

# Bond Resonance Energy and Verification of the Isolated Pentagon Rule

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**Abstract:** The isolated pentagon rule (IPR) states that fullerenes with isolated pentagons are kinetically much more stable than their fused pentagon counterparts. This rule can be verified in terms of a graph-theoretically defined bond resonance energy. In general, a  $\pi$  bond shared by two pentagons has a large negative bond resonance energy, thus contributing significantly to the increase in kinetic instability or chemical reactivity of the molecule. The existence of such highly antiaromatic local structures sharply distinguishes IPR-violating fullerenes from isolated-pentagon isomers.  $\pi$  bonds shared by two pentagons are shared by many antiaromatic conjugated circuits but not by relatively small aromatic conjugated circuits.

## Introduction

Fullerenes with up to several hundred carbon atoms are now being studied by laser vaporization of graphite.<sup>1–8</sup> A spheroidal conjugated system in every possible fullerene consists of a suitable number of hexagonal and 12 pentagonal rings. Although many different fullerenes are observable in the gas phase immediately following cluster formation, only a few of them are isolable.<sup>4–8</sup> This implies that many fullerenes are fairly comparable in thermodynamic stability but are markedly different in kinetic stability. Typically, fullerenes 1–8 in Figure 1 form abundantly in the gas phase.<sup>4–8</sup> Among them, C<sub>60</sub> (I<sub>h</sub>) (3) and C<sub>70</sub> (D<sub>5h</sub>) (8) are isolable, but all others are not capable of survival during the synthetic process.

As all isolable fullerenes do not have abutting pentagons, it is generally believed that there must be no abutting pentagons in chemically stable or isolable fullerenes.<sup>4,9–12</sup> This belief is called the isolated pentagon rule (IPR). The IPR has been interpreted primarily in terms of aromaticity.<sup>4,10–12</sup> As a pentalene molecule (9) is highly antiaromatic and extremely reactive,<sup>13</sup> the kinetic instability of fullerenes with local pentalene structures or abutting pentagons has been attributed to such substructures.<sup>4,10–12</sup> In our view, however, there is no decisive evidence supporting such an interpretation of the IPR.

Aromaticity arises from extra thermodynamic stabilization due to cyclic conjugation. The conjugated-circuit resonance energy (CCRE) per carbon atom is one of the conventional measures of aromaticity.<sup>14–17</sup> Schmalz et al. found a rough correlation between the CCRE per carbon atom and the ratio

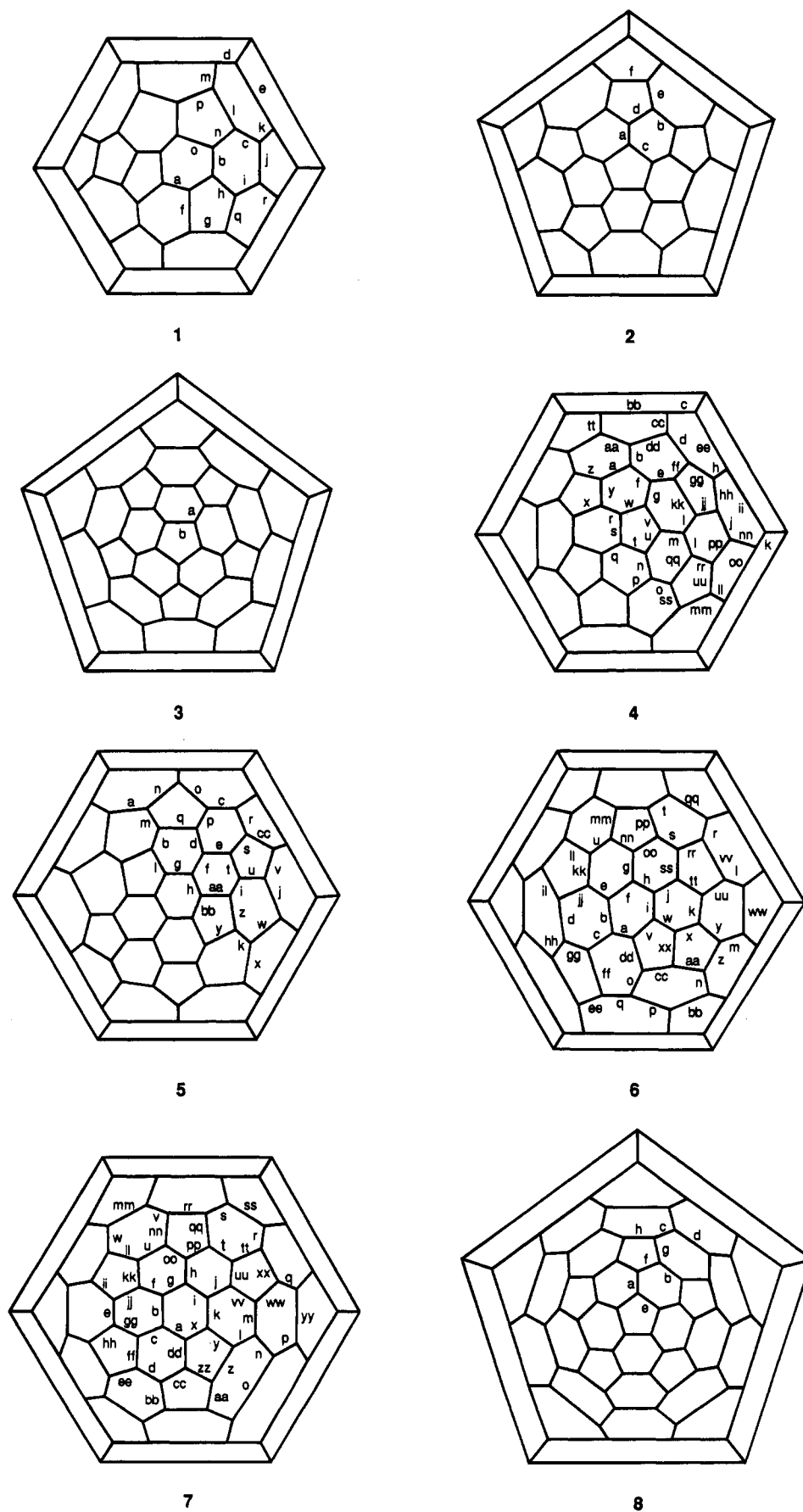
of the number of abutments between pairs of pentagons to the number of carbon atoms.<sup>10–12</sup> IPR-violating fullerenes turned out to be thermodynamically less stable and less aromatic than the IPR-observing, or isolated-pentagon, isomers.<sup>8,10–12</sup> However, in general, larger fullerenes must have larger CCREs per carbon atom. Therefore, it is not easy to explain from such a correlation a marked difference in chemical reactivity between IPR-observing and -violating fullerenes.

