HÜCKEL AND MÖBIUS CYCLIC CONJUGATED MOLECULES

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Abstract

Generalized graphs represent Hückel-type and Möbius-type polycyclic conjugated systems. We show that the number of generalized graphs with different spectra for a given parent graph is not larger than $2^{N(R)}$ and is equal to $2^{N(R)}$ if no two rings are equivalent, $N(R)$ being the number of rings (fundamental circuits) in the parent graph. We demonstrate that the rule for the stability of generalized graphs, proved in a previuos paper, and the information on the relative magnitudes of the effects of individual circuits enable one to predict the stabilities of generalized graphs without performing numerical calculations.

1. Introduction

Hückel's $4n+2$ rule is one of the most fundamental rules of chemistry and has been widely used by organic chemists [1]. This rule states that planar monocyclic systems containing $(4n+2)$ π-electrons are stable and exhibit aromaticity, while those containing $4n$ π-electrons are unstable and exhibit antiaromaticity. This rule was extended to polycyclic conjugated systems (the generalized Hückel rule) [2].

Heilbronner presented the fascinating idea that large-ring polyenes might be twisted once to give Möbius systems, and showed that the stability of Möbius annulenes shows an opposite tendency to the stability of (usual) annulenes [3]. The stability of Möbius annulenes obeys the anti-Hückel rule. This rule was applied to cyclic transition states in certain chemical reactions [4]. In the case of a simple HMO approach, a conjugated molecule is represented by a graph in which each edge has weight 1 [5]. A Möbius annulene is represented by a graph in which one edge has weight -1, indicating the change of the phase for the overlapping of adjacent π-orbitals [6]. The Möbius concept was extended to polycyclic conjugated systems [4,7]. Generalized polycyclic graphs in which each edge has weight 1 or -1 represent Hückel and Möbius polycyclic conjugated molecules [7].

Magnetic properties (London susceptibility, ring current and NMR chemical shift) of cyclic conjugated systems, which have been used as indices for aromaticity [8], were proved to obey a rule similar to the Hückel rule [9]. Further, it was shown that the London susceptibilities of Möbius monocyclic systems obey a modulo 4 rule which shows an opposite tendency to magnetic susceptibilities of conjugated molecules [10].

In a previous paper, we proved the rule for the stability of generalized graphs [11]. This rule states that the sign of the contribution of a circuit in a generalized (poly)cyclic graph to the thermodynamic stability is determined by the type of circuit (Hückel or Möbius) and by the number of vertices in the circuit (see table 1). Since generalized graphs represent Hückel-type and Möbius-type cyclic systems, this rule is valid for Hückel-type and Möbius-type polycyclic systems and thus contains the Hückel rule, the generalized Hückel rule, and the anti-Hückel rule as special cases.

Table 1

Rule for stability of generalized graphs: (a) number of vertices in a circuit; (b) number of vertices in a pair of disjoint circuits

	Types of circuit and pair of disjoint circuits	Effects of circuit and pair of disjoint circuits
(a) $N(C_j) = 4n$	Hückel	destabilize
	Möbius	stabilize
$N(C_j) = 4n+2$	Hückel	stabilize
	Möbius	destablize
(b) $N(C_j)+N(C_k) = 4n$	Hückel, Hückel	stabilize
	Möbius, Möbius	stabilize
	Hückel, Möbius	destabilize
$N(C_j)+N(C_k) = 4n+2$	Hückel, Hückel	destabilize
	Möbius, Möbius	destabilize
	Hückel, Möbius	stabilize

Randić and Zimmerman [12] discussed the stabilities of Möbius polycyclic systems in terms of conjugated circuits [13]. However, they used the assumptions that a Möbius conjugated circuit of size $4n$, $M(n)$, stabilizes Möbius systems, that one of size $4n+2$, $N(n)$, destabilizes Möbius systems, and that the absolute magnitudes of $M(n)$ and $N(n)$ decrease with increasing size of the conjugated circuits. In this paper, we shall study the stabilities of generalized graphs without such assumptions. The aim of the paper is to show that the rule for the stability of generalized graphs enables one to predict the stabilities of generalized graphs without performing numerical calculations.

2. Rule for stability of generalized graphs

The rule for the stability of generalized graphs was proved by applying a Coulson integral formula [14] to the topological resonance energy *TRE* theory [15]. This rule holds for any generalized graphs as long as the systems have completely filled bonding and empty antibonding molecular orbitals and no odd-membered circuits. In this section, we will explain the meanings of the rule.

The topological resonance energy *TRE* is an excellent index for aromaticity of a conjugated molecule [15]. A conjugated molecule with positive (or negative) *TRE* value is predicted to be stable (or unstable). The *TRE* value of a conjugated molecule represented by graph G was defined as the difference between the total π-electron energy calculated from the characteristic polynomial $P(G;X)$ and that calculated from the reference polynomial $R(G;X)$. The difference arises from the presence of circuits in the system because the characteristic polynomial contains the contributions of all the Sachs graphs of G, while the reference polynomial contains the contributions of the acyclic Sachs graphs only [5, 16]. If the system G has completely filled bonding and empty antibonding molecular orbitals, then the *TRE* value of G can also be calculated from the integral expression for *TRE* [15]:

$$TRE = (1/\pi) \int_{-\infty}^{\infty} \ln |P(G;\mathrm{i}X)/R(G;\mathrm{i}X)| \, \mathrm{d}X, \tag{1}$$

where $\mathrm{i} = \sqrt{-1}$.

