General Rules for Constructing Hückel Molecular Orbital Characteristic Polynomials

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Abstract: Graph-theoretical rules for evaluating the coefficients of an HMO characteristic polynomial, applicable to all conjugated systems, are presented. They represent an extension of earlier graph-theoretical formulas for conjugated hydrocarbons. The topological nature of the coefficients of the HMO characteristic polynomial can straightforwardly be understood by means of these rules. Moreover, they are essential to the graphical theory of aromaticity recently formulated by us. A quantitative expression is given between the same coefficients and the total π energy for heteroconjugated systems.

The direct expansion of an HMO secular determinant of a conjugated compound into a polynomial, i.e., an HMO characteristic polynomial, is neither practical nor does it clarify any relation between the values of the coefficients and the geometry of the π-electron network. In order to overcome this difficulty, considerable effort has been devoted to finding graphical (or graph-theoretical) techniques for constructing the characteristic polynomial.[1]

In 1972, the first general solution of this problem, applicable to conjugated hydrocarbons, was presented by Graovac et al.[2,3] They pointed to a method for enumerating the coefficients of the characteristic polynomial for these compounds by means of Sachs' graph-theoretical theorem (Sachs theorem).[4] On the assumption that all resonance integrals have a constant value, the coefficients were nicely expressed with his graph-theoretical terms. Hosoya independently presented an alternate method for enumerating the same coefficients[5] by correlating them with his topological index.[6] It can easily be shown that these two approaches are equivalent.[3]

Assuming constant resonance integrals, Mallion et al. extended the graphical method for constructing the characteristic polynomial to conjugated systems with heteroatoms.[7] However, the assumption of constant resonance integrals itself is of limited chemical interest because a realistic consideration of actual conjugated systems with heteroatoms leads to two or more types of resonance integrals.[8] Even for conjugated hydrocarbons, bond alternation diversifies the resonance integrals.[8] Their approach must hence be extended to be suitable to any conjugated systems.

On the other hand, we recently developed a graphical theory of aromaticity.[9] An HMO reference polynomial was therein defined by excluding from the coefficients of the characteristic polynomial all contributions from cyclic components in the π system. The reference polynomial could be interpreted as a characteristic polynomial for the aromaticity-free reference structure. The resonance energy was then defined as the difference between the total π energy calculated from the characteristic polynomial and that calculated from the reference polynomial. Our theory of aromaticity thus requires the values of the coefficients of the characteristic polynomial. In order to extend this theory to heteroconjugated systems, a graphical method for constructing the characteristic polynomials is indispensable. For these reasons, we undertook to seek the method for graphically constructing the characteristic polynomial for conjugated systems with heterobonds.

On a Graph-Theoretical Formula for Heteroconjugated Systems. We begin by recalling the graphical method presented by Mallion et al.[7] for constructing the characteristic polynomial. According to them, a molecular graph (i.e., a π-electron network) of a conjugated compound with heteroatoms can be depicted by the use of a so-called self-loop representation.[10] Each heteroatom in the molecular graph is specified by the addition of a self-loop with a weight of h (its heteroatom parameter). The self-loop can hence be considered as a hypothetical π bond, both ends of which reach the same heteroatom. Such a self-loop can also be counted as one of the components of a Sachs graph. Only one atom is assigned to it. A definition of the Sachs graph has previously been described in detail.[2,3,11] In brief, it is a subgraph of the molecular graph which has no components other than disjoint π bonds and/or disjoint π cycles. When a given self-loop is counted, the neighboring π bonds must not be counted in the same Sachs graph.

A characteristic polynomial $P^*(X)$ for a conjugated system is then expressed with their Sachs formula as

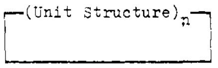
$$P^*(X) = \sum_{t=0}^{N} C_t^* X^{N-t} \tag{1}$$

where

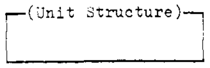
$$C_t^* = \sum_{s\epsilon S_t} \left\{ (-1)^{c(s)} 2^{r(s)} \prod_{\alpha} h_\alpha \right\} \tag{2}$$

Here, N is the number of atoms in the entire π system, S_t the set of all possible Sachs graphs which contain t atoms, $c(s)$ the number of components of a Sachs graph s, $r(s)$ the number of cyclic components of the Sachs graph s, and h_α the heteroatom parameter associated with each self-loop in the same Sachs graph; α runs over all self-loops in the Sachs graph. Asterisks in eq 1 and 2 signify that the quantities concerned are all related to the assumption that all resonance integrals in the π system have a constant value.