The topological resonance energy (TRE) is also a measure of extra thermodynamic stabilization due to cyclic conjugation.<sup>18–25</sup> The % TRE represents the degree of aromaticity, which is defined as 100 times the TRE, divided by the total  $\pi$ -binding energy of the graph-theoretically defined polyene reference.<sup>20–22,24</sup> The TREs and the % TREs for fullerenes 1–8 are summarized in Table 1. It is noteworthy that whether they obey the IPR or not, sizable fullerene molecules are all moderately aromatic with moderately large % TREs. There is no sharp difference in the % TRE between isolable and IPR-violating fullerenes. For example, the % TRE of 3 is comparable to that of 7 although the latter is not isolable. The IPR cannot be explained in terms of such measures as the CCRE and the TRE.

The problem is that the CCRE per carbon atom and the % TRE are not measures of kinetic stability or chemical inertness. Manolopoulos et al. found an interesting correlation between the kinetic stabilities of C<sub>34</sub> to C<sub>70</sub>, as determined by simple Hückel theory highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy separations, and the intensities of photoionization signals from carbon clusters produced by laser vaporization of graphite.<sup>7</sup> Liu et al. likewise presumed that all fullerenes with a HOMO–LUMO gap greater than 0.344  $|\beta|$  (the value for the known stable C<sub>76</sub> molecule) will be kinetically stable enough to survive during

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**Figure 1.** Schlegel diagrams for  $C_{44}$  ( $D_2$ ) (1),  $C_{50}$  ( $D_{5h}$ ) (2),  $C_{60}$  ( $I_h$ ) (3),  $C_{62}$  ( $C_2$ ) (4),  $C_{64}$  ( $D_2$ ) (5),  $C_{66}$  ( $C_2$ ) (6),  $C_{68}$  ( $C_2$ ) (7), and  $C_{70}$  ( $D_{5h}$ ) (8).

the synthetic process.<sup>12</sup> Thus, the HOMO–LUMO energy separation is very promising as an indicator of the tendency to react or decompose. However, this idea has not been applied to the interpretation of the IPR.

We were interested in the graph-theoretical interpretation of the IPR. It is still very true that various electronic aspects of a conjugated system can be elucidated using TRE theory.<sup>20</sup> In this paper the bond resonance energy (BRE), *i.e.*, the contribu-

**Table 1.** % TREs of Fullerenes

species	TRE/ $ \beta $	% TRE	$\pi$ -binding energy per carbon atom/ $ \beta $
C <sub>44</sub> (D <sub>2</sub> ) (1)	0.439	0.656	1.532
C <sub>50</sub> (D <sub>5h</sub> ) (2)	0.708	0.928	1.539
C <sub>60</sub> (I <sub>h</sub> ) (3)	1.643	1.795	1.553
C <sub>62</sub> (C <sub>2</sub> ) (4)	1.206 <sup>a</sup>	1.275 <sup>a</sup>	1.545
C <sub>64</sub> (D <sub>2</sub> ) (5)	1.610 <sup>a</sup>	1.649 <sup>a</sup>	1.550
C <sub>66</sub> (C <sub>2</sub> ) (6)	1.559 <sup>a</sup>	1.549 <sup>a</sup>	1.549
C <sub>68</sub> (C <sub>2</sub> ) (7)	1.606 <sup>a</sup>	1.725 <sup>a</sup>	1.552
C <sub>70</sub> (D <sub>5h</sub> ) (8)	2.036 <sup>b</sup>	1.906 <sup>b</sup>	1.554

<sup>a</sup> Estimated on the assumption that the  $\pi$ -binding energy per carbon atom of the polyene reference is equal to that for C<sub>60</sub> (I<sub>h</sub>) (3). <sup>b</sup> Reference 25.