For convenience, directed and edge-weighted graphs are studied here instead of generalized graphs [11, 17]. The results obtained for directed and edge-weighted graphs are of course valid for generalized graphs, because the former graphs contain the latter graphs as special cases.

Let G^* be a directed and edge-weighted graph for a given parent graph G. This graph G^* is obtained by replacing the edge $r-s$ in G with two directed edges with weights given by

$$w_{rs} = \exp(\mathrm{i}v_{rs}) \qquad \text{for the edge } r \to s,$$

$$w_{sr} = \exp(\mathrm{i}v_{sr}) \qquad \text{for the edge } s \to r. \tag{2}$$

We assume that the v_{rs}'s satisfy the condition:

$$v_{sr} = -v_{rs}. \tag{3}$$

This assumption ensures that the roots of the characteristic polynomial of G^* are real numbers. Figure 1 shows a directed and edge-weighted graph for the naphthalene graph.

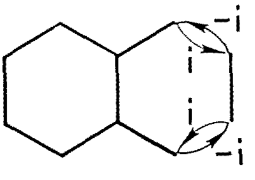

Fig. 1. Directed and edge-weighted graph for naphthalene.

The weights w_{rs} have no effect on the coefficients of the reference polynomial of any graph, and we thus have:

$$R(G^*;X) = R(G;X). \tag{4}$$

The characteristic polynomial of G^* can be expressed in terms of the reference polynomials of certain subgraphs for the parent graph G as follows [11,18]:

$$P(G^*;X) = R(G;X) - 2\sum_j R(G \ominus C_j;X)\cos(V(C_j))$$
$$+ 4\sum_{j>k}\sum R(G \ominus C_j \ominus C_k;X)\cos(V(C_j))\cos(V(C_k)) - \ldots . \tag{5}$$

In eq. (5), $V(C_j)$ is the sum of v_{rs} over all the edges in the circuit C_j along one direction; $G \ominus C_j$ is the subgraph of G obtained by deleting the circuit C_j and all the edges incident to C_j; $G \ominus C_j \ominus C_k$ is the subgraph of G obtained by deleting the pair of disjoint circuits C_j and C_k and all the edges incident to C_j and/or C_k; the first sum runs over all the circuits found in G, and the second one over all possible pairs of disjoint circuits. Figure 2 shows three subgraphs $G \ominus C_j$ for the benzocyclobutene graph.

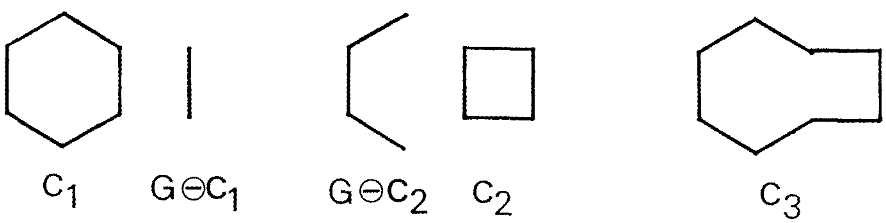

Fig. 2. Three circuits in the benzocyclobutene graph and subgraphs $G \ominus C_j$ for them.

Introduction of eq. (5) into eq. (1) gives the TRE value of the edge-weighted graph G^*:

$$TRE = (1/\pi)\int_{-\infty}^{\infty} \ln|1 - 2\sum_j A(C_j;\mathrm{i}X) + 4\sum_{j>k}\sum B(C_j, C_k;\mathrm{i}X) - \ldots|\,\mathrm{d}X, \tag{6}$$

where

$$A(C_j;\mathrm{i}X) = [R(G \ominus C_j;\mathrm{i}X)/R(G;\mathrm{i}X)]\cos(V(C_j)) \tag{7}$$

and

$$B(C_j, C_k; \mathrm{i}X) = [R(G \ominus C_j \ominus C_k; \mathrm{i}X)/R(G; \mathrm{i}X)]\cos(V(C_j))\cos(V(C_k)). \quad (8)$$

The term $A(C_j; \mathrm{i}X)$ represents the contribution of circuit C_j to the *TRE* and the term $B(C_j, C_k; \mathrm{i}X)$ represents the contribution of the pair of disjoint circuits C_j and C_k.

We classified circuits in directed and edge-weighted graphs into two types: Hückel-type circuits with a positive value of $\cos(V(C))$ and Möbius-type circuits with a negative value of $\cos(V(C))$ [11]. For example, the $\cos(V(C_1))$ value for circuit C_1 in the graph shown in fig. 1 is 1, $\cos(V(C_2)) = \cos(V(C_3)) = -1$ and so C_1 is Hückel-type, C_2 and C_3 are Möbius-type, where C_3 is the sum of the two fundamental circuits C_1 and C_2.