General Rules for Constructing Characteristic Polynomials. We consider hypothetical monocyclic conjugated systems with n unit structures as before.[9,12-14] A general formula for such π systems is illustrated as I. The unit structure in brackets is so chosen that the entire system with $n = 1$ becomes the compound (II) under consideration. For example, when we are concerned with fulvene, the unit structure of a corresponding type-I system is -C(=CH$_2$)—CH=CH—CH=CH-. A secular equation for a type-I system with n unit structures can be reduced to n algebraic equations of the same degree as the number of atoms (N) in the π system of every unit structure.[9,12,14] They are written in the form



I



II

$$P_{nm}(X) = \sum_{t=0}^{N} A_t(\cos \Lambda_{nm})\, X^{N-t} = 0 \tag{3}$$

where

$$\Lambda_{nm} = \frac{2m\pi}{n} \qquad m = 0, 1, \ldots, n-2, n-1 \tag{4}$$

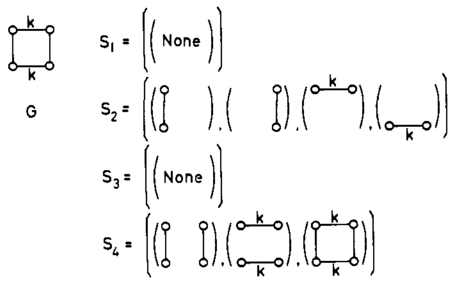


Figure 1. Norbornadiene-type four-π-electron systems.

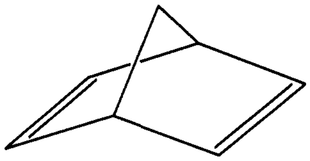
Here, the coefficients A_t are linear functions of cos Λ_{nm}. A characteristic polynomial $P(X)$ for a corresponding type-II system is

$$P(X) = \sum_{t=0}^{N} C_t X^{N-t} \qquad (C_0 = 1) \tag{5}$$

As pointed out in a previous paper,[9] both $P_{nm}(X)$ and $P(X)$ have many common coefficients. In particular, it is noteworthy that, for a monocyclic conjugated hydrocarbon with constant resonance integrals, all contributions from Sachs graphs which have cyclic components can be distinguished by noticing the cosines in the $A_t(\cos \Lambda_{nm})$ for a corresponding type-I system. If a cyclic component of a given type-II molecular graph is enumerated with a weight of 2 cos Λ_{nm}, the $A_t(\cos \Lambda_{nm})$ for a corresponding type-I system can be obtained. Conversely, the C_t for a given type-II system can readily be obtained by replacing the factors of 2 cos Λ_{nm} by 2 in the $A_t(\cos \Lambda_{nm})$ for a corresponding type-I system. This aspect of $P_{nm}(X)$-type polynomials gives an important clue to the present problem. The cosines in the $A_t(\cos \Lambda_{nm})$ for any type-I system with heterobonds might also mark the contributions from cyclic components of the molecular graph for a corresponding type-II system.

Before going ahead, let C_{ts} be the contribution from the Sachs graph s to the coefficient C_t of the characteristic polynomial for a given π system. C_t is then given by summing the C_{ts} over all Sachs graphs which contain t atoms. Let all resonance integrals be assumed to have a constant value, and these C_{ts} values can easily be determined from eq 2. These are used as initial C_{ts} values. At this stage C_t is equal to $C_t{}^*$.