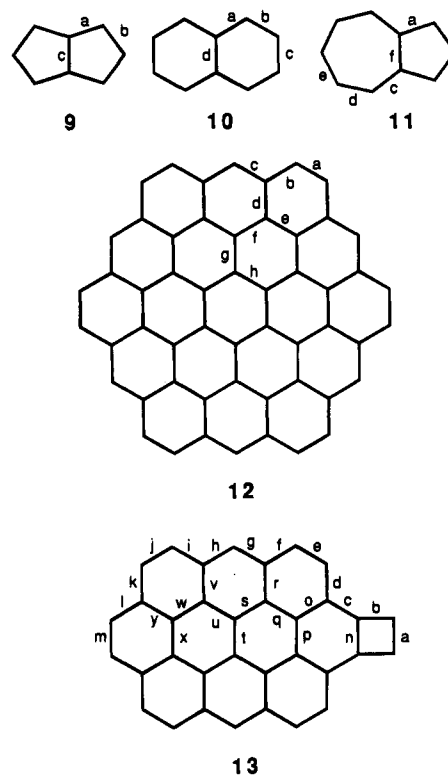
tion of every  $\pi$  bond to aromaticity, is defined within the framework of this theory. It is a practical index for determining the contribution of a given  $\pi$  bond to aromaticity. For IPR-violating fullerenes, the BRE widely varies from  $\pi$  bond to  $\pi$  bond. Just as highly antiaromatic molecules are very reactive,<sup>18,19,26,27</sup> molecules with highly antiaromatic local structures must likewise be very reactive and fragile. We found that the BRE is best suited for elucidating the kinetic instability of IPR-violating fullerenes.

### Definition of the Bond Resonance Energy (BRE)

In chemical graph theory, the term "circuit" means a cyclic path which can be chosen from a cyclic  $\pi$ -electron system.<sup>28,29</sup> For example, there are three circuits in **9**, one peripheral eight-membered and two five-membered ones. Aromaticity and antiaromaticity arise from all possible circuits in a  $\pi$ -electron system. Herndon,<sup>14,15</sup> Randić,<sup>16,17</sup> and Hosoya et al.<sup>30</sup> extensively studied such a geometric aspect of aromaticity. In brief, small  $(4n + 2)$ -membered conjugated circuits contribute much to the stabilization of the molecule, whereas small  $4n$ -membered conjugated circuits contribute much to the destabilization of the molecule.<sup>14-17</sup> The CCRE is an index of aromaticity devised along this way of reasoning.<sup>14-17</sup>

We utilize simple Hückel molecular orbital theory to define the BRE. A polynomial obtained by expanding the Hückel secular determinant is known as a characteristic polynomial, which is usually denoted by  $\mathbf{P}(X)$ . Its coefficients can be enumerated by inspecting the arrangement of  $\pi$  bonds and circuits in a given  $\pi$ -electron system.<sup>28,29</sup> TRE theory enables us to define a characteristic polynomial for the polyene reference of a mono- or polycyclic  $\pi$ -electron system graph-theoretically.<sup>18-25</sup> This polynomial is called a reference or matching polynomial, which is denoted by  $\mathbf{R}(X)$ .

We previously reported that for a monocyclic  $\pi$ -electron system,  $\mathbf{R}(X)$  can be expressed in the form of a secular determinant.<sup>31,32</sup> This kind of determinant is obtained in the following manner. First, an adjacency matrix is constructed for a given monocyclic  $\pi$ -electron system. Then, one  $\pi$  bond, say, the C<sub>p</sub>-C<sub>q</sub> bond, is chosen arbitrarily from the  $\pi$ -electron ring in it. One of the two off-diagonal matrix elements corresponding to this bond is multiplied by  $i$ , and the other by  $-i$ , where  $i$  is the square root of  $-1$ . All other elements in the



**Figure 2.** Molecular graphs for pentalene (**9**), naphthalene (**10**), azulene (**11**), dodecabenzocoronene (**12**), and cyclobut[*d*]ovalene (**13**).

matrix are kept unchanged. A secular determinant obtained with this partly modified adjacency matrix is identical with  $\mathbf{R}(X)$ .<sup>31,32</sup>

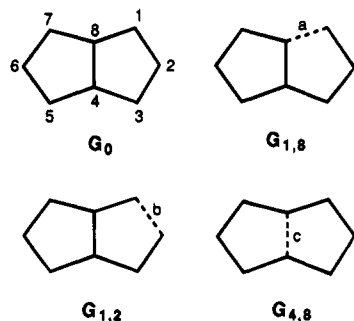
Conversely,  $\mathbf{R}(X)$  is obtainable by expanding the secular determinant defined in this manner. Since a single circuit in the monocyclic  $\pi$ -electron system does not contribute to the coefficients of  $\mathbf{R}(X)$ ,<sup>18-20</sup> the total  $\pi$ -binding energy obtained by solving the equation  $\mathbf{R}(X) = 0$  is devoid of any aromatic stabilization. Therefore, this energy can be interpreted as that of the polyene reference for the molecule in question. Coefficients and zeroes of  $\mathbf{R}(X)$  are always real because the matrix from which the polynomial is derived is Hermitian.<sup>31,32</sup>

Let us consider what happens if the same procedure is applied to a polycyclic  $\pi$ -electron system. First, an adjacency matrix is written for any polycyclic  $\pi$ -electron molecule. Then, one of the two off-diagonal elements corresponding to an arbitrarily chosen  $\pi$  bond, say, the C<sub>p</sub>-C<sub>q</sub> bond, is multiplied by  $i$ , and the other by  $-i$ . All other elements in the matrix are kept unchanged. A secular determinant is constructed with this partly modified adjacency matrix. By expanding the determinant, we obtain the polynomial  $\mathbf{Q}_{p,q}(X)$ , which is neither equal to  $\mathbf{R}(X)$  nor to  $\mathbf{P}(X)$ .

