Cyclopent[*cd*]azulene	16.366	0.220[b]	0.101
Aceheptylene	18.911	0.229[b]	0.106
Anthracene	19.314	0.66[a]	0.475
Phenanthrene	19.448	0.77[a]	0.546
Pyrene	22.505	0.81[a]	0.598

[a] Reference 7. [b] Reference 9. [c] Reference 29.

paring the π energy of the ion with that of a corresponding open-chain system. According to this principle, Dewar presented PPP results on the aromaticity of some carbocyclic ions.[40] Hobey estimated the resonance energies of annulene ions with a free electron molecular orbital (FEMO) model.[41] However, one of the difficulties in using an acyclic conjugated system as a reference structure is that the geometry of the ion and the number of π bonds are not preserved in it. To make matters worse, the FEMO model cannot reproduce even the established additivity of π-bond energies for a neutral species. Our reference energies are evidently free from these difficulties. The contributions from all π bonds are counted in the reference energies. It goes without saying that the applicability of methods A-I and A-II is not restricted to the above carbocyclic ions. The methods can be applied to any monocyclic ion.

Resonance Energies of Polycyclic Hydrocarbons

In the preceding sections, we have repeatedly verified the validity of method A-II by comparing the results with those obtained by methods HS and A-I. As far as the monocyclic conjugated systems are concerned, it can be concluded that the A-II resonance energies are as reasonable as the A-I resonance energies, in that they precisely correlate with the HS resonance energies. It seems to us that even some ambiguity in the HS resonance energies can be avoided by using either method A-I or method A-II. For example, the HS resonance energy of oxirene (Table III) is negligible, although it has never been isolated. The resonance energy of this compound appears to be much improved by our two methods.

Unfortunately, method A-I can be applied only to monocyclic conjugated systems. In other words, the periodic type-I system cannot be imagined for any polycyclic conjugated system, although many polycyclic systems are known as aromatic. Since the $P_{nm}(X)$-type polynomial cannot be defined for these systems, the reference energy cannot be derived from eq 8. Method A-II in its original form cannot be applied to the polycyclic systems, either, because there is no $P_{nm}(X)$-type polynomial from which the reference polynomial must be derived.

In order to overcome this difficulty, let us stop using eq 9 and 10 as a definition of the reference polynomial. Instead, we adopt eq 15 as a new definition of the reference polynomial. By inspection of the reference polynomials for various monocyclic hydrocarbons, we noticed before that all the contributions from cyclic components of the molecular graph are missing in the coefficients of the reference polynomial. As far as the monocyclic hydrocarbons are concerned, the aromaticity is undoubtedly associated with the cyclic structure of the π system. On this basis, we assume that the reference polynomial for a polycyclic conjugated hydrocarbon can also be obtained by excluding from the coefficients of the HMO characteristic polynomial all the contributions from cyclic components of the corresponding molecular graph. For example, the HMO characteristic polynomial for naphthalene is

$$P(X) = X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9 \quad (22)$$

while the reference polynomial for the same compound is then given as

$$R(X) = X^{10} - 11X^8 + 41X^6 - 61X^4 + 31X^2 - 3 \quad (23)$$

The resonance energy for a polycyclic hydrocarbon is defined as before from these two types of polynomials. Since this definition necessarily includes that given to the monocyclic conjugated hydrocarbon, the obtained resonance energy is similarly termed the A-II resonance energy.

However, the definition of the A-II resonance energy for a polycyclic hydrocarbon is not based on a physical inter-

Table VII. Resonance Energies in Units of β of Polycyclic Heterocyclic Compounds

Compd	Total π energy	Resonance energy	
		Method HS	Method A-II
Indole	11.236	0.466[a]	0.375
Benzofuran	10.526	0.356[a]	0.272
Benzo[*b*]thiophene	11.011	0.443[b]	0.349
Quinoline	12.598	0.516[c]	0.356
Isoquinoline	12.559	0.514[c]	0.351
Cycl[3.2.2]azine	14.136	0.475[a]	0.400
Cycl[3.3.3]azine	16.424	0.015[a]	0.145
Tetrathiofulvalene	7.669	0.282	0.032

[a] Reference 10. [b] Reference 12. [c] Reference 13.

pretation because a relation like eq 16 does not exist for the polycyclic system. The only way of judging the validity of method A-II in this extended form is to examine extensively the numerical results with a variety of polycyclic conjugated hydrocarbons. The A-II resonance energies for these compounds, calculated in this manner, are listed in Table VI. They are therein compared with the HS resonance energies.

