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Conjugated Systems with Identical Circuit Resonance Energies

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Circuit resonance energy CE defined by Aihara is one of indices for local aromaticity. The CE for a circuit of a polycyclic conjugated molecule is calculated from the roots of the reference polynomial and circuit characteristic polynomial. It is reported that there exist polycyclic conjugated molecules which have identical reference polynomials and identical circuit characteristic polynomials and thus identical circuit resonance energies.

Since 1972 when Clar published a book[1] "The Aromatic Sextet" it became evident that aromaticity is not a global property of polycyclic conjugated molecules, but that an aromatic character can be associated with particular rings of the conjugated systems. A large number of topological indices for measuring the local aromaticity have been proposed,[2] among which the circuit resonance energy plays a significant role. Within the framework of the topological resonance energy (TRE) theory[3] circuit resonance energy was defined in two different manners: by Aihara[4] and by Gutman and Bosanac.[5] In both of these approaches the circuit resonance energy of a given circuit C_n, CE(C_n), is a measure of the contribution of the circuit to the TRE of the respective molecule. Since the stability of a (poly)cyclic conjugated molecule (which can be predicted from the TRE value of the molecule) obeys the generalized Hückel $4n+2$ rule,[6] it is desirable that circuit resonance energies also obey similar rules. Unfortunately the circuit resonance energies calculated by the method of Gutman and Bosanac[5] for some hydrocarbons violate the Hückel rule. On the other hand one of the authors[7] has recently shown that the CE's defined by Aihara strictly obey the Hückel rule. Moreover the same author extended the notion of CE to Möbius-type circuits and proved that $4n+2$ rules apply to these circuits as well.

The actual relation between TRE and the circuit resonance energies is nowadays not completely understood. The ideal case would be if TRE could be represented as a sum of the pertinent circuit resonance energies. However, in reality the situation is somewhat more complicated, because TRE depends not only on effects of individual circuits but also on collective effects of pairs, triplets etc. of circuits. Only for monocyclic systems TRE coincides with circuit resonance energy. Anyway, the circuit resonance energy can be interpreted as the part of TRE which originates from the respective circuit of the conjugated system considered.

The present paper is concerned with Aihara's circuit resonance energy. Until now it has not been reported that there exist topologically nonequivalent conjugated systems having identical circuit resonance energies. Here we point out a whole class of such conjugated systems.

The Main Results

Let G be a graph representing the π-electron network of a polycyclic conjugated molecule without bond alternation. Denote the reference polynomial of G in the topological resonance energy theory[3] by $R(\mathrm{G};X)$. This polynomial is also called the matching polynomial and can be expressed in the form

$$R(\mathrm{G};X)=\sum_k (-1)^k\, m(\mathrm{G},k)\, X^{N-2k}, \tag{1}$$

where N is the number of vertices of the graph G and where $m(\mathrm{G},k)$ denotes the number of k-matchings of G. The circuit characteristic polynomial for a circuit C_n in G, $P(\mathrm{G}/C_n;X)$, is expressed in terms of reference polynomials as

$$P(\mathrm{G}/C_n;X)=R(\mathrm{G};X)-2R(\mathrm{G}\ominus C_n;X), \tag{2}$$

where $\mathrm{G}\ominus C_n$ is a subgraph of G obtaind by deleting all the vertices in C_n and edges incident to C_n from G.[7] The second term on the right-hand side of Eq. 2 represents the contribution of the circuit C_n. The reference polynomial R(G;X) has no contribution from any circuit. Circuit resonance energy of the circuit C_n defined by Aihara is given by

$$\mathrm{CEA}(C_n)=\sum_J g_J X_J(P(\mathrm{G}/C_n)-\sum_J g_J X_J(R(\mathrm{G})), \tag{3}$$

where $X_J(P(\mathrm{G}/C_n))$ and $X_J(R(\mathrm{G}))$ denote the J-th roots of $P(\mathrm{G}/C_n,X)$ and of $R(\mathrm{G};X)$, respectively and g_J is the occupation number of the J-th MO.

If two graphs G′ and G″ satisfy the following two equations at the same time

$$R(\mathrm{G}';X)=R(\mathrm{G}'';X) \text{ and } P(\mathrm{G}'/\mathrm{C}';X)=P(\mathrm{G}''/\mathrm{C}'';X),$$

i.e.

$$R(\mathrm{G}';X)=R(\mathrm{G}'';X) \text{ and } R(\mathrm{G}'\ominus\mathrm{C}';X)=R(\mathrm{G}''\ominus\mathrm{C}'';X), \tag{4}$$

where C′and C″ are circuits in G′ and in G″, then we have

$$\mathrm{CEA}(\mathrm{C}' \text{ in } \mathrm{G}')=\mathrm{CEA}(\mathrm{C}'' \text{ in } \mathrm{G}'').$$

We now find graphs which satisfy Eq. 4.