Molecular graphs for true pentalene (**9**) and those corresponding to the partly modified adjacency matrices are shown in Figure 3.  $G_0$  and  $G_{p,q}$  stand for such true and hypothetical  $\pi$ -electron systems, respectively. In the latter graphs, the C<sub>p</sub>-C<sub>q</sub> bond to which imaginary matrix elements are assigned is denoted by a dashed line. For example, a secular determinant for  $G_{1,2}$  in Figure 3 is

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$$\mathbf{Q}_{1,2}(X) = \begin{vmatrix} -X & i & 0 & 0 & 0 & 0 & 0 & 1 \\ -i & -X & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -X & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -X & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & -X & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -X & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & -X & 1 \\ 1 & 0 & 0 & 1 & 0 & 0 & 1 & -X \end{vmatrix} \\ = X^8 - 9X^6 + 24X^4 - 2X^3 - 20X^2 + 4X + 2 \quad (1)$$



**Figure 3.** Molecular graphs for pentalene ( $G_0$ ) and related structures ( $G_{1,8}$ ,  $G_{1,2}$ , and  $G_{4,8}$ ). Dashed lines indicate hypothetically olefinic  $\pi$  bonds.

In order to analyze the coefficients of  $Q_{p,q}(X)$  graph-theoretically, the following two types of products are defined for the elements  $a_{ij}$  in a secular determinant:<sup>20,30</sup>

$$B = a_{ij}a_{ji} \quad (2)$$

$$C = a_{ij}a_{jk}a_{kl}\dots a_{rs}a_{st}a_{ti} + a_{it}a_{ts}a_{sr}\dots a_{lk}a_{kj}a_{ji} \quad (3)$$

For a true conjugated system  $G_0$ ,  $B$  vanishes unless conjugated atoms  $i$  and  $j$  form a  $\pi$  bond, whereas  $C$  vanishes unless conjugated atoms  $i, j, k, l, \dots, r, s,$  and  $t$  form a closed circuit. For a hypothetical  $\pi$ -electron system  $G_{p,q}$ , some type- $C$  products vanish even if the conjugated atoms concerned form a circuit. All type- $B$  products do not change on going from  $G_0$  to  $G_{p,q}$ . For a hypothetical conjugated hydrocarbon  $G_{p,q}$ ,  $B$  and  $C$  take the following values:

$$B = 1 \text{ for all } \pi \text{ bonds including the } C_p-C_q \text{ bond} \quad (4)$$

$$C = 0 \text{ for all circuits along which the } C_p-C_q \text{ bond lies} \quad (5)$$

$$C = 2 \text{ for all other circuits} \quad (6)$$

Here, we assumed that there is no bond-length alternation in  $G_{p,q}$ . Note that  $G_{p,q}$  is characterized by eq 5, which does not hold for a true conjugated system.

Coefficients of  $P(X)$  can be enumerated by appropriately combining type- $B$  and  $-C$  products in eqs 2 and 3, whereas those of  $R(X)$  are enumerated by appropriately combining the type- $B$  products only.<sup>18-20</sup> Coefficients of  $Q_{p,q}(X)$  can likewise be enumerated by appropriately combining nonzero type- $B$  and  $-C$  products in eqs 4-6. Coefficients and zeroes of  $Q_{p,q}(X)$  are all real because a partly modified adjacency matrix is Hermitian. It is evident from eqs 4-6 that  $Q_{p,q}(X) = Q_{q,p}(X)$ . If the  $C_p-C_q$  and  $C_r-C_s$  bonds are shared by the same set of circuits but not by others,  $Q_{p,q}(X) = Q_{r,s}(X)$ . For **9**,  $Q_{1,2}(X) = Q_{2,1}(X)$  and  $Q_{1,2}(X) = Q_{1,8}(X)$ . If conjugated atoms  $p$  and  $q$  belong to a side chain or an acyclic substituent,  $Q_{p,q}(X)$  is identical with  $P(X)$ .

We see from eq 5 that all circuits passing through the  $C_p-C_q$  bond do not contribute to the coefficients of  $Q_{p,q}(X)$ , although this bond has  $\pi$ -bond character. All circuits not sharing the  $C_p-C_q$  bond in  $G_{p,q}$  contribute fully to the coefficients as in the case of  $P(X)$ . Since the  $C_p-C_q$  bond does not contribute at all to aromaticity in the molecule, it can be interpreted as a hypothetically olefinic (*i.e.*, polyene-like)  $\pi$  bond. This bond behaves as if it were a  $\pi$  bond in acyclic polyene. In other words, the  $C_p-C_q$  bond in a cyclic conjugated hydrocarbon can be made olefinic by setting  $a_{p,q} = i$  and  $a_{q,p} = -i$ . However, this bond still works as a full weight when circuits not sharing it are enumerated. Therefore, zeroes of  $Q_{p,q}(X)$  represent the  $\pi$ -orbital energies of  $G_{p,q}$  in which the  $C_p-C_q$  bond alone is made olefinic artificially.

**Table 2.** Topological Resonance Energies (TREs) for Planar Polycyclic Conjugated Hydrocarbons

species	TRE/ $ \beta $	% TRE
pentalene ( <b>9</b> )	-0.215	-2.017
naphthalene ( <b>10</b> )	0.389	2.924
azulene ( <b>11</b> )	0.151	1.143
dodecabenzocoronene ( <b>12</b> )	2.096	2.696
cyclobut[ <i>d</i> ]ovalene ( <b>13</b> )	0.512	1.059

It naturally follows that the total  $\pi$ -binding energy obtained by solving the equation  $Q_{p,q}(X) = 0$  is free from aromatic stabilization due to the circuits sharing the  $C_p-C_q$  bond but contains the stabilization energy due to all other circuits. Therefore, the difference between the total  $\pi$ -binding energies of  $G_0$  and  $G_{p,q}$  can be interpreted as a measure of bond aromaticity, namely, a contribution of the  $C_p-C_q$  bond in  $G_0$  to the aromaticity in it. This energy difference may be called the bond resonance energy (BRE) for the  $C_p-C_q$  bond. The BRE vanishes for all  $\pi$  bonds in acyclic substituents. This corresponds to the fact that substituents are olefinic even if they are conjugated with the  $\pi$ -electron ring.