If graph G represents an alternant conjugated polycyclic system with an even number of vertices, then $A(C_j; \mathrm{i}X)$ for any circuit in G is a real function of X and has a definite sign for any X. This is true also for $B(C_j, C_k; \mathrm{i}X)$ for any pair of disjoint circuits. From eq. (6), it is seen that if $A(C_j; \mathrm{i}X)$ is negative (or positive) for any X, then the sign of the contribution of circuit C_j to the *TRE* is positive (or negative) and thus graph G is stabilized (or destabilized) by that circuit, and that if $B(C_j, C_k; \mathrm{i}X)$ is positive (or negative) for any X, then graph G^* is stabilized (or destabilized) by the pair of disjoint circuits C_j and C_k. The sign of $A(C_j; \mathrm{i}X)$ (and of $B(C_j, C_k; \mathrm{i}X)$) is determined by the size and type of the circuit C_j (and of the pair of disjoint circuits C_j and C_k). Table 1 shows the signs of $A(C_j; \mathrm{i}X)$ and $B(C_j, C_k; \mathrm{i}X)$.

3. A property of generalized graphs

By giving a weight 1 or -1 to each edge of the graph representing a polycyclic conjugated molecule, one can obtain a number of generalized graphs. The number of generalized graphs for a given parent graph is $2^{N(B)}$, $N(B)$ being the number of edges in the graph. For example, we have $2^9 (=512)$ generalized graphs for the benzocyclobutene graph. Figure 3 shows four of them. However, most of them have

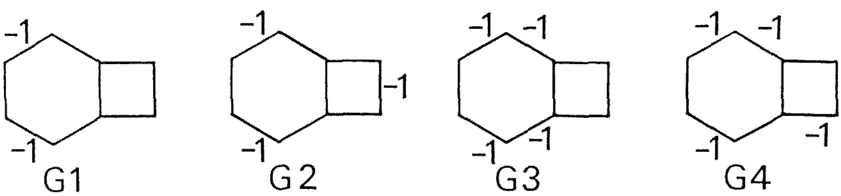

Fig. 3. Four generalized graphs for benzocyclobutene.

the same spectrum or the same set of roots as the characteristic polynomial. Calculations show that the two graphs $G1$ and $G3$ in fig. 3 have the same spectrum. However, it is not easy to understand this without calculation. The aim of this section is to obtain a simple way of finding generalized graphs with the same spectrum and the number of generalized graphs with different spectra for a given parent graph.

Even if the various v_{rs} values are assigned to G^*, these graphs do not always have different spectra. From eq. (5), it is seen that weights in the form of eq. (2) have no effect on the characteristic polynomials of any acyclic systems. This means that any generalized graphs for an acyclic graph have the same spectrum. Equation (5) shows that $P(G^*;X)$ depends on the $V(C_j)$ values for the circuits only (not on the v_{rs} values for individual edges). We showed in a previous paper [19] that the $V(C_j)$ values for all the circuits are not independent and that the number of independent $V(C_j)$ quantities is equal to the number of fundamental circuits (called rings). For instance, in the case of graphs with two fused rings such as naphthalene, $V(C_j)$'s for two fundamental circuits C_1 and C_2 are independent and $V(C_3)$ is equal to $V(C_1) + V(C_2)$. This result corresponds to the fact that by means of a unitary transformation, the adjacency matrix of G^* can be transformed into the adjacency matrix of a graph in which all edges except one edge in each fundamental circuit in G have weight 1 [20]. Thus, it is seen that $P(G^*;X)$ depends on the $V(C_j)$ values for the fundamental circuits only. For example, it is seen that the graph in fig. 1 and graph $G6$ in fig. 4 have the same spectrum.

In the case of the generalized graph, the value of $\cos(V(C))$ for any Hückel-type circuit is equal to 1 and that for any Möbius-type circuit is equal to -1. Thus, it follows that the number of generalized graphs with different spectra for a given parent graph is determined by the types of fundamental circuits found in the graphs. From this, we can obtain the important result that the number of generalized graphs with different spectra for a given parent graph is $2^{N(R)}$, $N(R)$ being the number of fundamental circuits in the parent graph [21]. Generalized graphs can be divided into two categories, Möbius-type graphs which contain at least one Möbius-type circuit and Hückel-type graphs which contain no Möbius-type circuit. So, the number of Möbius-type generalized graphs with different spectra for a given parent graph is $2^{N(R)} - 1$. For example, for the benzocyclobutene graph we can find four generalized graphs with different spectra. The four graphs are $G8$–$G11$, shown in fig. 4. Table 2 shows the types of these four generalized graphs and the types of circuits found in them. Now it is easily seen that the spectra of $G1$, $G2$, $G3$ and $G4$ are equal to the spectra of $G8$, $G10$, $G8$ and $G11$, respectively.

In the above, we have not considered the equivalence of rings. If a given parent graph has equivalent fundamental circuits (rings), then the number of generalized graphs with different spectra for the given parent graph is less then $2^{N(R)}$. Here, the term "equivalent" means that if subgraph $G \ominus C_j$ is identical with $G \ominus C_k$, then the two circuits are equivalent. For instance, the number of generalized graphs with different spectra for naphthalene is $2^2 - 1 = 3$, because the naphthalene graph $G5$ (see fig. 4) has two equivalent rings C_1 and C_2. The three graphs are $G5$–$G7$, shown in fig. 4. Let $G6'$ be a generalized graph for the naphthalene graph in which $\cos(V(C_1)) = -1$ and $\cos(V(C_2)) = 1$. The characteristic polynomial of this graph is