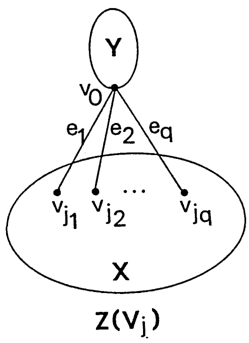


Fig. 1. Graph $Z(\mathbf{V}_j)$.

Consider a molecular graph $Z(\mathbf{V}_j)$ shown in Fig. 1, which is constructed as follows. Let X be a graph possessing p vertices $v_1, v_2, \cdots, v_p$ which satisfy

$$R(X-v_1)=R(X-v_2)=\cdots=R(X-v_p). \tag{5}$$

Let Y be another graph and v_0 its certain vertex. Denote the set $\{v_1, v_2, \cdots, v_p\}$ by $\mathbf{V}$. Let $\mathbf{V}_j=\{v_{j_1}, v_{j_2}, \cdots, v_{j_q}\}$ be a certain q-element subset of $\mathbf{V}$. Construct the graph $Z=Z(\mathbf{V}_j)$ by connecting the vertex v_0 of Y with the vertices $v_{j_1}, v_{j_2}, \cdots, v_{j_q}$ of X. Hence q new edges are to be introduced; they are denoted by $e_1, e_2, \cdots, e_q$, respectively.

Proposition I. Suppose that q is a fixed number. Then the reference polynomial of Z is the same for all choices of the subsets $\mathbf{V}_j$. Moreover

$$R(Z)=R(X)\cdot R(Y)-qR(X-v)\cdot R(Y-v_0), \tag{6}$$

where v is an arbitrary element of $\mathbf{V}_j$.

Proof of Proposition I. Denote by $G_1 \cup G_2$ the graph composed of two disconnected components G_1 and G_2. Recall that $R(G_1 \cup G_2)=R(G_1)\cdot R(G_2)$. Divide the k-matchings of $Z(\mathbf{V}_j)$ as follows:

a) The matchings which do not contain the edges $e_1, e_2, \cdots e_q$; there are $m(X \cup Y,k)$ such matchings.

b) The matchings which contain one of the edges $e_1, e_2, \cdots e_q$, say e_i; these matchings cannot contain the edges $e_1, e_2, \cdots e_{i-1}, e_{i+1}, e_q$; their number is equal to $m(Z-v_{j_i}-v_0,k-1)=m(X-v_{j_i} \cup Y-v_0,k-1)$.

Consequently

$$m(Z,k)=m(X \cup Y,k)+\sum_{i=1}^{q} m(X-v_{j_i} \cup Y-v_0,k-1). \tag{7}$$

When substituted into Eq. 1 relation 7 gives

$$R(Z)=R(X \cup Y)-\sum_{i=1}^{q} R(X-v_{j_i} \cup Y-v_0). \tag{8}$$

Now

$$R(X \cup Y)=R(X)\cdot R(Y),$$

$$R(X-v_{j_i} \cup Y-v_0)=R(X-v_{j_i})\cdot R(Y-v_0).$$

Since the vertices from $\mathbf{V}_j$ satisfy Eq. 5, Proposition I follows.

Proposition IIa: Suppose that $q \geqq 3$. Let C_1 be a circuit of $Z(\mathbf{V}_j)$ containing (among others) the vertices v_0, v_{j_1} and v_{j_2}. Then $Z \ominus C_1$ is independent of the choice of the vertices $v_{j_3}, \cdots, v_{j_q}$.

Proof of Proposition IIa. If we delete from $Z(\mathbf{V}_j)$ the vertices of the circuit C_1 then we also must delete all edges of Z incident to v_0. This means that $Z \ominus C_1$ dose not contain the edges $e_3, \cdots, e_q$ and therefore the actual choice of the vertices $v_{j_3}, \cdots, v_{j_q}$ is immaterial.

Proposition IIb: Suppose that $q \geqq 2$. Let C_2 be a circuit containing (among others except the vertex v_0) all the vertices satisfying Eq. 5. Then $Z \ominus C_2$ is independent of the choice of the vertices of the subset $\mathbf{V}_j$.

This proposition should be evident from the definition of the circuit C_2.

Thus we found that a series of graphs derived from $Z(\mathbf{V}_j)$ satisfy Eq. 4. Therefore Propositions I and IIa lead to Proposition IIIa, and Propositions I and IIb to Proposition IIIb.

Proposition IIIa: The circuit C_1 has identical CEA for all the graphs of the form $Z(\mathbf{V}_j)$.

Proposition IIIb: The circuit C_2 has identical CEA for all the graphs of the form $Z(\mathbf{V}_j)$.

