

## Partly Olefinic Reference Structure Defined to Evaluate Bond Resonance Energy and the Ring Current It Would Sustain\*

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The concept of bond resonance energy (BRE) is useful for estimating the degree of kinetic stability for a variety of polycyclic  $\pi$ -systems. In evaluating the BRE for a given  $\pi$  bond in a polycyclic  $\pi$ -system, the corresponding partly olefinic reference structure has been defined, in which cyclic conjugation *via* the  $\pi$  bond is forbidden. The ring-current pattern expected for such a hypothetical  $\pi$ -system were estimated graph-theoretically. Such a ring-current pattern proved very useful to visualizing and characterizing the mode of cyclic conjugation in a partly olefinic  $\pi$ -system.

### INTRODUCTION

Chemical graph theory, to the construction of which Professor Nenad Trinajstić and his school made an enormous contribution, has been applied to elucidate many physical and chemical aspects of cyclic  $\pi$ -systems.<sup>1–3</sup> In 1995, we defined bond resonance energy (BRE) within the same theoretical framework as the contribution of a given  $\pi$  bond to the topological resonance energy (TRE).<sup>4–14</sup> BRE is identical with the energy difference between a cyclic  $\pi$ -system and the reference  $\pi$ -system of the same geometry but with one  $\pi$  bond being made olefinic or polyene-like artificially.<sup>4</sup> This hypothetical  $\pi$ -system differs from an actual one, in that the resonance integrals for one of the  $\pi$  bonds are  $\pm i\beta$ , where  $i$  is the unit of an imaginary number and where  $\beta$  is the standard resonance integral for CC bonds. A hypothetical  $\pi$ -system thus defined may be called a partly olefinic

reference structure or a partly olefinic  $\pi$ -system because at least one  $\pi$  bond is olefinic by definition.

The smallest or minimum BRE in a  $\pi$ -system has been used successfully as an index of kinetic stability for a variety of cyclic  $\pi$ -systems.<sup>4–14</sup> In this context, we have been interested in exploring physical properties expected for partly olefinic reference structures. In such hypothetical  $\pi$ -systems, cyclic conjugation is interrupted at the hypothetically olefinic  $\pi$  bond. Therefore, one can safely assume that a current would not be induced magnetically through the  $\pi$  bond even if it is a constituent of a polycyclic  $\pi$ -system. We then attempted to examine the magnetic response of the partly olefinic  $\pi$ -systems for typical polycyclic conjugated hydrocarbons. In this paper, we estimate the ring-current patterns of these partly olefinic reference structures and compare them with those of the actual  $\pi$ -systems. This must be the best

\* Dedicated to Professor Nenad Trinajstić on the occasion of his 65<sup>th</sup> birthday.

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way to visualize and characterize the mode of cyclic conjugation in the reference structures used for BRE calculations.

## THEORY

We found that at the limit of zero magnetic field the ring-current pattern of an actual polycyclic  $\pi$ -system is given as a superposition of currents induced independently in all possible circuits.<sup>15–19</sup> Here the circuits signify all possible cyclic paths in the  $\pi$ -system.<sup>1,2</sup> If an external magnetic field is perpendicular to the molecular plane, diatropic and paratropic currents are induced in counterclockwise and clockwise directions, respectively, along cyclic paths.

Let the entire  $\pi$  system of a polycyclic hydrocarbon be denoted by  $G$  and a current intensity,  $I_i$ , induced in the  $i$ th circuit,  $r_i$ , is expressed in the form:<sup>18,19</sup>

$$\frac{I_i}{I_0} = 18 \frac{S_i}{S_0} \sum_j^{\text{occ}} \frac{P_{G-r_i}(X_j)}{P'_G(X_j)} \quad (1)$$

Here  $I_0$  is the current intensity induced in the benzene ring;  $S_i$  and  $S_0$  are the areas of  $r_i$  and the benzene ring, respectively;  $G-r_i$  is the subsystem of  $G$ , obtained by deleting  $r_i$  from  $G$ ;  $P_G(X)$  and  $P_{G-r_i}(X)$  are the characteristic polynomials for  $G$  and  $G-r_i$ , respectively;  $X_j$  is the  $j$ th largest zero of  $P_G(X)$ ; and  $j$  runs over all occupied  $\pi$  molecular orbitals. If  $G$  has degenerate  $\pi$  orbitals, this formula must be replaced by others.<sup>15,18</sup> Positive and negative values for  $I_i/I_0$  denote diamagnetic and paramagnetic circuit currents, respectively. Current intensities will be given in units of that for benzene.