The TRE of a cyclic  $\pi$ -electron system is not additive with respect to the constituent  $\pi$  bonds. It cannot be obtained by summing up the BREs. For example, the BRE for each  $\pi$  bond in benzene is equal to the TRE of the molecule ( $0.273|\beta|$ ).<sup>18-20</sup> If one  $\pi$  bond in benzene is made olefinic, all other  $\pi$  bonds are necessarily made olefinic. Therefore, the sum of the BREs over all  $\pi$  bonds is six times as large as the TRE. A polycyclic  $\pi$ -electron system is in a much more complicated situation. Most  $\pi$  bonds in a polycyclic system are shared by two or more circuits, and every circuit is formed by three or more  $\pi$  bonds. Thus, the BRE is never suited for estimating the degree of aromaticity in an entire molecule. However, as will be seen below, the BRE is a good index for predicting the kinetic stability or chemical reactivity of individual  $\pi$  bonds.

### BREs for Planar Hydrocarbons

Before going to fullerenes, it is instructive to examine the BREs for planar polycyclic conjugated hydrocarbons **9-12** given in Figure 2. The TREs for these molecules and the BREs for all nonidentical  $\pi$  bonds in them are listed in Tables 2 and 3, respectively.

Pentalene (**9**) is antiaromatic with a large negative % TRE.<sup>20</sup> Apparently this molecule can be seen as perturbed cyclooctatetraene as bond *c* does not create additional conjugated circuits.<sup>14-17</sup> Planar cyclooctatetraene is highly antiaromatic with a % TRE of -5.802.<sup>20</sup> Bond *a* in **9** is highly antiaromatic with a large negative BRE, whereas bond *c* is aromatic with a large positive BRE. This suggests that the peripheral eight-membered conjugated circuit dominates aromatic character of this molecule but that bond *c* is very effective in diminishing the degree of high antiaromaticity due to the peripheral circuit. Since bonds *a* and *b* are shared by the same set of circuits, both have the same BRE.

All  $\pi$  bonds in naphthalene (**10**) are aromatic with large positive BREs, which is consistent with the fact that all these bonds participate in the formation of aromatic conjugated circuits. Bonds *a*, *b*, and *c* are highly aromatic since they are shared by one six-membered and one ten-membered conjugated circuit. Bond *d* has the largest BRE since it is shared by two six-membered conjugated circuits. Smaller ( $4n + 2$ )-membered conjugated circuits contribute more to aromaticity.<sup>14-17</sup>

Azulene (**11**) is moderately aromatic.<sup>18-20,26,27</sup> This molecule can be viewed as perturbed [10]annulene because bond *f* creates no additional conjugated circuits. [10]Annulene is moderately aromatic with a % TRE of 1.247.<sup>20</sup> Bond *f* in **11** has a very

**Table 3.** Bond Resonance Energies (BREs) for Planar Polycyclic Conjugated Hydrocarbons

bond	BRE/ $ \beta $	bond order
(A) Pentalene (9)		
a	-0.232	0.524
b	-0.232	0.650
c	0.327	0.531
(B) Naphthalene (10)		
a	0.210	0.555
b	0.210	0.725
c	0.210	0.603
d	0.267	0.518
(C) Azulene (11)		
a	0.143	0.596
b	0.143	0.656
c	0.129	0.586
d	0.129	0.664
e	0.129	0.639
f	0.003	0.401
(D) Dodecabenzenocoronene (12)		
a	0.122	0.772
b	0.122	0.505
c	0.170	0.605
d	0.209	0.510
e	0.212	0.530
f	0.220	0.535
g	0.189	0.510
h	0.210	0.533
(E) Cyclobut[ <i>d</i> ]ovalene (13)		
a	-0.657	0.854
b	-0.657	0.246
c	0.029	0.630
d	0.076	0.498
e	0.076	0.782
f	0.076	0.488
g	0.146	0.629
h	0.146	0.578
i	0.148	0.524
j	0.148	0.752
k	0.148	0.530
l	0.164	0.545
m	0.164	0.736
n	-0.411	0.554
o	0.096	0.465
p	0.155	0.559
q	0.200	0.538
r	0.197	0.501
s	0.222	0.538
t	0.190	0.512
u	0.206	0.528
v	0.217	0.518
w	0.215	0.527
x	0.218	0.521
y	0.235	0.534

small positive BRE. In many polycyclic systems, a  $\pi$  bond not shared by conjugated circuits acts as a perturber, which tends to diminish the degree of aromaticity or antiaromaticity due to adjacent conjugated circuits. Bond c in **9** and bond f in **11** are such examples.

Circumcoronene or dodecabenzenocoronene (**12**) is predicted to be highly aromatic although it has not been synthesized yet. This molecule may resemble fullerenes, in that it has many carbon atoms bonded to three other carbon atoms. As in the case of **10**, all  $\pi$  bonds in **12** have large positive BREs since they are shared by many aromatic conjugated circuits but not by antiaromatic conjugated circuits. Unlike fullerenes, there are no antiaromatic conjugated circuits in **10–12**.

Cyclobut[*d*]ovalene (**13**) is also a hypothetical hydrocarbon. This molecule is predicted to be as moderately aromatic as azulene (**11**) but must be very reactive because there is a highly antiaromatic four-membered circuit in it. Such a situation can be visualized by evaluating the BREs.  $\pi$  bonds located along

the four-membered ring in **13** have very large negative BREs. Just as a highly antiaromatic molecule is very fragile,<sup>18,19,26,27</sup> such a molecule with highly antiaromatic local structures will be very unstable against chemical reaction and then will be very difficult to isolate. Whenever chemically active species encounter **13**, they must first attack the four-membered ring in order for the entire molecule to be stabilized thermodynamically.