It is clear from Table VI that the agreement between these two sets of resonance energies is excellent for all polycyclic hydrocarbons investigated. As the A-II resonance energies were calculated independently by quite a different method, it is strongly suggested that the agreement is not accidentally attained. We emphasize that, in line with the HS resonance energies, the A-II resonance energies are all satisfactorily of Dewar type. This fact indicates that the reference energy derived from the reference polynomial can always be regarded as the total HMO π energy of the aromaticity-free reference structure.

All benzenoid hydrocarbons are predicted to be stable enough. The introduction of a four-membered ring results in a great decrease in the stability of the entire π system. Symmetric fulvalenes and *as*-indacene are predicted to be antiaromatic, whereas asymmetric fulvalenes and *s*-indacene are predicted to be aromatic. Two Hafner hydrocarbons,[42] cyclopent[*cd*]azulene and aceheptylene, are suggested to be slightly aromatic. The correlation between the resonance energies for these compounds and their chemical behavior has been fully examined and discussed by Hess and Schaad[7-9] and Gleicher et al.[29]

From the above comparative study, it has been established that, as in the case of a monocyclic hydrocarbon, the resonance energy of a polycyclic hydrocarbon is closely related to the cyclic structure of the π system. In this sense, method A-II in its extended form fulfills our chemical sense that the aromatic stabilization must arise from the cyclic structure of the π system.

The following consideration might give a further understanding of the A-II resonance energies. By Dewar's definition,[3,4] the reference structure of any conjugated hydrocarbon is a hypothetical polyene. Therefore, it should be alternant. It must be remembered that the reference polynomial $R(X)$ for a polycyclic hydrocarbon is correspondingly constructed in the same manner as the HMO characteristic polynomial for an alternant acyclic polyene,[22,24] neglecting all the contribution from cyclic components of the molecular graph. As in the case of a monocyclic hydrocarbon, it is an even function of X, because the conjugated hydrocarbons of interest are all even membered. Therefore, when X_i is a root of $R(X) = 0$, $-X_i$ is also a root. We also remember that the alternant hydrocarbon is characterized by such a pairing theorem.[43] Accordingly, the assumption of Hess and Schaad[7] that the reference structure for a cyclic conjugated hydrocarbon can be constructed with appropriate π bonds of acyclic polyenes seems to be visualized by the omission of cyclic components of the molecular graph.

From this viewpoint, method A-II in its extended form may give an exact reference energy for any conjugated hydrocarbon, because the obtained reference polynomial satisfies the pairing theorem. If this is true, method A-II must be preferred to method A-I. In this case, it is necessary that the additivity of π-bond energies must be modified for the olefinic reference structure. When method A-II is employed, the reference energy often deviates slightly from strict additivity of π-bond energies. For example, the A-I reference energy of benzene (7.639) is exactly half the A-I reference energy of [12]annulene. However, it is not true for the A-II reference energies; the A-II reference energies are 7.727 for benzene and 15.322 for [12]annulene. In all events, the difference between the A-I and A-II reference energies is slight, and of no practical significance.

Resonance Energies of Polycyclic Heterocyclic Compounds

The surprising success of method A-II in predicting the aromaticities of polycyclic hydrocarbons suggests that, if a graph-theoretical method for constructing the HMO characteristic polynomial for a heteroatom-containing polycyclic system were available, method A-II could be used to predict the aromaticity of the heterocycle in the same manner.

In 1974, Mallion et al. reported on the method for graphically determining the coefficients of the HMO characteristic polynomial for the heterocyclic compound, on the assumption that the resonance integrals are all equal in the π system.[44] For the present purpose an extension of this method including the hetero-bond parameters has now been developed, and a computer program written to carry out the tedious enumeration of the coefficients.[45] The reference polynomial for the heterocycle again has cyclic components of the molecular graph excluded.

The A-II resonance energy for a heterocycle is analogously defined as the difference between the total π energy calculated from the HMO characteristic polynomial and that calculated from the corresponding reference polynomial. The A-II resonance energies for heteroatom-containing monocyclic systems (Table III) are of course in harmony with this definition.[45] Table VII contains a list of the A-II resonance energies calculated for the polycyclic compounds containing heteroatoms.