The ring-current distribution in a partly olefinic  $\pi$ -system can be obtained in essentially the same manner. It is given as a superposition of currents induced in all circuits but the ones passing through the  $\pi$  bond in question (*e.g.*, the  $k$ th  $\pi$  bond). By definition,  $G_k$  is a partly olefinic  $\pi$ -system of the same geometry as  $G$  in which the  $k$ th  $\pi$  bond is made olefinic artificially. All circuits passing through the  $k$ th  $\pi$  bond are missing in this reference structure. In other words, cyclic motion of  $\pi$  electrons is forbidden along these circuits. Eq. (1) can be used to evaluate circuit currents induced in  $G_k$  if  $G$  is replaced by  $G_k$  and if  $X_j$  is replaced by the  $j$ th largest zero of  $P_{G_k}(X)$ .

Such a graph-theoretical variant of the Hückel-London ring-current model is the only one that can prove explicitly that a ring current can be obtained in an additive manner.<sup>13–19</sup> The validity of Eq. (1) can be checked by examining if it reproduces the ring-current pattern obtained by standard procedures.<sup>20–22</sup> All  $\pi$  bonds are assumed to have equal resonance integrals. A circuit-current analysis has so far made for relatively small polycyclic aromatic hydrocarbons, such as naphthalene, azulene, and biphenylenes.<sup>18,19</sup> We analyze below the

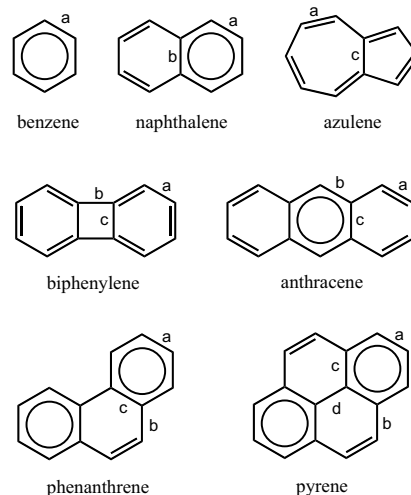


Figure 1. Seven aromatic hydrocarbons investigated.

ring currents induced in seven typical aromatic hydrocarbons in Figure 1 and related partly olefinic reference structures.

## RESULTS AND DISCUSSION

The BREs calculated for different  $\pi$  bonds in seven aromatic hydrocarbons are presented in Figure 2. They are given in units of  $|\beta|$ . If one of the  $\pi$  bonds in benzene is made olefinic by multiplying the resonance integrals by  $\pm i$ , all other  $\pi$ -bonds are naturally made olefinic. Likewise, if a given  $\pi$  bond in a polycyclic  $\pi$ -system is made olefinic, all  $\pi$  bonds on the same arc made of  $\pi$  bonds are made olefinic and hence have the same BREs. In Figure 1, representative  $\pi$  bonds that belong to different arcs are denoted by lower-case alphabetical letters. For example, naphthalene consists of two groups of  $\pi$  bonds with different BREs. Pyrene comprises four groups of  $\pi$  bonds.

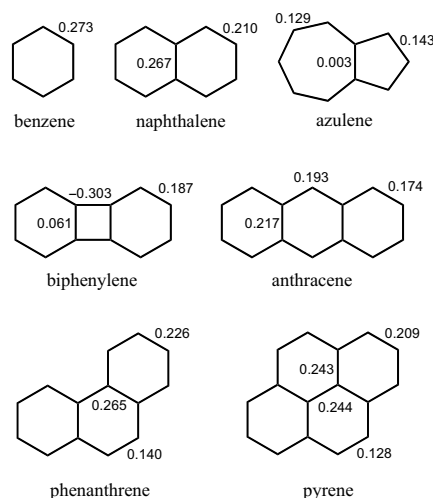


Figure 2. Bond resonance energies (BREs) in units of  $|\beta|$  for seven aromatic hydrocarbons.