In Table 3, every BRE is compared with the corresponding  $\pi$ -bond order. When a given ring in a polycyclic  $\pi$ -electron system have two or more peripheral  $\pi$  bonds, they usually have very different bond orders. However, they have the same BREs. For example, bonds a and b in **13** have the same BREs although their bond orders are extremely different. Thus, as far as relatively small  $\pi$ -electron systems are concerned, there is no definite correlation between the BRE and the  $\pi$ -bond order. When a  $\pi$ -electron system is sufficiently large, a rough correlation is found between them. Even in this case, many peripheral  $\pi$  bonds are exceptional.

### Isolated Pentagon Rule (IPR)

According to Zhang et al., fullerenes **1–8** are the most stable isomers of such even-numbered carbon clusters.<sup>8</sup> The BREs calculated for all  $\pi$  bonds in **1–8** are listed in Table 4.  $C_{60}$  ( $I_h$ ) (**3**) and  $C_{70}$  ( $C_{5h}$ ) (**8**) satisfy the IPR, whereas all others do not.

A  $\pi$  bond shared by an  $m$ -membered ring and an  $n$ -membered ring is denoted by an  $m/n$  bond. On this basis, carbon–carbon  $\pi$  bonds in fullerenes can be classified into three types: 6/6, 5/6, and 5/5 bonds. As can be seen from Table 4, most 6/6 bonds have not only large positive BREs but also relatively large bond orders. Most 5/6 bonds have small positive or negative BREs. In contrast, all 5/5 bonds have large negative BREs, together with very small bond orders. This indicates that these 5/5 bonds are thermodynamically much less stable than the carbon–carbon bonds in acyclic polyenes. Therefore, it follows that abutting pentagons are never favorable to the stabilization of the fullerene  $\pi$ -electron system. Thus, the existence of extremely unstable 5/5 bonds is closely related to the IPR.

As already stated, conjugated circuits are primary contributors to aromaticity or antiaromaticity in  $\pi$  bonds.<sup>14–17</sup> In addition, Hosoya et al. pointed out that any two isolated hexagons contribute to the stabilization of the molecule, but that any two isolated pentagons contribute significantly to the destabilization of the molecule.<sup>30</sup> Although every five-membered circuit itself is not a conjugated circuit, two isolated pentagons tend to decrease the total  $\pi$ -binding energy of the molecule. If there are many ways to choose two isolated pentagons from the  $\pi$ -electron system, they contribute significantly to the destabilization of the molecule.<sup>30</sup> These aspects of conjugated and nonconjugated circuits can be used to explain qualitatively why 5/5 bonds in IPR-violating fullerenes are highly antiaromatic.

When a 6/6 bond in a fullerene molecule is made olefinic, two six-membered conjugated circuits are lost. Considering that six-membered conjugated circuits are most highly aromatic in nature, the loss of two six-membered circuits must result in a large decrease in aromaticity. It is presumably for this reason that most 6/6 bonds have large positive BREs. When a 6/6 bond is made olefinic, some ten-membered and some twelve-membered conjugated circuits are also lost. When a 5/6 bond is made olefinic, one six-membered conjugated circuit, together with some ten- and twelve-membered conjugated circuits, is lost. This leads to a relatively small decrease or increase in aromaticity.

When one of the 5/5 bonds in IPR-violating fullerene is made olefinic, neither small aromatic nor small antiaromatic conjugated circuits are lost. However, many twelve-membered antiaromatic conjugated circuits are lost. In addition, two