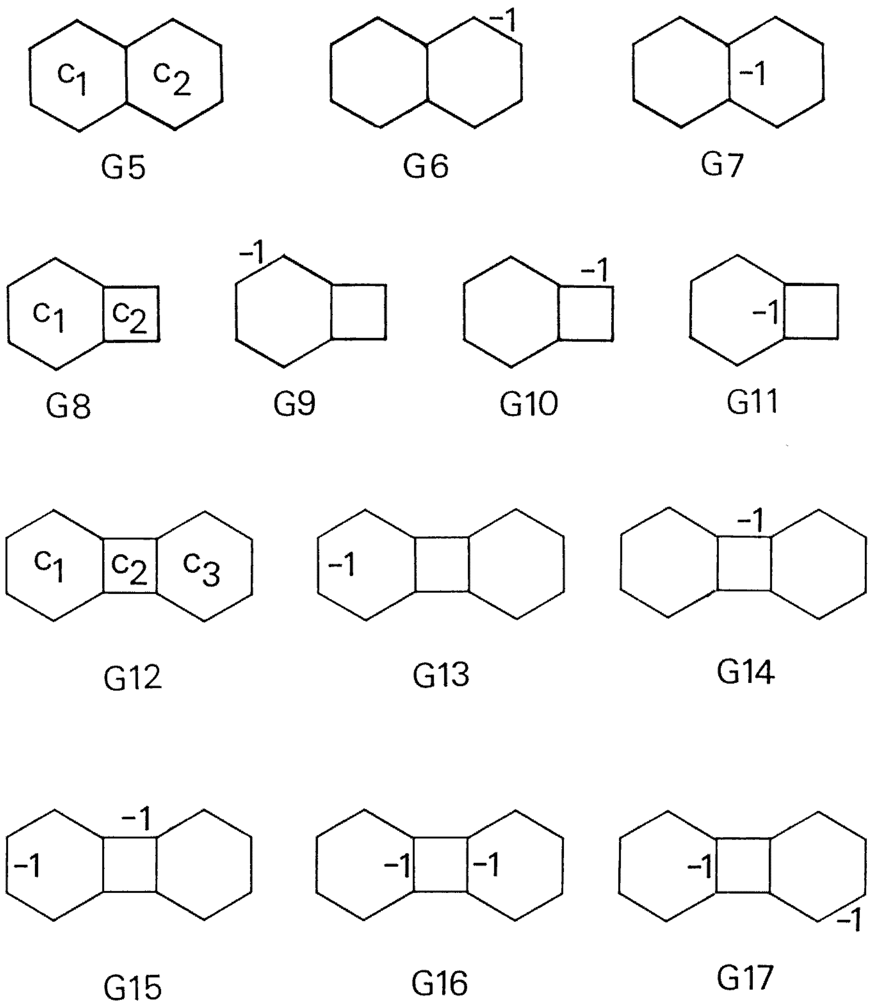

Fig. 4. Generalized graphs with different spectra for three parent graphs.

Table 2

Types of graphs $G5-G11$ (see fig. 4) and types of circuits found in them. Circuit C_3 is the sum of C_1 and C_2

	Type of circuit			Type of graph
Graph	C_1	C_2	C_3	
5	Hückel	Hückel	Hückel	Hückel
6	Hückel	Möbius	Möbius	Möbius
7	Möbius	Möbius	Hückel	Möbius
8	Hückel	Hückel	Hückel	Hückel
9	Möbius	Hückel	Möbius	Möbius
10	Hückel	Möbius	Möbius	Möbius
11	Möbius	Möbius	Hückel	Möbius

$$P(G6';X) = R(G5;X) + 2R(G5 \ominus C_1;X) - 2R(G5 \ominus C_2;X) + 2R(G5 \ominus C_3;X). \tag{9}$$

Since $G5 \ominus C_1$ is identical with $G5 \ominus C_2$, the characteristic polynomial of $G6'$ is identical with that of $G6$. Table 2 shows the types of generalized graphs $G5-G7$ and the types of circuits found in them

Although table 1 shows the effects of individual circuits on stability, the results obtained in this section mean that all the circuits found in a generalized graph do not independently contribute to the stability of the graph. It should be noted that generalized graphs with the same spectrum are different from so-called isospectral graphs [22] because the former graphs have the same skeleton but the latter graphs do not. The *TRE* values of isospectral graphs may be different because the reference polynomials for these graphs may be different. On the other hand, generalized graphs with the same spectrum have the same *TRE* value because they have the same characteristic polynomial and the same reference polynomial.

4. Stabilities of generalized graphs

The rule for stability of generalized graphs enables one to predict without numerical calculation the signs of the effects of each circuit and each pair of disjoint circuits in a generalized graph to the *TRE* value. So, for generalized graphs which contain circuits with the effect of stabilization (or destabilization) only, we can directly find from the rule the signs of the *TRE* values of these graphs. However, for generalized graphs which contain both circuit(s) with the effect of stabilization and circuits(s) with the effect of destabilization we need information on the relative magnitudes of the effects of individual circuits and those of pairs of disjoint circuits.