The BRE for a  $\pi$ -bond shared by two six-membered rings, such as bond **b** in naphthalene, bond **c** in anthracene, bond **c** in phenanthrene, and bonds **c** and **d** in pyrene, is fairly large, suggesting that all six-membered circuits contribute significantly to aromaticity.<sup>16,17</sup> In contrast, the  $\pi$  bond shared by two odd-membered rings in azulene (bond **c**) has a very small BRE, which implies that both five- and seven-membered circuits contribute little to aromaticity. For semibenzenoid biphenylene, a central four-membered ring is formed with four  $\pi$  bonds with small positive or large negative BREs (bonds **b** and **c**). The four-membered circuit must make a large negative contribution to aromaticity.

Ring-current patterns of seven aromatic hydrocarbons are summarized in Figure 3. Positive and/or negative values indicated around the molecular structures represent the intensities of diatropic and paratropic currents, respectively. Currents flowing through individual  $\pi$  bonds may be referred to as bond currents. Bond currents flowing through  $\pi$  bonds shared by two rings are not presented, which can easily be calculated using Kirchhoff's law. The nucleus-independent chemical shift (NICS) values<sup>23,24</sup> are given in boldface at individual ring centers. Positive and negative NICS values indicate paratropic and diatropic environments, respectively.

Figure 3 shows that the NICS value at a given ring center is primarily determined by the current that the ring sustains. For example, two benzene rings in biphenylene are diatropic with a small negative NICS value, whereas the central four-membered ring is paratropic with a large positive NICS value. Benzene rings in other species are all diatropic in the sense that the NICS values concerned are positive in sign. In Figure 1 Clar structures are depicted for five benzenoid hydrocarbons.<sup>8,25</sup> Here circles represent aromatic sextets in Clar's sense.<sup>25</sup> It is noteworthy that benzene rings in which circles are written sustain larger diatropic currents. In general, peripheral  $\pi$  bonds

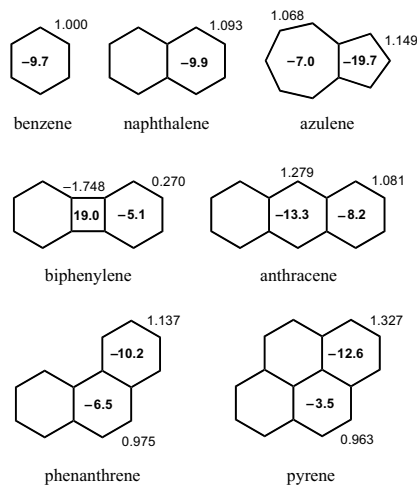


Figure 3. Ring currents induced in seven aromatic hydrocarbons. All current intensities are given in units of that for benzene. Values in individual rings are the NICS values cited from Refs. 23 and 24.

with large positive BREs belong to rings with large negative NICS values. Among such  $\pi$  bonds are bond **b** in anthracene and bonds **a** in phenanthrene and pyrene.

All non-identical circuits in seven hydrocarbons, together with currents induced in them, are presented in Figure 4. A ring current in any polycyclic  $\pi$ -system is