Table 4. Bond Resonance Energies (BREs) for Typical Fullerenes

bond	bond type	BRE/ $ \beta $	bond order	bond	bond type	BRE/ $ \beta $	bond order	bond	bond type	BRE/ $ \beta $	bond order	bond	bond type	BRE/ $ \beta $	bond order				
(A) C <sub>44</sub> (D <sub>2</sub> ) (1)								(F) C <sub>66</sub> (C <sub>2</sub> ) (6)											
a	6/6	0.131	0.631	j	5/6	-0.053	0.481	a	6/6	0.097	0.567	z	5/6	-0.031	0.442				
b	6/6	0.068	0.624	k	5/6	0.001	0.536	b	6/6	0.111	0.477	aa	5/6	-0.026	0.555				
c	6/6	0.162	0.549	l	5/6	-0.016	0.533	c	6/6	0.115	0.528	bb	5/6	-0.022	0.529				
d	6/6	0.057	0.524	m	5/6	-0.077	0.577	d	6/6	0.084	0.607	cc	5/6	-0.059	0.557				
e	5/6	0.009	0.456	n	5/6	-0.006	0.470	e	6/6	0.154	0.580	dd	5/6	-0.075	0.488				
f	5/6	0.013	0.453	o	5/6	-0.086	0.437	f	6/6	0.147	0.506	ee	5/6	-0.080	0.468				
g	5/6	0.001	0.570	p	5/5	-0.263	0.390	g	6/6	0.181	0.572	ff	5/6	-0.038	0.543				
h	5/6	-0.050	0.465	q	5/5	-0.221	0.405	h	6/6	0.160	0.494	gg	5/6	-0.023	0.471				
i	5/6	-0.105	0.638	r	5/5	-0.268	0.389	i	6/6	0.141	0.513	hh	5/6	0.023	0.475				
(B) C <sub>50</sub> (D <sub>5h</sub> ) (2)								(G) C <sub>68</sub> (C <sub>2</sub> ) (7)											
a	6/6	0.100	0.625	d	5/6	-0.035	0.455	a	6/6	0.156	0.523	aa	5/6	0.015	0.570				
b	6/6	0.115	0.543	e	5/6	-0.070	0.560	b	6/6	0.165	0.496	bb	5/6	0.026	0.461				
c	5/6	0.026	0.460	f	5/5	-0.308	0.383	c	6/6	0.174	0.559	cc	5/6	0.069	0.520				
(C) C <sub>60</sub> (I <sub>h</sub> ) (3)								(H) C <sub>70</sub> (D <sub>5h</sub> ) (8)											
a	6/6	0.193	0.601	b	5/6	0.082	0.476	a	6/6	0.192	0.597	e	5/6	0.078	0.477				
(D) C <sub>62</sub> (C <sub>2</sub> ) (4)								(I) C <sub>70</sub> (D <sub>5h</sub> ) (8)											
a	6/6	0.174	0.558	y	5/6	0.005	0.476	b	6/6	0.176	0.602	f	5/6	0.083	0.479				
b	6/6	0.147	0.522	z	5/6	0.080	0.509	c	6/6	0.192	0.545	g	5/6	0.052	0.469				
c	6/6	0.139	0.557	aa	5/6	-0.013	0.582	d	6/6	0.165	0.488	h	5/6	0.118	0.534				
d	6/6	0.089	0.626	bb	5/6	-0.008	0.542												
e	6/6	0.089	0.538	cc	5/6	-0.016	0.459												
f	6/6	0.162	0.495	dd	5/6	-0.041	0.446												
g	6/6	0.130	0.544	ee	5/6	0.060	0.485												
h	6/6	0.167	0.601	ff	5/6	-0.047	0.454												
i	6/6	0.147	0.539	gg	5/6	0.027	0.462												
j	6/6	0.129	0.586	hh	5/6	0.037	0.488												
k	6/6	0.106	0.629	ii	5/6	0.016	0.462												
l	6/6	0.102	0.504	jj	5/6	0.001	0.474												
m	6/6	0.128	0.533	kk	5/6	-0.022	0.532												
n	6/6	0.075	0.516	ll	5/6	-0.060	0.539												
o	6/6	0.116	0.549	mm	5/6	-0.049	0.556												
p	6/6	0.138	0.512	nn	5/6	0.029	0.472												
q	6/6	0.050	0.563	oo	5/6	-0.053	0.434												
r	6/6	0.080	0.611	pp	5/6	-0.052	0.497												
s	5/6	0.015	0.481	qq	5/6	-0.089	0.496												
t	5/6	-0.097	0.516	rr	5/6	-0.119	0.560												
u	5/6	-0.112	0.477	ss	5/6	-0.097	0.488												
v	5/6	-0.019	0.539	tt	5/5	-0.263	0.380												
w	5/6	-0.048	0.457	uu	5/5	-0.279	0.435												
x	5/6	-0.018	0.451																
(E) C <sub>64</sub> (D <sub>2</sub> ) (5)																			
a	6/6	0.182	0.604	p	5/6	0.094	0.511												
b	6/6	0.169	0.603	q	5/6	0.042	0.470												
c	6/6	0.188	0.567	r	5/6	0.093	0.528												
d	6/6	0.186	0.560	s	5/6	0.084	0.569												
e	6/6	0.173	0.526	t	5/6	0.015	0.456												
f	6/6	0.165	0.491	u	5/6	0.047	0.464												
g	6/6	0.183	0.543	v	5/6	0.093	0.528												
h	6/6	0.181	0.544	w	5/6	0.064	0.474												
i	6/6	0.134	0.622	x	5/6	0.059	0.470												
j	6/6	0.188	0.567	y	5/6	0.033	0.461												
k	6/6	0.173	0.603	z	5/6	0.033	0.461												
l	5/6	0.030	0.461	aa	5/6	0.015	0.459												
m	5/6	0.072	0.476	bb	5/6	0.100	0.541												
n	5/6	0.059	0.470	cc	5/5	-0.121	0.425												
o	5/6	0.064	0.474																

pentagonal circuits sharing the 5/5 bond disappear. This is accompanied by the loss of many possible ways to choose two isolated pentagons from the  $\pi$ -electron system, which also contribute to the decrease in the total  $\pi$ -binding energy.<sup>30</sup> Thus, the 5/5 bond in IPR-violating fullerene contributes little to aromaticity but much to antiaromaticity. This must be the main reason why every 5/5 bond in fullerene has a large negative BRE.

By contrast, the 5/5 bond in pentalene (9) has a large positive BRE, stabilizing the entire  $\pi$ -electron system to a large extent.

This can also be accounted for in terms of conjugated circuits. The 5/5 bonds in IPR-violating fullerenes are shared by many antiaromatic conjugated circuits. However, the 5/5 bond in 9 is not shared by any antiaromatic conjugated circuits, so is never highly antiaromatic.

It may be interesting to examine in some detail aromatic character of  $\pi$  bonds in C<sub>68</sub> (C<sub>2</sub>) (7). Bond b in 7 is a 6/6 bond surrounded by four benzene rings. This bond participates in the formation of two six-membered and six ten-membered conjugated circuits. All these aromatic circuits make bond b