The following two homoconjugative systems are especially instructive to infer the role of heterobond parameters (k) in the actual C_{ts} because we do not need to take any heteroatom parameters (h) into consideration. A heterobond is defined as a π bond whose resonance integral is not equal to β. Norbornadiene (III) has an antihomoaromatic four-π-electron system,[15] in which π bonds strongly alternate. The heterobond parameter k is related to the resonance integral between nonbonded sp^2-carbon atoms and should hence be much less than unity. The characteristic polynomial for this π system is



III

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

whereas the $P_{nm}(X)$ for a corresponding type-I system is represented by

$$P_{nm}(X) = X^4 - (2 + 2k^2)X^2 + (1 + k^4 - 2k^2 \cos \Lambda_{nm}) \tag{7}$$

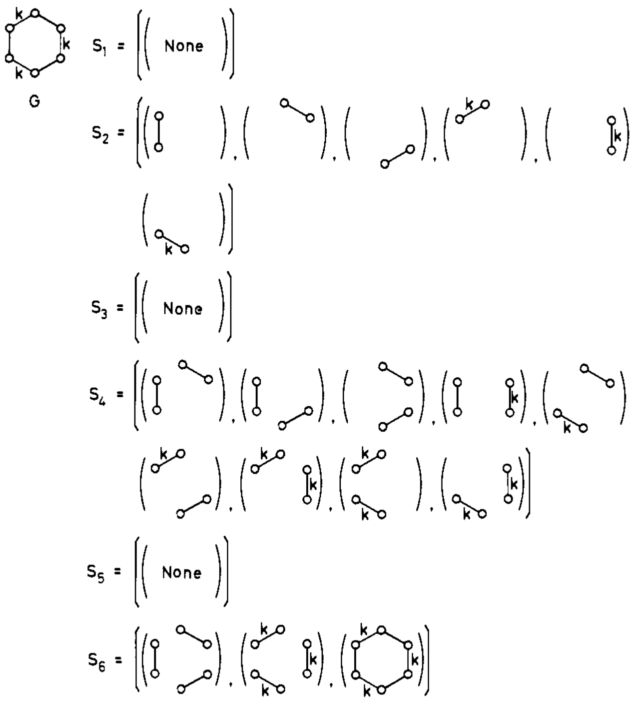
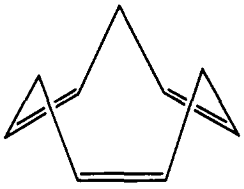


Figure 2. Cyclononatriene-type six-π-electron systems.

On the other hand, cyclononatriene (IV) has a homoaromatic six-π-electron system[15] in which π bonds also strongly alternate. For this system, the two types of polynomials are written as



IV

$$P(X) = X^6 - (3 + 3k^2)X^4 + (3 + 3k^2 + 3k^4)X^2 - (1 + k^6 + 2k^3) \tag{8}$$

and

$$P_{nm}(X) = X^6 - (3 + 3k^2)X^4 + (3 + 3k^2 + 3k^4)X^2 - (1 + k^6 + 2k^3 \cos \Lambda_{nm}) \tag{9}$$

In eq 7 and 9 the cosines in the coefficients suggest that the corresponding terms in the $P(X)$ are related to the Sachs graphs which have cyclic components, and the other terms may necessarily be related to the Sachs graphs which are formed with disjoint π bonds only. On this basis the coefficients C_t of the $P(X)$ for these two compounds tempt us to imagine the following generalized Sachs graphs, shown in Figures 1 and 2, which will later prove correct. Molecular graphs are shown with G. All Sachs graphs are drawn within parentheses and the set of all Sachs graphs S_t are denoted in brackets.

By comparing eq 7 and 9 with these possible Sachs graphs, the following two rules are found to govern the actual coefficients of the characteristic polynomials: (1) when each disjoint heterobond is counted in the Sachs graph s, the initial C_{ts} must every time be multiplied by its heterobond parameter squared; (2) when each π cycle with heterobonds is counted in the same Sachs graph, the C_{ts} must further every time be multiplied by the product of all heterobond parameters in the π cycle. These