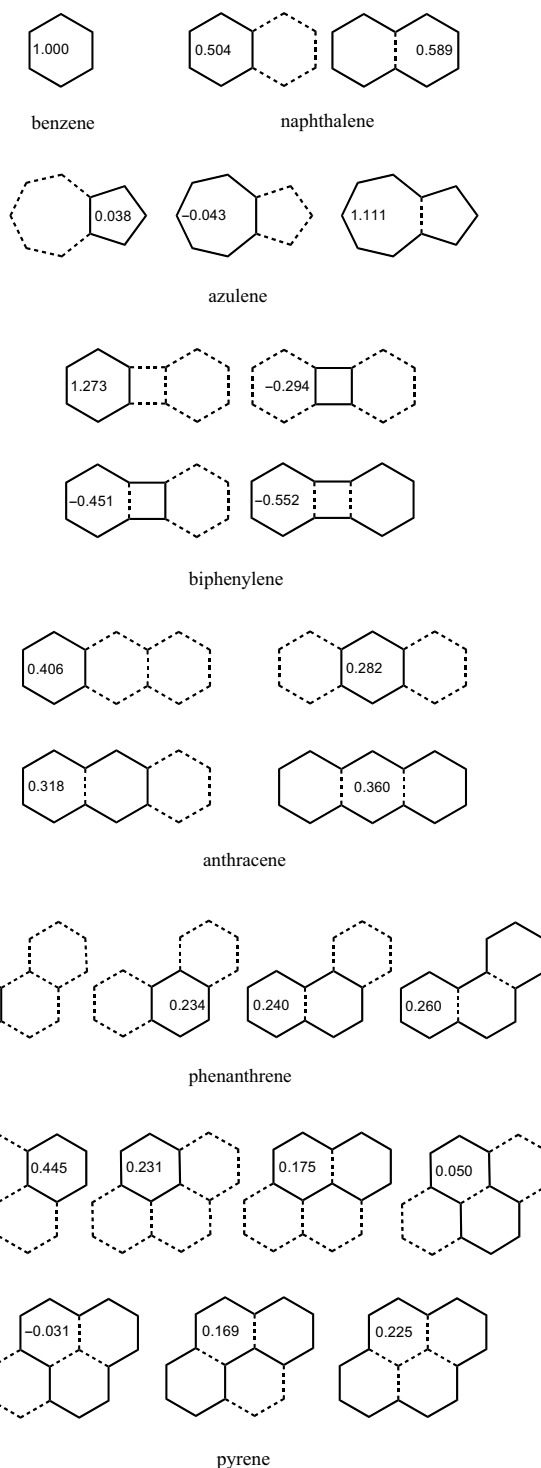


Figure 4. Non-identical circuits and circuit currents for seven aromatic hydrocarbons. All current intensities are given in units of that for benzene.

obtainable by superposing such circuit currents. One may suspect that in symmetric polycyclic benzenoid hydrocarbons, such as naphthalene, anthracene, and pyrene, a ring current is induced mainly along the periphery of the  $\pi$ -system since inner  $\pi$  bonds sustain no or little current. Typically, the central  $\pi$  bond shared by two rings in naphthalene (bond **b**) sustains no current. It then appears that the only circuit current in naphthalene is the one induced in the peripheral ten-membered circuit. This picture is consistent with Platt's perimeter model, which states that peripheral conjugation is a determinant for the aromaticity of a polycyclic  $\pi$ -system.<sup>26</sup> However, this way of reasoning does not hold for polycyclic benzenoid hydrocarbons.

We should remember that three different circuit currents are induced in naphthalene. As shown in Figure 4, all of them are diatropic or diamagnetic in nature. Currents induced in two six-membered circuits are as strong as that induced in the peripheral ten-membered circuit. Therefore, the NICS value of  $-9.9$  at each ring center<sup>23</sup> must be attributed not only to the six-membered circuits but also to the ten-membered one. It follows that the absence of a bond current at bond **b** is due to the complete cancellation of diatropic currents induced in two adjacent six-membered circuits. Thus, by analyzing relevant circuit currents, we can imagine explicitly that a current and a countercurrent of the same intensity flow simultaneously through the central  $\pi$  bond of naphthalene.

Azulene is the only non-alternant hydrocarbon investigated. Large negative NICS values were calculated at two odd-membered rings in it.<sup>23</sup> On this sole basis, one may presume that these two rings might be as highly aromatic as benzene rings in naphthalene. A ring current in azulene likewise is given as a superposition of three circuit currents. However, the currents induced in five- and seven-membered circuits are negligibly small. This is consistent with the very small BRE for bond **c**. The five- and seven-membered circuits are only slightly diatropic and paratropic, respectively. Therefore, we can safely say that the ring current in azulene is determined primarily by the current induced in the peripheral ten-membered circuit. A negative NICS value does not always indicate that a diatropic current is induced in the ring concerned.<sup>27</sup> It simply implies that the center of the ring is in the diatropic environment.

As for biphenylene, bond **b** has a large negative BRE. This  $\pi$  bond is shared by one four-, two eight-, and one twelve-membered circuit, which are all paratropic and antiaromatic. In general, the sign or direction of a circuit current formally obeys the Hückel ( $4n + 2$ ) rule even if the circuit belongs to a polycyclic  $\pi$ -system;<sup>28</sup>  $4n$ - and  $(4n + 2)$ -membered circuits are paratropic and diatropic, respectively. This Hückel-like rule is consistent with the conjugated circuit theory<sup>29,30</sup> and with the extended Hückel rule proposed by Hosoya *et al.*<sup>31</sup> Paratropic circuits in biphenylene are all  $4n$ -membered ones. Odd-membered circuits, such as those in azulene, are es-

entially non-aromatic as predicted by Herndon, Randić, and Hosoya *et al.*<sup>28–30</sup>