**Table 5.** Smallest Localization Energies for Fullerenes

species	SCLE/ $ \beta $	SALE/ $ \beta $
C <sub>44</sub> (D <sub>2</sub> ) (1)	2.510	1.848
C <sub>50</sub> (D <sub>5h</sub> ) (2)	2.501	1.793
C <sub>60</sub> (I <sub>h</sub> ) (3)	2.767	2.490
C <sub>62</sub> (C <sub>2</sub> ) (4)	2.472	1.774
C <sub>64</sub> (D <sub>2</sub> ) (5)	2.571	2.140
C <sub>66</sub> (C <sub>2</sub> ) (6)	2.502	1.802
C <sub>68</sub> (C <sub>2</sub> ) (7)	2.517	1.936
C <sub>70</sub> (D <sub>5h</sub> ) (8)	2.701	2.385

highly aromatic with a large positive BRE. High antiaromaticity in 5/5 bonds can be explained in the same manner. There are two 5/5 bonds in **7**. Each is shared by eight twelve-membered conjugated circuits but by no small aromatic conjugated circuits. Furthermore, every 5/5 bond is relevant to 20 antiaromatic pairs of isolated pentagons. That is, if it is lost, the number of ways to choose two isolated pentagons from the  $\pi$ -electron system decreases by 20. These roughly constitute the reason why 5/5 bonds are highly antiaromatic with a BRE of  $-0.197$ . Every 5/6 bond participates in the formation of one six-membered, some ten-membered, and some twelve-membered conjugated circuits. Therefore, it is neither highly aromatic nor highly antiaromatic.

Different reactivity indices strongly reflect the distribution of highly antiaromatic  $\pi$  bonds with large negative BREs. The well-known localization energy<sup>33,34</sup> is not an exception. This index is used to predict the sites of high reactivity toward electrophiles or nucleophiles in conjugated hydrocarbons.<sup>33,34</sup> The smallest cation localization energies (SCLEs) and the smallest anion localization energies (SALEs) for fullerenes **1–8** are listed in Table 5. All these SCLEs and SALEs are associated with the carbon atoms shared by two or three pentagons. Therefore, we can say that IPR-violating fullerenes undergo electrophilic and nucleophilic reactions preferentially at these carbon atoms. Since a highly antiaromatic 5/5 bond is lost in the  $\sigma$ -complex intermediate formed during the reaction, the corresponding localization energy becomes very small.

For polycyclic benzenoid hydrocarbons, the SCLE and the SALE are the same in magnitude because they are alternant hydrocarbons. For most of these molecules, the cation and anion localization energies at carbon atoms bonded to three other carbon atoms are larger than  $2.7|\beta|$ . For example, both the SCLE and the SALE for this type of carbon atoms in **13** are  $2.785|\beta|$ , which occur at the carbon atoms located along the central hexagon. Both the SCLE and the SALE for all fullerenes are smaller than those for carbon atoms bonded to three other carbon atoms in polycyclic benzenoid hydrocarbons. Of course, the most reactive sites in polycyclic benzenoid hydrocarbons are peripheral carbon atoms.

Fullerenes, such as buckminsterfullerene (**3**) and C<sub>70</sub> (**8**), tend to form molecular anions since the lowest unoccupied molecular orbitals are very low in energy.<sup>7</sup> Therefore, they tend to undergo nucleophilic rather than electrophilic reactions. In line with this, the SALE is smaller than the SCLE for all fullerenes. Above all, IPR-violating fullerenes are predicted to be extremely reactive toward nucleophiles since the SALEs for these molecules are much smaller than those for carbon atoms shared by three  $\pi$  bonds in polycyclic benzenoid hydrocarbons. It now is clear that even if IPR-violating fullerenes are moderately

aromatic, they must be very reactive in harsh experimental conditions. Note that fullerenes are produced in the harsh environment full of active chemical species, such as in arc discharge or laser vaporization chambers.<sup>1–6</sup>

### Concluding Remarks

We previously evaluated two representative reactivity indices, localization energy<sup>33,34</sup> and superdelocalizability,<sup>35,36</sup> for all sites in various nonbenzenoid hydrocarbons and their polyene references, and pointed out that many nonbenzenoid hydrocarbons are chemically reactive even if they are sufficiently aromatic.<sup>37</sup> The present BRE model can settle this kind of problems without referring to the reactivity toward particular chemical species, thus being best suited for discussing general kinetic instability of IPR-violating fullerenes.

The reasons given earlier for pentalene substructures leading to instability in fullerenes proved to be incorrect. It is very reasonable to presume that the IPR-violating fullerenes are very unstable against chemical reaction, not because eight-membered conjugated circuits are highly antiaromatic but because  $\pi$  bonds shared by two pentagons are highly antiaromatic. These  $\pi$  bonds are shared by many antiaromatic conjugated circuits. It is such a marked difference in bond aromaticity that sharply distinguishes IPR-violating fullerenes from isolated-pentagon isomers. The BRE alone can verify the high chemical reactivity of IPR-violating fullerenes.

Edge-sharing pentagons may introduce additional strain to the fullerene cage.<sup>9–11,38</sup> The IPR is apparently consistent with this trend in  $\sigma$  strain.<sup>10,12</sup> As repeatedly stated, this rule is related closely to kinetic stability. High-lying molecular orbitals in fullerenes consist mainly of carbon 2p<sub>z</sub> orbitals.<sup>39</sup> In general, it is such high-lying molecular orbitals that play a predominant role in determining the degree of kinetic stability or chemical reactivity. This way of reasoning is consistent with the fact that the simple Hückel theory HOMO–LUMO energy separation can be used as an indicator of the tendency for a fullerene molecule to react or decompose.<sup>7,12</sup> Therefore, it is highly probable that antiaromatic character of some  $\pi$  bonds, rather than an increase in  $\sigma$  strain, is primarily responsible for the high reactivity of IPR-violating fullerenes. The present approach, based solely on  $\pi$ -electron molecular orbitals, can be justified from this point of view.

Our graph theory is totally based on the Hückel bonding model in its simplest form. No attempt was made to correct for departure from planarity. However, we believe that the verification of the IPR given in this study will survive the seeming naivité of the Hückel bonding model.<sup>7,10</sup>

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