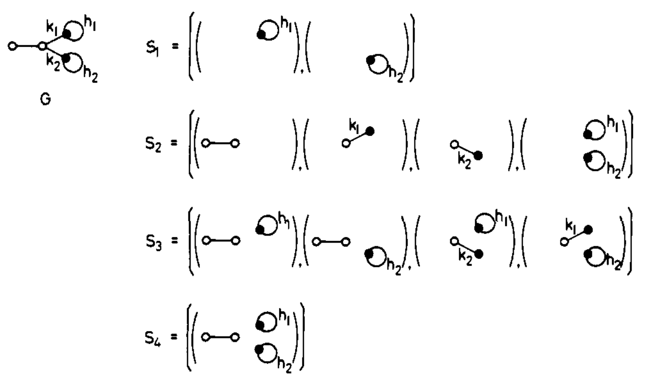


Figure 3. 1-Bromo-1-chloroethylene-like systems.

two rules are sufficient to construct a characteristic polynomial for any conjugated system. They define a weighted Sachs graph formed with disjoint π bonds and/or disjoint π cycles, each weighted with heterobond parameters.

The above two rules prove mathematically self-evident if we follow the original graph-theoretical development by Sachs.[4] The set of Sachs graphs represent all possible permutations of nonzero elements (a_{ij}) in the secular determinant. Counting a given disjoint π bond between the ith and jth atoms corresponds to taking a product $a_{ij}a_{ji}$. Counting a given cyclic component corresponds to taking two products in such a manner as $a_{ij}a_{jk}a_{kl} \ldots a_{pq}a_{qr}a_{ri}$ and $a_{ji}a_{kj}a_{lk} \ldots a_{qp}a_{rq}a_{ir}$; these are the products of matrix elements related to the π cycle. Accordingly, when some of these elements are different from unity, the initial C_{ts} value must necessarily be multiplied by them. This gives a proof on our inference of the graphical rules generalized for constructing the characteristic polynomials.

Application of General Rules to Heteroconjugated Systems. We shall illustrate the use of our rules presented above by some examples outlined below. Sachs graphs are indicated in the same formalism.

(1) 1-Bromo-1-chloroethylene-like systems (Figure 3). Therefore,

$$C_1 = (-1)^1 2^0 h_1 + (-1)^1 2^0 h_2 = -h_1 - h_2 \tag{10a}$$

$$C_2 = (-1)^1 2^0 + (-1)^1 2^0 k_1^2 + (-1)^1 2^0 k_2^2 + (-1)^2 2^0 h_1 h_2 = -1 - k_1^2 - k_2^2 + h_1 h_2 \tag{10b}$$

$$C_3 = (-1)^2 2^0 h_1 + (-1)^2 2^0 h_2 + (-1)^2 2^0 h_1 k_2^2 + (-1)^2 2^0 h_2 k_1^2 = h_1 + h_2 + h_1 k_2^2 + h_2 k_1^2 \tag{10c}$$

$$C_4 = (-1)^3 2^0 h_1 h_2 = -h_1 h_2 \tag{10d}$$

and the characteristic polynomial is

$$P(X) = X^4 - (h_1 + h_2)X^3 - (1 + k_1^2 + k_2^2 - h_1 h_2)X^2 + (h_1 + h_2 + h_1 k_2^2 + h_2 k_1^2)X - h_1 h_2 \tag{11}$$

(2) Pyrrole-like systems (Figure 4). Therefore,

$$C_1 = (-1)^1 2^0 h = -h \tag{12a}$$

$$C_2 = (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^0 k^2 + (-1)^1 2^0 k^2 = -3 - 2k^2 \tag{12b}$$

$$C_3 = (-1)^2 2^0 h + (-1)^2 2^0 h + (-1)^2 2^0 h = 3h \tag{12c}$$

$$C_4 = (-1)^2 2^0 + (-1)^2 2^0 k^2 + (-1)^2 2^0 k^2 + (-1)^2 2^0 k^2 + (-1)^2 2^0 k^2 = 1 + 4k^2 \tag{12d}$$

$$C_5 = (-1)^3 2^0 h + (-1)^1 2^1 k^2 = -h - 2k^2 \tag{12e}$$

and the characteristic polynomial is

$$P(X) = X^5 - hX^4 - (3 + 2k^2)X^3 + 3hX^2 + (1 + 4k^2)X - (h + 2k^2) \tag{13}$$