Circuit currents induced in anthracene and phenanthrene can be interpreted in the same manner. All circuits in these two hydrocarbons are diatropic ( $4n + 2$ )-membered ones. Currents induced in the edge six-membered circuits are larger than that induced in the central six-membered circuit. It is noteworthy that currents induced in six-, ten-, and fourteen-membered cir-

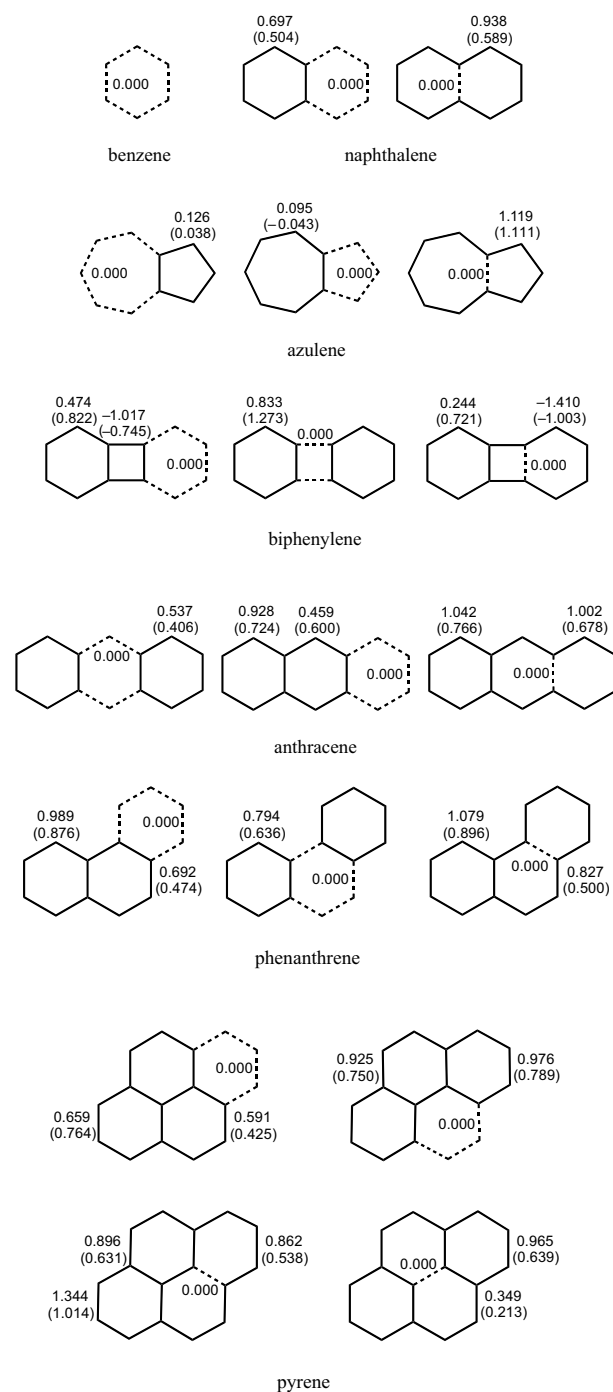


Figure 5. Ring currents that are supposedly induced in all non-identical partly olefinic reference structures for seven aromatic hydrocarbons. All current intensities are given in units of that for benzene.

cuits are of comparable intensity, which obviously reflects the fact that larger  $(4n + 2)$ -membered circuits are less aromatic but larger in size.<sup>16</sup> Pyrene has two twelve-membered non-conjugated circuits, together with many  $(4n + 2)$ -membered conjugated ones. In general, non-conjugated circuits sustain very weak currents even if they are even-membered ones.<sup>16</sup>

We proceed to explore some physical properties of the ring-current distributions in the partly olefinic reference structures defined to evaluate BREs. Figure 5 shows the ring-current patterns for all non-identical partly olefinic  $\pi$ -systems associated with seven aromatic hydrocarbons. Values in parentheses are the reference ring currents, which were estimated by subtracting from the actual ring-current patterns in Figure 3 the currents induced in all circuits sharing the hypothetically olefinic  $\pi$  bond. If a given  $\pi$  bond in a polycyclic  $\pi$ -system is made olefinic, all  $\pi$  bonds on the same arc are made olefinic and no longer sustain bond currents. In Figure 5 all  $\pi$  bonds thus made olefinic are denoted by dashed lines. The same partly olefinic  $\pi$ -system can be obtained by assigning the resonance integrals of  $\pm i\beta$  to any of the dashed bonds.

