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Matrix Representation of an Olefinic Reference Structure for Monocyclic Conjugated Compounds

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Synopsis. A reference polynomial which represents an olefinic reference structure of a monocyclic conjugated system can be expressed in the form of a Hermitian matrix. Some interesting features of the reference structure have been deduced from it.

The author has developed a graph theory of aromaticity,[1,2] in which the resonance energy due to aromaticity is given as the difference between the total π-electron energy of a conjugated compound and that of its olefinic reference structure. The reference energy of a conjugated hydrocarbon, *i.e.*, the total π-electron energy of its reference structure, has been defined by the following reference polynomial:[1]

$$R(X) = X^N + \sum_{r=1}^{[N/2]} (-1)^r p(r) X^{N-2r}, \tag{1}$$

where N is the number of sp^2-carbon atoms in a conjugated system, $[N/2]$ is the maximum integer not exceeding $N/2$, and $p(r)$ is the number of ways of choosing r disjoint π bonds from the conjugated system.[3] The reference energy is given as twice the sum of the larger $[N/2]$ roots of the equation

$$R(X) = 0. \tag{2}$$

A matrix representation of such a reference polynomial is possible for any monocyclic conjugated system, and is discussed below.

Consider a monocyclic conjugated hydrocarbon with N sp^2-carbon atoms, M of which constitute a closed π ring. The other carbon atoms, if any, belong to the substituent(s). Let an adjacency matrix[4] for this conjugated system be denoted by A and the elements by a_{ij}. The matrix element a_{ij} is therein equal to unity if there is a π bond between the atoms i-j. All the other matrix elements are zero. The eigenvalues of this matrix represent the orbital energies of a conjugated system.

The elements of the matrix A are then changed as follows. If matrix element a_{ij} corresponds to one of the M π bonds forming a π ring, it is weighted with a factor $\exp(i\eta_{ij}\theta)$, where the numerical value of θ is $\pi/(2M)$, and

$$\eta_{ij} = \begin{cases} +1 & \text{if atoms i}\to\text{j are arranged clockwise in a } \pi \text{ ring of a conjugated system, and} \\ -1 & \text{if not.} \end{cases}$$

The remaining matrix elements are left unchanged. The resulting matrix is denoted by B and the elements by b_{ij}. Matrix B is thus a weighted adjacency matrix.

Next, consider a secular determinant defined by

$$Q(X) = (-1)^N \det|B-EX|, \tag{4}$$

where E is a unit $N\times N$ matrix. On expansion, $Q(X)$ leads to a polynomial in X, the coefficients all being expressible in terms of the closed cyclic products of the type $b_{ij}b_{jk}\cdots b_{pq}b_{qi}$.[5] Such products of more than two matrix elements represent a cyclic array of π bonds, *i.e.*, a π ring, in a conjugated system. These products, however, vanish in the present case since

$$b_{ij}b_{jk}\cdots b_{pq}b_{qi} + b_{ji}b_{kj}\cdots b_{qp}b_{iq} = 2\cos\left(\frac{\pi}{2}\right) = 0. \tag{5}$$

The non-zero cyclic product is represented by

$$b_{ij}b_{ji} = \exp(0) = 1 \tag{6}$$

for each π bond. Then, apply an extended version of Sachs' graph-theoretical theorem[5] to the secular determinant $Q(X)$ with Eqs. 5 and 6 in mind, and the determinant will necessarily be expanded into the same polynomial as the reference polynomial for the same conjugated system, namely,

$$R(X) \equiv Q(X). \tag{7}$$

It has thus been proved that a reference polynomial for a monocyclic conjugated system can be expressed in the form of Eq. 4. Since matrix B is a Hermitian matrix, the eigenvalues of the matrix, *i.e.*, the roots of the equation $Q(X)=0$, are all real.

For example, matrix B for styrene in Fig. 1 is

$$B = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & z & 0 & 0 & 0 & z^* \\ 0 & 0 & z^* & 0 & z & 0 & 0 & 0 \\ 0 & 0 & 0 & z^* & 0 & z & 0 & 0 \\ 0 & 0 & 0 & 0 & z^* & 0 & z & 0 \\ 0 & 0 & 0 & 0 & 0 & z^* & 0 & z \\ 0 & 0 & z & 0 & 0 & 0 & z^* & 0 \end{pmatrix}, \tag{8}$$

where

$$z = \exp\left(\frac{\pi}{12}\,\mathrm{i}\right). \tag{9}$$

This matrix leads to the same polynomial as $R(X)$ for this compound, *i.e.*,

$$Q(X) = R(X) = X^8 - 8X^6 + 19X^4 - 14X^2 + 2. \tag{10}$$

From the present definition of matrix B, the following

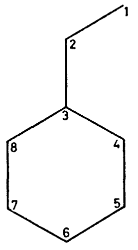

Fig. 1. A conjugated system of styrene.

equalities have been clarified for monocyclic conjugated hydrocarbons:

$$\mathrm{Tr}\,B = \mathrm{Tr}\,A = 0, \tag{11}$$

$$\mathrm{Tr}\,B^2 = \mathrm{Tr}\,A^2 = 2H, \tag{12}$$

where H is the number of π bonds in an entire conjugated system. Note that the trace of a matrix is the sum of the eigenvalues. Equation 11 indicates that the sum of the orbital energies vanishes both for a conjugated system and its reference structure. Equation 12 indicates that the sum of the orbital energies squared for a conjugated system is equal to that for its reference structure. According to extensive numerical analysis, these equalities appear to hold true for polycyclic conjugated hydrocarbons without exception. Since the sum of the orbital energies squared is preserved in the reference structure, it can be deduced that some of the occupied orbitals in a conjugated system must be energetically higher than the corresponding orbitals in its reference structure$^{6)}$ even if the conjugated system is aromatic with positive resonance energy.

A reference polynomial for a monocyclic heterocyclic conjugated system can also be derived from the secular determinant simply by weighting the matrix elements with the same factors $\exp(i\eta_{ij}\theta)$ as in the case of monocyclic conjugated hydrocarbons. It is interesting to note that, if $\theta=\pi/M$, matrix B represents a Möbius conjugated system, *i.e.*, a singly twisted conjugated system.$^{7)}$

References

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