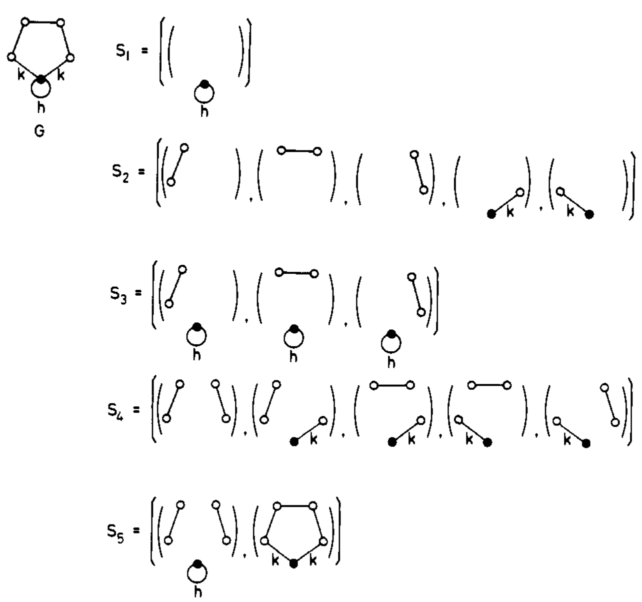
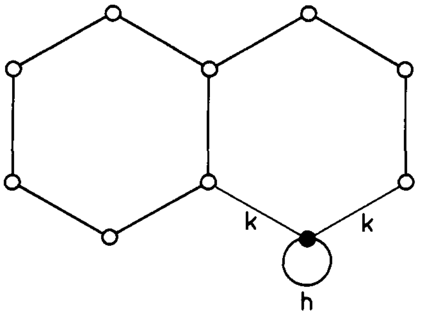


Figure 4. Pyrrole-like systems.

(3) Quinoline-like systems (V). Because there are too many Sachs graphs for this kind of π system, only the characteristic polynomial obtained is cited below:



V

$$P(X) = X^{10} - hX^9 - (9 + 2k^2)X^8 + 9hX^7 + (26 + 15k^2)X^6 - 26hX^5 - (29 + 36k^2)X^4 + 29hX^3 + (11 + 32k^2)X^2 - 11hX - 9k^2 \tag{14}$$

In all cases, the roots of $P(X) = 0$ are of course in exact accord with those derived from the secular determinant. A characteristic polynomial for any heteroconjugated system can now be obtained in such a graphical manner.

As stated before, when our own theory of aromaticity[9] is applied to any conjugated system, a reference polynomial for it is required. Owing to the present rules for constructing characteristic polynomials, we can also obtain the reference polynomial for any conjugated systems, including heterocycles, simply by ignoring π cycles in the Sachs graphs. To adduce examples, the reference polynomials $R(X)$ for pyrrole- and quinoline-like systems are, respectively,

$$R(X) = X^5 - hX^4 - (3 + 2k^2)X^3 + 3hX^2 + (1 + 4k^2)X - h \tag{15}$$

and

$$R(X) = X^{10} - hX^9 - (9 + 2k^2)X^8 + 9hX^7 + (26 + 15k^2)X^6 - 26hX^5 - (27 + 34k^2)X^4 + 27hX^3 + (7 + 24k^2)X^2 - 7hX - 3k^2 \tag{16}$$

The resonance energies derived from such reference polynomials have already been reported[9] and favorably compared with those of Hess and Schaad.[16] It goes without saying that the reference polynomial for any acyclic heteroconjugated system is identical with its characteristic polynomial. Therefore, acyclic systems are assuredly nonaromatic. These results are quite consistent with Dewar's theory of aromaticity.[17]