It can be seen readily from Figure 5 that the gross ring-current pattern expected for a partly olefinic reference structure can be predicted using the intensities of related circuit currents in the actual  $\pi$ -system. At least, the signs or directions of most bond currents in a partly olefinic  $\pi$ -system can be predicted in this manner. This fact implies that even in partly olefinic  $\pi$ -systems an entire  $\pi$ -system, including the olefinic portion, is responsible for the details of the ring-current pattern. As far as polycyclic benzenoid hydrocarbons are concerned, most of the circuit currents are intensified to some extent in the partly olefinic  $\pi$ -system.

Comparative study of Figures 3 and 5 further reveals that the ring-current pattern in a partly olefinic  $\pi$ -system reflects the corresponding BRE. When the partly olefinic  $\pi$ -system corresponds to a very large BRE, some of the bond currents in it are fairly small as compared to those in the actual  $\pi$ -system. For example, when bonds **a** in naphthalene, biphenylene, phenanthrene, and pyrene are made olefinic, some of the bond currents in the corresponding partly olefinic  $\pi$ -systems are appreciably diminished. The same thing occurs when bond **b** in anthracene is made olefinic. The partly olefinic  $\pi$ -system that corresponds to a negative BRE is more aromatic with large diatropic currents than the actual  $\pi$ -system. Such a situation occurs if bond **b** in biphenylene is made olefinic.

We then explore the mode of conjugation in individual partly olefinic  $\pi$ -systems by examining the ring-current patterns in some detail. For monocyclic benzene, the BRE is equal to the TRE. If one of the  $\pi$  bonds is made olefinic, the entire  $\pi$ -system no longer sustains any ring current. Two non-identical partly olefinic structures are conceivable for naphthalene. If bond **a** is made olefinic, one six-membered and one ten-membered circuit vanish and

only one six-membered circuit remains in the  $\pi$ -system. Therefore, this partly olefinic  $\pi$ -system can be viewed as a resonance hybrid of substituted benzene and substituted *o*-xylylene. It is well-known that *o*-xylylene derivatives are olefinic in nature. It may be for this reason that a smaller ring current is induced in the partly olefinic  $\pi$ -system even if the current induced in the six-membered circuit is intensified as compared to that in actual naphthalene. If bond **b** in naphthalene is made olefinic, the current induced in the ten-membered circuit is noticeably intensified as compared to that in the actual  $\pi$ -system.

As has been seen in Figure 4, five- and seven-membered circuits in azulene sustain very small circuit currents. Therefore, even if bond **c** is made olefinic, the ring-current pattern will remain almost unchanged. This was found to be the case. If bond **a** or **b** is made olefinic, the entire  $\pi$ -system is made essentially olefinic with a very small ring current. When bond **b** in biphenylene is made olefinic, all paratropic  $4n$ -membered circuits disappear and then large diatropic currents are induced in the two benzene rings. The resulting partly olefinic  $\pi$ -system can be seen as a biphenyl derivative.

Partly olefinic  $\pi$ -systems for anthracene are interesting in some respects. When bond **a** is made olefinic, the current induced in the central benzene ring becomes somewhat weaker than that induced in the edge benzene ring. This  $\pi$ -system may be depicted as a resonance hybrid of 2,3-disubstituted naphthalene and 2,3-dimethylenenaphthalene. Note that 2,3-dimethylenenaphthalene is much less aromatic than naphthalene. A smaller current induced in the central ring may possibly reflect such a resonance hybrid. When bond **b** is made olefinic, relatively weak diatropic currents are induced in the two isolated benzene rings. This ring-current pattern coincides with the fact that the  $\pi$ -system can be described formally as a combination of aromatic benzene and non-aromatic *o*-xylylene. When bond **c** is made olefinic, diatropic currents induced in large  $(4n + 2)$ -membered circuits are markedly intensified as in the case of naphthalene.