Such information is obtained from comparison of the magnitudes of $A(C_j;\mathrm{i}X)$ and $2B(C_j, C_k;\mathrm{i}X)$. The factor 2 before $B(C_j, C_k;\mathrm{i}X)$ arises from the fact that, as seen from eq. (5), $B(C_j, C_k;X)$ contributes to $P(G^*, X)$ in the form of $4B(C_j, C_k;X)$, while $A(C_j)$ does so in the form of $2A(C_j;X)$. The coefficient of the reference polynomial for a graph can be obtained by counting the number of mutually independent edges in the graph [5]. Therefore, by counting these numbers for $G \ominus C_j$ and $G \ominus C_j \ominus C_k$, we can estimate the relative magnitudes of $A(C_j;\mathrm{i}X)$ and $2B(C_j, C_k;\mathrm{i}X)$, and thus the relative magnitudes of the effects of individual circuits and the effects of pairs of disjoint circuits.

Let us study the stabilities of the generalized graphs shown in fig. 4.

4.1. GRAPHS $G5-G7$

Graph $G5$ contains three circuits C_1, C_2 and C_3 $(=C_1 + C_2)$. As seen in the previous section, the three generalized graphs with different spectra for the parent graph $G5$ are $G5-G7$. The types of the three circuits in the three graphs are shown

Table 3

Effects of circuits in graphs $G5-G11$ (see fig. 4) on their stabilities. Circuit C_3 is the sum of $C_1$and C_2

	Effect of circuit		
Graph	C_1	C_2	C_3
5	stabilize	stabilize	stablize
6	stabilize	destabilize	destabilize
7	destabilize	destabilize	stabilize
8	stabilize	destabilize	destabilize
9	destabilize	destabilize	stabilize
10	stabilize	stabilize	stabilize
11	destabilize	stabilize	destabilize

in table 2, and the numbers of vertices in the three circuits are 6, 6 and 10, respectively. Therefore, from the rule for the stability of generalized graphs we can see that the circuits in the three graphs have the effects as shown in table 3.

From this table, the following results are obtained. Graph $G5$ is stabilized by every circuit found in this graph and thus this graph is very stable. Graph $G6$ is stabilized by C_1 but destabilized by C_2 and C_3. Since the absolute value of $A(C_1;\mathrm{i}X)$ is equal to that of $A(C_2;\mathrm{i}X)$ and the two circuits C_1 and C_2 in graph $G6$ belong to different types, the effect of circuit C_1 on the stability of $G6$ is cancelled by the effect of C_2. Therefore, the stability of $G6$ is determined by the effect of circuit C_3 only and so $G6$ is unstable. Graph $G7$ is stabilized by C_3 but destabilized by C_1 and C_2. So, for the determination of the sign of the *TRE* value of $G7$, it is necessary to estimate qualitatively the relative magnitudes of the absolute values of the $A(C_j;\mathrm{i}X)$ terms (which are independent of the type of circuit).

By counting disjoint edges in the subgraphs $G5\ominus C_1$, $G5\ominus C_2$ and $G5\ominus C_3$, we can easily obtain

$$R(G5\ominus C_1;X) = R(G5\ominus C_2;X) = X^4 - 3X^2 + 1$$

and

$$R(G5\ominus C_3;X) = 1.$$

By comparing the coeffcients of the above polynomials, we find that

$$|R(G5\ominus C_1;\mathrm{i}X)| = |R(G5\ominus C_2;\mathrm{i}X)| > |R(G5\ominus C_3;\mathrm{i}X)| > 0 \quad \text{for any } X.$$

The above equation, with eq. (7), leads to

$$|A(C_1;\mathrm{i}X)| = |A(C_2;\mathrm{i}X)| > |A(C_3;\mathrm{i}X)| \quad \text{for any } X. \tag{10}$$

This equation means that the absolute magnitude of the effect of C_1 (or C_2) is larger than that of C_3. From this result and table 3, it is seen that $G7$ is more unstable than $G6$.

Thus, we have shown that the signs and order of the *TRE* values of $G5-G7$ are predicted to be as follows:

$$TRE(G5) > 0 > TRE(G6) > TRE(G7). \tag{11}$$

4.2. GRAPHS $G8-G11$

These four graphs, which have three circuits C_1, C_2 and C_3 (see fig. 3), are the generalized graphs with different spectra for the parent graph $G8$. The types of the three circuits in these four graphs are shown in table 2, and the numbers of vertices of the three circuits are 6, 4 and 10, respectively. Therefore, from the rule for the stability of generalized graphs it follows that the circuits in the four graphs have the effects as shown in table 3.

Table 3 shows that graph $G10$ is stabilized by all the circuits in this graph, and the other three graphs contain circuit(s) with the effect of stabilization and circuit(s) with the effect of destabilization at the same time. Thus, it follows that $G10$ has a positive *TRE* value and is the most stable graph of the four.