The resonance energies obtained by us can be understood logically as follows. The products of matrix elements related to every π cycle in the molecular graph are

$$\begin{aligned} a_{ij}a_{jk}a_{kl}\ldots a_{pq}a_{qr}a_{ri} &= (1/\beta^{w})\,\langle i|\mathcal{H}|j\rangle\langle j|\mathcal{H}|k\rangle\langle k|\mathcal{H}|l\rangle \\ &\quad \ldots\langle p|\mathcal{H}|q\rangle\langle q|\mathcal{H}|r\rangle\langle r|\mathcal{H}|i\rangle \end{aligned} \tag{17}$$

and

$$\begin{aligned} a_{ji}a_{kj}a_{lk}\ldots a_{qp}a_{rq}a_{ir} &= (1/\beta^{w})\,\langle j|\mathcal{H}|i\rangle\langle k|\mathcal{H}|j\rangle\langle l|\mathcal{H}|k\rangle \\ &\quad \ldots\langle q|\mathcal{H}|p\rangle\langle r|\mathcal{H}|q\rangle\langle i|\mathcal{H}|r\rangle \\ &= (1/\beta^{w})\,\langle i|\mathcal{H}|r\rangle\langle r|\mathcal{H}|q\rangle\langle q|\mathcal{H}|p\rangle \\ &\quad \ldots\langle l|\mathcal{H}|k\rangle\langle k|\mathcal{H}|j\rangle\langle j|\mathcal{H}|i\rangle \end{aligned} \tag{18}$$

where w is the number of π bonds in the π cycle, and $\mathcal{H}$ is the Hückel Hamiltonian. Note that these cyclic interactions are all ignored in the coefficients of the reference polynomial. Hence, our resonance energies can be associated with the contributions of π energy from such cyclic interactions, which appear to induce two opposite ring currents in the individual π cycles.

A Correlation between the Coefficients of the Characteristic Polynomial and the Total π Energy for Heteroconjugated Systems. In order to see a correlation between the coefficients of the characteristic polynomial and the total π energy for heteroconjugated systems, we arrange the roots of $P(X) = 0$ in a decreasing order as

$$X = X_1, X_2, \ldots, X_m, X_{m+1}, \ldots, X_{N-1}, X_N \tag{19}$$

The first m roots correspond to the energies of the occupied π orbitals in units of β; for these heteroconjugated systems, the m is not always equal to half the number of atoms in the conjugated system ($N/2$). The characteristic polynomial is rewritten with these roots in the form:

$$P(X) = \prod_{t=1}^{N} (X - X_t) \tag{20}$$

We will then derive a useful expression which is linear in X_t. Let us choose a constant K somewhat arbitrarily as

$$K \approx (1/3)\,\mathrm{Max}\,\{|X_t|\} \tag{21}$$

i.e., about one-third of the maximum absolute X_t value. In the case of conjugated hydrocarbons, the K can safely be equated to unity.[18] We define a new quantity Z^* with this K in this manner:

$$Z^* = K^{-NK}\,\{|P(iK)|\}^{K} = K^{-NK} \prod_{t=1}^{N} (K^2 + X_t{}^2)^{K/2} \tag{22}$$

where $i = \sqrt{-1}$. The logarithm of Z^* is then

$$\log Z^* = (K/2) \sum_{t=1}^{N} \log\{1 + (X_t/K)^2\} \tag{23}$$

The physical image of eq 23 can be visualized with the use of the following approximation:[18]

$$\log(1 + X^2) \approx 0.32870|X| \qquad \text{for } |X| \le 3.0 \tag{24}$$

This approximation holds fairly well in the indicated region. Since for all X_t

$$|X_t/K| \le 3.0 \tag{25}$$

the above approximation can be used to make eq 23 linear in every X_t, namely,

$$\log Z^* \approx (0.32870/2) \sum_{t=1}^{N} |X_t| \tag{26}$$

It should be noted that for most conjugated hydrocarbons the product $X_m X_{m+1}$ is negative.[18,19] The same product is also negative for most heteroconjugated systems. The total π energy for a heteroconjugated system E_π can hence be written in the form:

$$E_\pi = 2 \sum_{t=1}^{m} X_t = \sum_{t=1}^{N} |X_t| + \sum_{\alpha} h_\alpha \tag{27}$$

where α runs over all heteroatoms in the π system. By combining eq 27 with eq 26, we arrive at a desired expression for the total π energy of the heteroconjugated system:

$$\begin{aligned} E_\pi &\approx 6.0846 \log Z^* + \sum_{\alpha} h_\alpha \\ &= 6.0846 \log\left[K^{-NK}\left\{\left|\sum_{t=0}^{N} C_t (iK)^{N-t}\right|\right\}^{K}\right] + \sum_{\alpha} h_\alpha \end{aligned} \tag{28}$$