Phenanthrene is more or less similar in diatropicity to anthracene. When bond **a** in phenanthrene is made olefinic, the current induced in the central benzene ring becomes much weaker than that induced in the edge benzene ring. In harmony with this, the partly olefinic  $\pi$ -system can be depicted as a resonance hybrid of naphthalene and 1,2-dimethylenenaphthalene derivatives. When bond **b** is made olefinic, the  $\pi$ -system becomes a kind of biphenyl or stilbene derivative. Therefore, diatropic currents induced in the two edge benzene rings are larger than those in the partly olefinic anthracene  $\pi$ -system in which bond **b** is made olefinic. When bond **c** is made olefinic, the currents induced in large  $(4n + 2)$ -membered circuits are appreciably intensified.

Four different partly olefinic  $\pi$ -systems are conceivable for pyrene. When bond **a** is made olefinic, the  $\pi$ -system becomes a resonance hybrid of 1- and 9-methylenephthalene

derivatives. This might explain why two benzene rings near the olefinic portion sustain fairly small diatropic currents as compared to the remaining benzene ring. When bond **b** in pyrene is made olefinic, the  $\pi$ -system becomes a phenanthrene derivative and the ring-current pattern is similar to that in phenanthrene. When bond **d** is made olefinic, the  $\pi$ -system becomes a kind of metacyclophane, in which two six-membered circuits sustain large diatropic currents.

## CONCLUDING REMARKS

In 1995 a partly olefinic  $\pi$ -system was defined to estimate the BREs for a polycyclic  $\pi$ -system. Since it is a hypothetical reference structure, we have been using it without imaging its physical characteristics. We found that the circulation of  $\pi$ -electrons in such a reference structure can be visualized and characterized by graph-theoretically evaluating the ring current induced in it. All circuit currents in a partly olefinic  $\pi$ -system still obey the extended Hückel rule. As has been seen, the ring-current pattern in a partly olefinic  $\pi$ -system reflects not only the magnitude of the corresponding BRE but also the classical resonance structures that can be written for it. Thus, the mode of conjugation in the partly olefinic reference can be read from its ring-current pattern. Further analysis of the ring-current pattern would deepen our understanding of the BRE concept. BRE cannot be defined for a partly olefinic  $\pi$ -system.

In fact, the BRE concept can be traced back to the work carried out by Gutman *et al.*<sup>32,33</sup> In 1978 they reported that the TRE can be partitioned exactly among the constituent  $\pi$  bonds in a cyclic  $\pi$ -system. In the present study, however, we utilized our own definition of BRE.<sup>4-14</sup> It is suited at least for discussing the effect of individual circuits on aromaticity and chemical reactivity. Our BRE can easily be calculated for any of very large  $\pi$ -systems even if TRE cannot be calculated for it.

As repeatedly mentioned, a partly olefinic  $\pi$ -system was defined by multiplying the resonance integrals for one of the  $\pi$  bonds in an actual  $\pi$ -system by  $\pm i$ . This approach in principle is essentially an extension of that employed to construct the secular determinant for the polyene reference of a monocyclic  $\pi$ -system.<sup>34,35</sup> Analogous approaches have since be devised not only to construct a secular determinant for the polyene reference of a symmetric bicyclic  $\pi$ -system<sup>36</sup> but also to estimate the degree of superaromaticity in super-ring molecules such as kekulene and cyclacenes.<sup>37</sup>

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**SAŽETAK****Djelomična olefinska referentna struktura uvedena za računanje rezonancijske energije veze i struje prstenova****Jun-ichi Aihara, Rika Sekine i Sumio Oe**

Koncepcija o rezonancijskoj energiji veze pokazala se pogodnom za predviđanje stupnja kinetičke stabilnosti različitih policikličkih konjuguiranih molekula. Izračunavanje rezonancijske energije veze za određenu  $\pi$  vezu u nekoj policikličkoj konjugiranoj molekuli temelji se na djelomično olefinskoj referentnoj strukturi u koju nije uključena ciklička konjugacija koja sadrži tu vezu. Očekivani izgled struje prstenova za takav hipotetski sustav dobijen je pomoću teorije grafova. Izgled struje prstenova pokazao se vrlo pogodnim za vizualiziranje i karakteriziranje načina cikličke konjugacije u djelomično olefinskim sustavima.