Equation 4 is a necessary condition for non-isomorphic molecules to have identical circuit resonance energies. So, as a result of the sum of Eq. 3, molecules not belonging to $Z(\mathbf{V}_j)$ may have identical circuit resonance energies even if they don't satisfy Eq. 4. But these molecules may not have identical circuit resonance energies when they are in ionic state. Molecules represented by $Z(\mathbf{V}_j)$ have identical circuit resonance energies even when they are in ionic state because they have identical reference polynomials and identical circuit characteristic polynomials. This is a significance of the finding of molecules represented by $Z(\mathbf{V}_j)$.

The fact that circuits in different molecular graphs can have equal circuit resonance energies reveals that CEA depends on some, but not on all details of the molecular structure. It infers that structural features other than the size of the circuit have a relatively small influence on CEA. This may be considered as the chemically most relevant conclusion of the present work. By finding distinct conjugated systems with equal CEA's we demonstrated that the theory of circuit resonance energy has reached a level when the dependence of CEA on molecular structure is almost fully understood.

Examples

One can construct arbitrarily many graphs belonging to the class $Z(\mathbf{V}_j)$. In actual applications of the propositions proved above the concept "equivalent vertices" is very useful. The vertices $v_1, v_2, \cdots, v_p$ of a graph X are said to be equivalent if $X-v_1=X-v_2=\cdots=X-v_p$. These vertices , of course, satisfy Eq. 5.

Some typical examples of molecular graphs belonging to class $Z(\mathbf{V}_j)$ are depicted in Fig. 2.

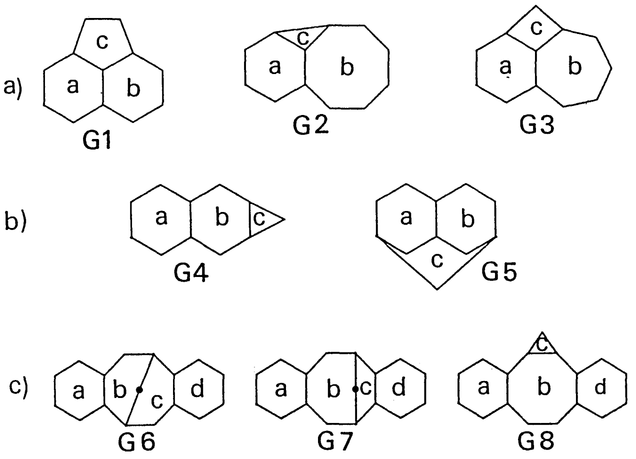


Fig. 2. Some molecular graphs belonging to the class $Z(\mathbf{V}_j)$.

a) Graphs G1, G2, and G3. In this case X is the [11]annulene graph, Y is the inner vertex and q=3; each six-membered circuit in these graphs corresponds to the circuit C_1 in Proposition IIa and each circuit **b**+**c** also corresponds to the circuit C_1; each peripheral circuit corresponds to the circuit C_2 in Proposition IIb because the peripheral circuits contain all the equivalent vertices in the [11]annulene graph. Therefore, it is seen from Proposition IIIa that the six-membered circuits in the graphs **G1**, **G2**, and **G3** have identical CEA's, the circuits **b**+**c** have identical CEA's and from Proposition IIIb that the peripheral circuits have identical CEA's.

b) Graphs G4 and G5. In this case X is the naphthalene graph, Y is one vertex, and q=2; each circuit **a**+**b** in these graphs corresponds to the circuit C_2 in the Proposition IIb because the circuits contain all the equivalent vertices in the naphthalene graph. Therefore, from Proposition IIIb it is seen that the circuits **a**+**b** in the graphs **G4** and **G5** have identical CEA's.

c) Graphs G6, G7, and G8. In this case q=2 and the graph X is the graph **G9** depicted in Fig. 3. In Fig. 3 also a set of equivalent vertices of **G9** is indicated. We can find only the circuits corresponding to the circuit C_2. According to Proposition IIIb it is seen that

CEA(**b**+**c** in **G6**) = CEA(**b**+**c** in **G7**) = CEA(**b** in **G8**), (9)

CEA(**a**+**b**+**c** in **G6**) = CEA(**a**+**b**+**c** in **G7**)
= CEA(**a**+**b** in **G8**), (10)

CEA(**b**+**c**+**d** in **G6**) = CEA(**b**+**c**+**d** in **G7**)
= CEA(**b**+**d** in **G8**), (11)

CEA(**a**+**b**+**c**+**d** in **G6**) = CEA(**a**+**b**+**c**+**d** in **G7**)
= CEA(**a**+**b**+**d** in **G8**), (12)

The cases described above, of course, are not the only examples of non-isomorphic molecular graphs having identical circuit resonance energies. By appropriate combinatorial reasoning we can construct many other examples of this kind.