This expression gives a quantitative relation between the total π energy and the coefficients C_t of the characteristic polynomial. Since each coefficient is a function of Sachs graphs, we can see from this expression how the total π energy is dependent upon the connectivity of the π-electron network. A contribution from a given π cycle in the π system can be estimated merely by removing from eq 28 all terms C_{t}s related to the Sachs graphs which have the other π cycles as the components. For most heterocyclic systems, the sign and the magnitude of the resonance energy can be predicted from the same expression by examining whether or not the entire set of Sachs graphs which have cyclic components positively contribute to the total π energy. In this sense, this expression is a good example which visually shows a structure of the π-electron network in terms of the C_t.

Concluding Remarks

A graph-theoretical method for evaluating the coefficients C_t of an HMO characteristic polynomial has been outlined for any kind of conjugated system. The method enables one to apply our graphical theory of aromaticity[9] to all kinds of conjugated systems or their ionic species. As exemplified by eq 28, the obtained coefficients C_t are key quantities for graphically understanding the π-electron network for these systems. By constructing a polynomial whose coefficients are functions of Sachs graphs from which all π cycles but a given one are excluded, we can predict the resonance energy assignable to the remaining π cycle in the Sachs graphs. Work in this area is in progress. It must be emphasized that the present approach maintains all the simplicity and elegance of the HMO theory and can be viewed as a promising extension of the HMO theory.

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References and Notes

(1) Typical works carried out in relation to this area are as follows: I. Samuel, *C. R. Acad. Sci.*, **229**, 1236 (1949); E. Heilbronner, *Helv. Chim. Acta*, **36**, 170 (1953); R. Gourané, *J. Rech. C. N. R. S.*, **34**, 81 (1956); L. Collatz and U. Sinogowitz, *Abhandl. Math. Sem. Univ. Hamburg*, **21**, 63 (1957); F. Harary, *J. Math. Phys.*, **38**, 104 (1959); *SIAM Rev.*, **4**, 202 (1962); L. Spialter, *J. Am. Chem. Soc.*, **85**, 2012 (1963); *J. Chem. Doc.*, **4**, 261 (1964).
(2) A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theor. Chim. Acta*, **26**, 67 (1972).
(3) I. Gutman and N. Trinajstić, *Top. Curr. Chem.*, **42**, 49 (1973).
(4) H. Sachs, *Publ. Math.* (*Debrecen*), 11, 119 (1963); the method presented by Graovac et al. can be considered as an interpretation of the Sachs theorem in terms of chemistry.
(5) H. Hosoya, *Theor. Chim. Acta*, **25**, 215 (1972).
(6) H. Hosoya, *Bull. Chem. Soc. Jpn.*, **44**, 2332 (1971); H. Hosoya, K. Kawasaki,

and K. Mizutani, *ibid.*, **45**, 3415 (1972); H. Hosoya, *Fibonacci Q.*, **11**, 255 (1973).
(7) R. B. Mallion, A. J. Schwenk, and N. Trinajstić, *Croat. Chem. Acta*, **46**, 171 (1974); R. B. Mallion, N. Trinajstić, and A. J. Schwenk, *Z. Naturforsch. A*, **29**, 1481 (1974).
(8) See, e.g., A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, Chapters 4 and 5.
(9) J. Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976).
(10) This is a symbolic representation for discriminating heteroatoms. It permits one to graphically interpret the secular determinant for the heteroconjugated system.
(11) The term "Sachs graph" is used here as it was adopted in ref 3, 4, and 7. A different term reflecting priority (see ref 1) might also be assigned to the same concept.
(12) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305 (1971).
(13) J. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 517 (1975).
(14) J. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 1501 (1975).
(15) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).
(16) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 3657, 5299 (1972); **31**, 295 (1975); B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **95**, 3907 (1973).
(17) 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, A. J. Harget, and N. Trinajstić, *ibid.*, **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).
(18) J. Aihara, *J. Org. Chem.*, **41**, 2488 (1976).
(19) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations", Pergamon Press, Oxford, 1965.