The correlation between the A-II and HS resonance energies for these compounds seems to be reasonable, as compared with the correlation for the polycyclic hydrocarbons. The A-II resonance energies for indole, benzofuran, and benzo[*b*]thiophene are distributed between the resonance energies for benzene and naphthalene (Tables I and VI). The A-II resonance energies for quinoline and isoquinoline are comparable to that for naphthalene. The same situation is encountered among the HS resonance energies. In accord with the prediction of Hess et al.,[10] cycl[3.2.2]azine is predicted to be much more aromatic than cycl[3.3.3]azine.

However, the A-II resonance energy for tetrathiofulvalene is considerably smaller than the HS resonance energy for it. According to the HMO calculation, the highest occupied π orbital of this compound has an antibonding character. The iso-π-electronic hydrocarbon, heptafulvalene, was predicted to be antiaromatic (Table VI). In addition, this compound is easily oxidized to the cation radical.[46] Considering these properties of tetrathiofulvalene, our prediction of the resonance energy for it appears to be more probable.

In a previous paper,[15] we suggested that the electronegativity of the heteroatom influences the π energies of the nearby π bonds. Owing to this effect, when the carbon–heteroatom bonds are predominant in the π system, the deviation of the HS resonance energy from the A-I resonance energy may sometimes be magnified. A good example is oxirene, for which the HS resonance energy is much larger than the A-II or A-I resonance energy (Table III). Another example may be tetrathiofulvalene, because eight of its eleven π bonds are carbon–sulfur bonds.

Concluding Remarks

As has been seen above, it has been clearly established that method A-II gives Dewar-type resonance energies for all kinds of conjugated systems, including conjugated hydrocarbons, heterocycles, and cyclic conjugated ions, within the framework of the HMO theory. It has also been verified that the Dewar-type resonance energy is a topological quantity, depending solely upon the cyclic structure of the π system. The HMO theory is only one MO theory which can verify the topological nature of calculated resonance energies. Method A-II, based on graph theory,[22] can now be considered as a much more straightforward and less ambiguous method for obtaining the Dewar-type resonance energy, although quite a similar result can be obtained by method HS. This is exclusively ascribed to the reference polynomial defined without ambiguity. The uniqueness of the obtained resonance energy is characteristic of method A-II.

A comparison of the HMO results with the PPP results[4] has been made by Schaad and Hess,[2] and these methods along with resonance theory results have been compared by Herndon and Ellzey.[17] They concluded that the HS resonance energies are at least as reasonable as those derived by the PPP method. The same conclusion applies to our A-II resonance energies. We have neglected some energy terms, such as strain energy and σ-compression energy, in the HMO calculations. Nevertheless, a good correlation found between calculated resonance energies and experimental properties for a wide variety of conjugated systems evidently supports that the A-II resonance energies can be regarded as excellent aromaticity indices.

Acknowledgment. The author wishes to thank Professor Kimio Ohno for helpful discussions. The use of the facilities of the Hokkaido University Computing Center is acknowledged.

References and Notes

(1) For reviews, see (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961; (b) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y., 1966; (c) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.

(2) (a) L. J. Schaad and B. A. Hess, Jr., *J. Am. Chem. Soc.*, **94**, 3068 (1972); (b) *J. Chem. Educ.*, **51**, 640 (1974).

(3) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692 (1965).

(4) M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

(5) 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).

(6) N. C. Baird, *Can. J. Chem.*, **47**, 3535 (1969); *J. Chem. Educ.*, **48**, 509 (1971).

(7) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305 (1971).

(8) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 2413 (1971).

(9) B. A. Hess, Jr., and L. J. Schaad, *J. Org. Chem.*, **36**, 3418 (1971).

(10) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 3657 (1972).

(11) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 5299 (1972).

(12) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **95**, 3907 (1973).

(13) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **31**, 295 (1975).

(14) J. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 517 (1975).

(15) J. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 1501 (1975).

(16) W. C. Herndon, *J. Am. Chem. Soc.*, **95**, 2404 (1973); *J. Chem. Educ.*, **51**, 10 (1974).

(17) W. C. Herndon and M. L. Ellzey, Jr., *J. Am. Chem. Soc.*, **96**, 6631 (1974).