Möbius-type Circuits

The anti-Hückel rule[8] states that stabilities of Möbius annulenes show opposite tendencies to those of Hückel annulenes. The graph representing a Möbius annulene is obtained by giving weight −1 to one edge in the (Hückel) annulene graph. The concept of Möbius annulene was extended to polycyclic conjugated molecules.[9] Polycyclic Möbius graphs contain two types of circuits, Möbius-type and Hückel-type circuits. A circuit is said to be Hückel-type if it contains an even number (or no) of edges with weight −1, Möbius-type if it contains an odd number of edges with weight −1.[9]

By giving weight −1 to one of the edges in **G9** one obtains various Möbius graphs. Figure 4 shows two of them, **G10** and **G11**. For instance, in **G10**, three circuits **a**, **a**+**b** and **a**+**b**+**c** are Möbius-type whereas the other circuit **b**+**c** is Hückel-type. It should be noted that vertices which are equivalent in the (parent) Hückel graph need not be equivalent in the Möbius graph. As indicated in Fig. 4, the two Möbius graphs **G10** and **G11** have different sets of equivalent vertices from that of graph **G9**. It can be shown, however, that if some vertices of a Hückel graph G satisfy Eq. 5 then they satisfy Eq. 5 also in the case of any Möbius graph derived from G. Therefore the results of the previous two sections are immediately applicable to Möbius systems as well.

If the circuit C_n is a Möbius-type circuit, then Eq. 2 has to be replaced by[7]

$$P(\mathrm{G}/C_n;X) = R(\mathrm{G};X) + 2\,R(\mathrm{G}\ominus C_n;X). \tag{13}$$

The coefficients of the reference polynomial of a graph G remains to be the same even if some edges of G are weighted by −1.[9] This means that any Möbius graph, obtained from the parent graph by giving weight −1 to the set of certain edges, has the same reference polynomial as that of the parent graph.[9] This observation leads to an important conclusion, namely that the statements of Propositions I, IIa, and IIb (which hold for Hückel-type circuits) can be

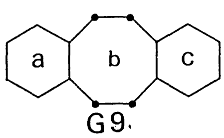


Fig. 3. Graph **G9**.

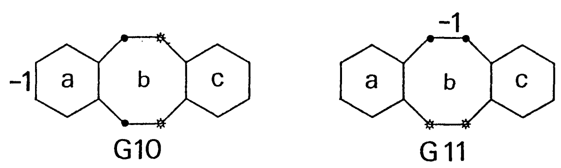
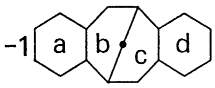
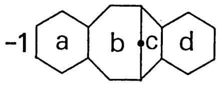


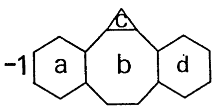
Fig. 4. Möbius graphs for graph **G9**.



G 12



G 13



G 14

Fig. 5. Some Möbius-type graphs belonging to the class $Z(\mathbf{V}_j)$.

straightforwardly extended to apply to Möbius-type circuits as well. This, on the other hand, implies that Propositions IIIa and IIIb remain valid also if $Z(\mathbf{V}_j)$ is a Möbius graph.

Consider one example of the application of the above result. When the graph **G10** is chosen as X in $Z(\mathbf{V}_j)$ we have three Möbius-type polycyclic graphs, viz. **G12**, **G13**, and **G14** depicted in Fig. 5; these should be compared with **G6**, **G7**, and **G8**, respectively.

The graphs **G12**, **G13**, and **G14** have identical CEA's shown by Eqs. 9—12.

As an additional remark to the above discussion we note that in the case of polycyclic Möbius graphs it is quite easy to find examples with identical circuit resonance energies. Let G be a Hückel graph and G′ and G″ be two Möbius graphs obtained from G by associating weights -1 to some of its edges. Then G′ and G″ satisfy Eq. 4. Bearing Eqs. 2 and 13 in mind we arrive at the conclusion that the CEA of a Hückel circuit is the same in all Möbius graphs derived from a given parent (Hückel) graph. The same holds for the CEA's of a Möbius circuit. For example, the circuits c in the graphs **G9**, **G10**, and **G11** have equal CEA's. The same holds for the circuits **a+b** in the graphs **G10** and **G11**.

Concluding this work we wish to point out the recently obtained rules[7] for predicting the signs of Aihara's circuit resonance energies. These rules state that

a) CEA of a $(4n+2)$-membered circuit is positive if the circuit is Hückel-type and negative if it is Möbius-type;

b) CEA of a $(4n)$-membered circuit is negative if the circuit is Hückel-type and positive if it is Möbius-type;

c) CEA of an odd-membered circuit is positive regardless of the type of the circuit.

Hence the sign of CEA can be predicted just by counting the number of vertices in the respective circuit.

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