By counting disjoint edges in the subgraphs $G8 \ominus C_1$, $G8 \ominus C_2$ and $G8 \ominus C_3$, we may easily obtain the reference polynomials of the subgraphs as follows:

$$R(G8 \ominus C_1; X) = X^2 - 1,$$

$$R(G8 \ominus C_2; X) = X^4 - 3X^2 + 1,$$

$$R(G8 \ominus C_3; X) = 1.$$

From the above equations, we can obtain:

$$|R(G8 \ominus C_2; iX)| > |R(G8 \ominus C_1; iX)| > |R(G8 \ominus C_3; iX)| \quad \text{for any } X. \tag{12}$$

The above equation, with eq. (7), leads to

$$|A(C_2; iX)| > |A(C_1; iX)| > |A(C_3; iX)| \quad \text{for any } X.$$

This equation means that the absolute magnitude of the effect of the 4-membered circuit C_2 is larger than that of the 6-membered circuit C_1, which in turn is larger than that of the 8-membered circuit C_3. From this result and table 3, we can predict the order of the stabilities of graphs $G8-G11$ as follows:

$$TRE(G10) > TRE(G11) > TRE(G8) > TRE(G9). \tag{13}$$

The signs of the *TRE* values of graphs $G8$, $G9$ and $G10$ are predicted to be as follows:

$$TRE(G10) > 0 > TRE(G8) > TRE(G9).$$

Unfortunately, from eq. (12) we cannot determine the sign of the *TRE* value of graph $G11$.

4.3. GRAPHS $G12-G17$

From the result of the previous section, it is seen that we can find six generalized graphs with different spectra for the parent graph $G12$. The six graphs are $G12-G17$. These graphs have six circuits C_1, C_2, C_3, $C_4\,(=C_1+C_2)$, $C_5\,(=C_2+C_3)$, and $C_6\,(=C_1+C_2+C_3)$ and a pair of disjoint circuits C_1 and C_3. Table 4 shows the signs of the effects of the circuits and the pair of disjoint circuits in the six generalized graphs.

Table 4

Effects of circuits and a pair of disjoint circuits in graphs $G12-G17$ (see fig. 4) on their stabilities. Circuit C_4 is the sum of C_1 and C_2, C_5 is the sum of C_2 and C_3, and C_6 is the sum of C_1, C_2 and C_3

	Effects of circuit and pair of disjoint circuits			
Graph	C_1	C_2	C_3	
12	stabilize	destabilize	stabilize	
13	destabilize	destabilize	stabilize	
14	stabilize	stabilize	stabilize	
15	destabilize	stabilize	stabilize	
16	destabilize	destabilize	destabilize	
17	destabilize	stabilize	destabilize	
	C_4	C_5	C_6	C_1+C_3
12	destabilize	destabilize	destabilize	stabilize
13	stabilize	destabilize	stabilize	destabilize
14	stabilize	stabilize	stabilize	stabilize
15	destabilize	stabilize	destabilize	destabilize
16	stabilize	stabilize	destabilize	stabilize
17	destabilize	destabilize	stabilize	stabilize

Table 4 shows that graph $G14$ is stabilized by all the circuits and by the pair of disjoint circuits found in this graph, and the other five graphs contain both circuit(s) with the effect of stabilization and circuit(s) with the effect of destabilization. Therefore, it follows that $G14$ has a positive *TRE* value and is more stable than any of the other graphs. It is also seen from this table that graph $G16$ has a negative

TRE value and is the most unstable graph of the six because it is destabilized by all its circuits except C_5, and the effect of C_5 is cancelled by the effect of C_4.

By counting disjoint edges in the subgraphs $G12 \ominus C_j$, we can obtain

$$R(G12 \ominus C_1;X) = R(G12 \ominus C_3;X) = X^6 - 6X^4 + 9X^2 - 2, \tag{14}$$

$$R(G12 \ominus C_2;X) = X^8 - 6X^6 + 11X^4 - 6X^2 + 1, \tag{15}$$

$$R(G12 \ominus C_4;X) = R(G12 \ominus C_5;X) = X^4 - 3X^2 + 1, \tag{16}$$

$$R(G12 \ominus C_6;X) = 1, \tag{17}$$

and

$$R(G12 \ominus C_1 \ominus C_3;X) = 1. \tag{18}$$

Thus, we see that

$$\left.\begin{matrix} |A(C_1;\mathrm{i}X)| = |A(C_3;\mathrm{i}X)| \\ |A(C_2;\mathrm{i}X)| \end{matrix}\right\} > |A(C_4;\mathrm{i}X)| = |A(C_5;\mathrm{i}X)| > |A(C_6;\mathrm{i}X)| \quad \text{for any } X, \tag{19}$$

and

$$|A(C_1;\mathrm{i}X)| = |A(C_3;\mathrm{i}X)| > 2\,|B(C_1, C_3;\mathrm{i}X)| \quad \text{for any } X. \tag{20}$$

From eqs. (14) and (15), we cannot compare the magnitudes of $|A(C_1;\mathrm{i}X)|$ and $|A(C_2;\mathrm{i}X)|$. Equation (19) means that the absolute values of the effects of individual circuits decrease with increasing size of the circuit (except for the case of the two circuits C_1 and C_2). Equation (20) shows that the absolute values of the effects of circuits C_1 and C_3 are larger than that of the pair of disjoint circuits C_1 and C_3.