(18) C. F. Wilcox, Jr., *Tetrahedron Lett.*, 795 (1968); *J. Am. Chem. Soc.*, **91**, 2732 (1969); W. C. Herndon, *Tetrahedron*, **29**, 3 (1973).

(19) R. Swinborne-Sheldrake, W. C. Herndon, and I. Gutman, *Tetrahedron Lett.*, 755 (1975).

(20) I. Gutman, N. Trinajstić, and C. F. Wilcox, Jr., *Tetrahedron*, **31**, 143 (1975); C. F. Wilcox, Jr., I. Gutman, and N. Trinajstić, *ibid.*, **31**, 147 (1975).

(21) H. Hosoya, K. Hosoi, and I. Gutman, *Theor. Chim. Acta*, **38**, 37 (1975).

(22) 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); their graph theory is based on the Sachs theorem [H. Sachs, *Publ. Math. (Debrecen)*, **11**, 119 (1963)].

(23) At present there is no definite proof for eq 8. In order to confirm that the first j roots of $P_{nm}(X) = 0$ for any Λ_{nm} (i.e., $2\pi x$) represent occupied energy levels, every root of $P_{nm}(X) = 0$ must separately be traced as a function of x. It is, however, clear from a band-theoretical viewpoint[25] that eq 8 exactly holds as long as the infinitely large type-I system is nonmetallic. Even if the system is metallic, eq 8 seems to hold true mostly. Strictly speaking, the roots of $P_{nm}(X) = 0$ for a type-I system of finite size must also be examined in the same manner. In order to compute E_U according to eq 8, a function of x (integrand) must first be defined as the sum of the first j roots of $P_{nm}(X) = 0$, each root being x dependent. The function at $x = x'$ is evaluated by numerically solving $P_{nm}(X) = 0$ for the x'. Then the E_U is given by numerically integrating the function from $x = 0$ to 1.

(24) H. Hosoya, *Bull. Chem. Soc. Jpn.*, **44**, 2332 (1971); *Theor. Chim. Acta*, **25**, 215 (1972); *Fibonacci Q.*, **11**, 255 (1973).

(25) C. Kittel, "Introduction to Solid State Physics", Wiley, New York, N.Y., 1956, Chapter 11.

(26) R. P. Feynman, "Statistical Mechanics", W. A. Benjamin, Reading, Mass., 1972, Chapter 9.

(27) E. Hückel, *Z. Phys.*, **70**, 204 (1931); **78**, 628 (1932).

(28) B. A. Hess, Jr., and L. J. Schaad, *Aust. J. Chem.*, **25**, 2231 (1972).

(29) G. J. Gleicher, D. D. Newkirk, and J. C. Arnold, *J. Am. Chem. Soc.*, **95**, 2526 (1973).

(30) K. T. Finley in "The Chemistry of the Quinonoid Compounds", Part 2, S. Patai, Ed., Wiley, London, 1974, Chapter 17.

(31) A. Albert, "Heterocyclic Chemistry", Athlone Press, London, 1959, Chapter 7.

(32) S. Winstein, *Q. Rev., Chem. Soc.*, 141 (1969); P. J. Garratt, "Aromaticity", McGraw-Hill, London, 1971, Chapter 7.

(33) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).

(34) W. R. Roth, W. P. Bang, P. Göbel, R. L. Sass, R. B. Turner, and A. P. Yü, *J. Am. Chem. Soc.*, **86**, 3178 (1964).

(35) K. G. Untch and R. J. Kurland, *J. Mol. Spectrosc.*, **14**, 156 (1964).

(36) T. Sasaki, S. Eguchi, M. Sugimoto, and F. Hibi, *J. Org. Chem.*, **37**, 2317 (1972).

(37) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965.

(38) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations", Pergamon Press, Oxford, 1965.

(39) F. Sondheimer, *Acc. Chem. Res.*, **5**, 81 (1972); D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds", Elsevier, Amsterdam, 1966.

(40) Reference 1c, Chapter 5.

(41) W. D. Hobey, *J. Org. Chem.*, **37**, 1137 (1972).

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

(43) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Philos. Soc.*, **36**, 193 (1940).

(44) R. B. Mallion, A. J. Schwenk, and N. Trinajstić, *Croat. Chem. Acta*, **46**, 171 (1974).

(45) Unpublished work of the author.

(46) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1435 (1970); J. P. Ferraris, D. O. Cowan, V. V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).