Unrestricted Open-Shell Calculations by MINDO/3. Geometries and Electronic Structure of Radicals

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Abstract: The MINDO/3 semiempirical SCF-MO method has been expanded to an unrestricted open-shell treatment. The calculated heats of formation of radicals as well as their geometries compare reasonably well with experiment. Calculated spin densities predict the correct proton hyperfine splitting ordering for most EPR spectra.

The geometry and the electronic structure of radicals determining their chemical reactivity and spectroscopic properties is of great importance in many fields of organic chemistry.[1] Unlike in reactions where only closed-shell reactants are involved, the application of the Woodward–Hoffmann rules[2] is not clear cut[3] and calls for more detailed theoretical investigations.

Since at present reliable ab initio calculations cannot yet be carried out on larger systems of chemical interest, the chemist is forced to choose some semiempirical method for his purposes.

MINDO/3[4] has proven[5] to be the most reliable method of this type, although some shortcomings are well known and have been criticized.[5,6]

Calculated properties like energy, spin distribution, and dipole moment depend strongly upon the geometry of the species in question. This demands total geometry optimization in order to make the results independent of any arbitrary choice of geometrical variables.

To our experience, the original closed-shell program[7] fails to converge in some cases, probably since the bond order matrix in using the restricted half-electron method[8] is not invariant to small changes in geometry. Calculations failed to converge mainly for complex systems, where the number of geometrical variables was large.

Following Dewar's suggestion,[4] the MINDO/3 method has been expanded to a nonrestricted open-shell treatment, in which this difficulty has been avoided. Although this purpose was the main "driving force", nonrestricted calculations in addition feature the well-known advantages common to this approach: (a) negative spin densities (which are known to occur[9]) can be computed; (b) Koopmans' theorem[10] can be used to estimate ionization potentials; and (c) adiabatic ionization potentials of closed-shell systems can be calculated by comparing their energies with the energies of the optimized open-shell cations. Furthermore, calculations of this type might be regarded as an independent test upon the parameters used in MINDO/3.

Although the power of any semiempirical treatment lies in the computation of large systems, we shall focus mainly on small species in this communication in order to compare with experimental facts that are available.

Procedure

The derivation of the Roothaan equations for open-shell systems[11] is straightforward and can be found in any textbook.[12] Within the MINDO/3 framework, the elements of the F matrices take the following form:

$$F_{ii}{}^{\alpha} = H_{ii} + p_{ii}{}^{\beta} g_{ii} + \sum_{k \neq i}^{(m)} (p_{kk} g_{ik} - p_{kk}{}^{\alpha} h_{ik}) + \sum_{n \neq m} \gamma_{mn} \sum_{k}^{(n)} p_{kk} \tag{1}$$

$$F_{ij}{}^{\alpha}(m,m) = (2p_{ij} - p_{ij}{}^{\alpha}) h_{ij} - p_{ij}{}^{\alpha} g_{ij} \tag{2}$$

$$F_{ij}{}^{\alpha}(m,n) = H_{ij} - p_{ij}{}^{\alpha} \gamma_{mn} \tag{3}$$

where

$$p_{ij} = p_{ij}{}^{\alpha} + p_{ij}{}^{\beta} \tag{4}$$

$$g_{ij} = (ii|jj) \tag{5}$$

$$h_{ij} = (ij|ij) \tag{6}$$

$$H_{ii} = U_{ii} - \sum_{n \neq m} C_n \gamma_{mn} \tag{7}$$

and

$$H_{ij} = \beta_{ij}{}^{c} = S_{ij}(I_i + I_j) B_{mn} \tag{8}$$

The symbols have their conventional meanings.[12] Analogous expressions hold for $F_{ij}{}^{\beta}$ of course. Using this notation, the total energy of a molecule is given by