For complicated graphs such as graphs $G12-G17$, it is convenient to compare the stabilities in terms of a function $Q(G^*;X)$ defined by

$$Q(G^*;X) = -\sum_j A(C_j;X) + 2\sum_{j>k}\sum B(C_j, C_k;X)\ldots\,. \tag{21}$$

Compare the stabilities of $G13$ and $G15$. From table 4, $Q(G13;\mathrm{i}X)$, for example, can be obtained as follows:

$$\begin{aligned} Q(G13;\mathrm{i}X) = &-|A(C_1;\mathrm{i}X)| - |A(C_2;\mathrm{i}X)| + |A(C_3;\mathrm{i}X)| + |A(C_4;\mathrm{i}X)| \\ &- |A(C_5;\mathrm{i}X)| - |A(C_6;\mathrm{i}X)| - 2\,|B(C_1, C_3;\mathrm{i}X)|. \end{aligned}$$

Thus, we have

$$Q(G13;\mathrm{i}X) - Q(G15;\mathrm{i}X)$$
$$= -2\,|A(C_2;\mathrm{i}X)| + 2\,|A(C_6;\mathrm{i}X)| < 0 \quad \text{for any } X,$$

where we used eqs. (14) and (19). From the above equation and eq. (6), it is seen that

$$TRE(G13) < TRE(G15).$$

Next, compare the stabilities of $G13$ and $G16$. From table 4, we can obtain

$$Q(G13;\mathrm{i}X) - Q(G15;\mathrm{i}X)$$
$$= X^6 + 10X^4 + 12\,X^2 > 0 \quad \text{for any } X.$$

From the above equation and eq. (6), it is seen that

$$TRE(G13) > TRE(G16).$$

In a similar way, we can obtain

$$TRE(G14) > \begin{matrix} TRE(G12) \\ TRE(G15) \end{matrix} > \begin{matrix} TRE(G13) \\ TRE(G17) \end{matrix} > TRE(G16). \tag{22}$$

We cannot compare the magnitudes of $TRE(G12)$ and $TRE(G15)$ and the magnitudes of $TRE(G13)$ and $TRE(G17)$. In order to do so, we need other information in addition to eqs. (14)–(20).

Graph $G13$ has a negative TRE value because the effects of the circuits C_1 and C_4 are cancelled by those of C_3 and C_5, respectively, and

$$Q(G13;\mathrm{i}X) = -|A(C_2;\mathrm{i}X)| + |A(C_6;\mathrm{i}X)| - 2\,|B(C_1, C_3;\mathrm{i}X)|$$
$$= -X^8 - 6X^6 - 11X^4 - 6X^2 - 2 < 0 \quad \text{for any } X,$$

where eqs. (15), (17) and (18) were used. Thus, we have shown, as for the signs of the TRE values of graphs $G13$, $G14$ and $G16$, that

$$TRE(G14) > 0 > TRE(G13) > TRE(G16). \tag{23}$$

It is noteworthy that from eqs. (11), (13) and (22), we can estimate the order of the total π-electron energies of these graphs because the generalized graphs for a parent graph have the same reference energy (see eq. (4)).

Thus far, we have estimated the absolute magnitudes of the effects of individual circuits in terms of $A(C_j; \mathrm{i}X)$ and obtained eqs. (10), (12), (19) and (20) which show that the absolute magnitude of $A(C_j; \mathrm{i}X)$ decreases with increasing size of the circuit. However, this is not always true. Gutman and Polansky [23] evaluated the effects of circuits from the value of the integral $\int_{-\infty}^{\infty} |A(C_j; \mathrm{i}X)| \, \mathrm{d}X$. Numerical calculations for C_1 and C_2 in graph $G12$ give:

$$\int_{-\infty}^{\infty} |A(C_1; \mathrm{i}X)| \, \mathrm{d}X = 0.123 \quad \text{and} \quad \int_{-\infty}^{\infty} |A(C_2; \mathrm{i}X)| \, \mathrm{d}X = 0.103.$$

This result shows that the absolute magnitude of the effect of 6-membered circuit C_1 is larger than that of 4-membered circuit C_2. Gutman and Polansky demonstrated that the value of the integral $\int_{-\infty}^{\infty} |A(C_j; \mathrm{i}X)| \, \mathrm{d}X$ depends mainly on the constant term in $|R(G \ominus C_j; \mathrm{i}X)|$ [23]. The above values reflect that the constant term in $|R(G12 \ominus C_1; \mathrm{i}X)|$ is 2 (see eq. (14)), while that in $|R(G12 \ominus C_2; \mathrm{i}X)|$ is 1 (see eq. (15)).

5. Concluding remarks

We have studied generalized graphs which represent Hückel-type and Möbius-type polycyclic conjugated systems. We have shown that the number of generalized graphs with different spectra for a given parent graph is $2^{N(R)}$ if no two rings are equivalent, $N(R)$ being the number of rings (fundamental circuits) in the parent graph. By use of the Sachs theorem and the integral expression for *TRE*, we have estimated by hand the relative magnitude of the effects of individual circuits (and pairs of disjoint circuits). We demonstrated that the rule for the stability of generalized graphs and the information on the relative magnitudes of the effects of individual circuits enable one to predict, without performing numerical calculations, the signs and order of stabilities of generalized graphs for a given parent graph.

It should be noted that the term $A(C_j; X)$ cannot be used to estimate quantitatively the contribution of each circuit to *TRE*, because *TRE* depends not only on effects of individual circuits but also on collective effects of pairs, triplets, etc. of circuits. In order to estimate quantitatively the contribution of each circuit to *TRE*, the concept of circuit resonance energy *CE* was introduced in two different ways: by Aihara [24] and by Gutman and Bosanac [25]. We have recently shown that the *CE*'s defined by Aihara strictly obey the Hückel rule and that the *CE*'s of Möbius-type circuits also obey $4n + 2$ rules [26,27].

References

[1] E. Hückel, Z. Phys. 76(1932)628;
A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* (Wiley, New York, 1961);
M.J.S. Dewar, *The Molecular Orbital Theory of Organic Chemistry* (McGraw–Hill, New York, 1969).

[2] H. Hosoya, K. Hosoi and I. Gutman, Theor. Chim. Acta 38(1975)37;
I. Gutman, J. Chem. Soc. Faraday II 75(1979)799.
[3] E. Heilbronner, Tetrahedron Lett. (1964)1923.
[4] H.E. Zimmerman, J. Amer. Chem. Soc. 88(1966)1564; H.E. Zimmerman, *Quantum Mechanics for Organic Chemistry* (Academic Press, New York, 1975);
M.J.S. Dewar and R.C. Dougher, *The PMO Theory of Organic Chemistry* (Plenum Press, New York–London, 1975).
[5] A. Graovac, I. Gutman and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules* (Springer, Berlin, 1977);
I. Gutman and O.E. Polansky, *Mathematical Concepts in Organic Chemistry* (Springer, Berlin, 1986).
[6] N. Trinajstić, *Chemical Graph Theory* (CRC Press, Boca Raton, FL, 1983).
[7] A. Graovac and N. Trinajstić, Croat. Chem. Acta 47(1975)95.
[8] J.A. Elvidge and L.M. Jackman, J. Chem. Soc. (1961)859;
H.J. Dauben, Jr., J.D. Wilson and J.L. Laity, J. Amer. Chem. Soc. 91(1969)1991;
R.C. Haddon, V.R. Haddon and L.M. Jackman, Fortschr. Chem. Forsch., Topics Curr. Chem. 16(1971)103;
F. Sondheimer, Acc. Chem. Res. 5(1972)81;
R. Banassi, P. Lazzeretti and F. Taddei, J. Phys. Chem. 79(1975)848;
R.C. Haddon, J. Amer. Chem. Soc. 101(1979)1722;
J. Aihara, Bull. Chem. Soc. Japan 53(1980)1163;
R.B. Mallion, Pure Appl. Chem. 52(1980)1541;
J. Aihara, Pure Appl. Chem. 54(1982)1115, and references therein.
[9] N. Mizoguchi, Chem. Phys. Lett. 106(1984)451; N. Mizoguchi, Bull. Chem. Soc. 60(1987)2005.
[10] N. Mizoguchi, Chem. Phys. Lett. 134(1987)371; N. Mizoguchi, J. Mol. Struct. (THEOCHEM) 181(1988)245.
[11] N. Mizoguchi, J. Phys. Chem. 92(1988)2754.
[12] M. Randić and H.E. Zimmerman, Int. J. Quant. Chem. Symp. 20(1986)185.
[13] M. Randić, J. Amer. Chem. Soc. 99(1977)444;
J.A.N.F. Gomes and R.B. Mallion, Rev. Port. Quimica 21(1979)82; J.A.N.F. Gomes, Theor. Chim. Acta 59(1981)333.
[14] C.A. Coulson, Proc. Cambrudge Phil. Soc. 36(1940)201; C.A. Coulson and H.C. Longuet-Higgins, Proc. Roy. Soc. London, Ser. A 191(1947)39; 192(1947)16.
[15] J. Aihara, J. Amer. Chem. Soc. 98(1976)2750;
I. Gutman, M. Milun and N. Trinajstić, J. Amer. Chem. Soc. 99(1977)1692.
[16] H. Sachs, Publ. Math. (Debrecen) 11(1963)119;
I. Gutman, N. Trinajstić and T. Živković, Theor. Chim. Acta 26(1972)67.
[17] N. Mizoguchi, J. Amer. Chem. Soc. 107(1985)4419.
[18] J. Aihara, J. Amer. Chem. Soc. 101(1979)5913.
[19] N. Mizoguchi, Bull. Chem. Soc. 63(1990)765.
[20] R. McWeeny, Mol. Phys. 1(1958)311;
J. Gayoso and A. Boucekkine, C.R. Acad. Sci. Paris C272(1971)184;
R.B. Mallion, Proc. Roy. Soc. London, Ser. A 341(1975)42,
[21] This result was obtained by Merrifield and Simmons in a different way. However, our method can be applied to a wider range of graphs, including directed and edge-weighted graphs. See: R.E. Merrifield and H.E. Simmons, Chem. Phys. Lett. 74(1980)348.
[22] L. Collats and U. Sinogowitz, Abh. Math. Semin. Univ. Hamburg 21(1967)63;
M. Randić, N. Trinajstić and T. Živković, J. Chem. Soc. Faraday Trans. 2(1976)244, and references therein.
[23] I. Gutman and O.E. Polansky, Theor. Chim. Acta 60(1981)203.

[24] J. Aihara, J. Amer. Chem. Soc. 99(1977)2048.
[25] S. Bosanac and I. Gutman, Z. Naturforsch. 32a(1977)10;
I. Gutman and S. Bosanac, Tetrahedron 33(1977)1809.
[26] N. Mizoguchi, Chem. Phys. Lett. 158(1989)383;
[27] The circuit resonance energies calculated by the method of Gutman and Bosanac for some hydrocarbons violate the Hückel rule. See ref. [25].