# Bond Resonance Energy as an Indicator of Local Aromaticity

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By definition, bond resonance energy (BRE) represents the contribution of a given $\pi$-bond to aromaticity. The minimum BRE in a $\pi$-system is an excellent measure of kinetic stability. It was found that the BRE for a peripheral $\pi$-bond correlated not only to the harmonic oscillator model of aromaticity (HOMA) index for a ring, to which the $\pi$-bond belongs, but also to the corresponding bond-order index of aromaticity (BOIA) for local aromaticity. Thus, the BRE for a peripheral $\pi$-bond can be used as an energetic indicator of local aromaticity at least for polycyclic aromatic hydrocarbons (PAHs).

Clar's sextet formula with the largest number of disjoint aromatic sextets and the smallest number of localized double bonds was devised to characterize the chemistry of a polycyclic aromatic hydrocarbon (PAH).[1–3] Aromatic sextets or sextet rings are defined as six $\pi$-electrons localized in a single benzene ring separated from adjacent rings by formal single bonds. Fully benzenoid hydrocarbons, i.e., PAHs in which all $\pi$-electrons belong to sextet rings, are not only thermodynamically but also kinetically very stable.[1–3] In general, a PAH with a given number of aromatic sextets is more stable than its isomers with fewer aromatic sextets. These empirical facts strongly suggest that each ring in a PAH molecule must have different aromatic character.[4–14] Various theoretical measures have been proposed to quantify the degree of local aromaticity in PAHs.[4–24] Quite recently, Bultinck has published a comprehensive review on the local aromaticity concept.[24]

An aromatic molecule must be thermodynamically stable in nature. Therefore, it is desirable to define the degree of local aromaticity in energetic terms. In 1995, we proposed a new energetic quantity, bond resonance energy (BRE), to estimate the contribution of each $\pi$-bond to the aromaticity of a polycyclic $\pi$-system.[11,25–35] BRE has proven to be very useful for identifying the reactive sites in polycyclic $\pi$-systems, such as those in PAHs and fullerenes. BREs for fullerene $\pi$-bonds shared by two pentagonal rings are kinetically very unstable with BREs $< -0.100|\beta_0|$.[25,27] This is the origin of the isolated pentagon rule. BRE can also be used as an indicator of local aromaticity for PAHs. In this paper, the correlations of the BREs for peripheral $\pi$-bonds with two typical local aromaticity criteria, that is, the harmonic oscillator model of aromaticity (HOMA) index[15,16,18,20] and the bond-order index of aromaticity (BOIA) value,[22,24] are examined in some detail.

## Theory

BRE is defined within a Hückel framework as follows.[11,25,27] A hypothetical $\pi$-system, in which a given $\pi$-bond (e.g., the $C_p$–$C_q$ bond) interrupts the cyclic conjugation of $\pi$-electrons thereat, is constructed by assuming $\beta_{pq} = i\beta$ and $\beta_{qp} = -i\beta$, where $\beta$ is the standard resonance integral between two carbon $2p_z$ orbitals and $i$ is the square root of $-1$. In this $\pi$-system no circulation of $\pi$-electrons is expected along the circuits that share the $C_p$–$C_q$ bond in common. BRE for the $C_p$–$C_q$ bond can then be interpreted as a destabilization energy of this hypothetical $\pi$-system. All C–C $\pi$-bonds were assumed to have the same lengths. Peripheral $\pi$-bonds have the same BRE values if they belong to the same ring. The BRE for a peripheral $\pi$-bond will hereafter be referred to as a peripheral BRE.

In order to see if the peripheral BRE indeed was an indicator of local aromaticity, it was compared to the HOMA ring index[15,16,18,20] and the BOIA value.[22,24] These reference criteria of local aromaticity reflect the degree of bond-length alternation or variation in a given benzene ring straightforwardly. The HOMA index is a well-established structural index of aromaticity, whereas the BOIA value is representative of the so-called delocalization indices of aromaticity. If the peripheral BRE correlates to HOMA and BOIA values, it will be used as an energetic criterion of local aromaticity. BRE vanishes for olefinic $\pi$-bonds.

The HOMA index for each benzene ring in a PAH molecule is defined as:[15,16,18,20]

$$\mathrm{HOMA} = 1 - \frac{\alpha}{6}\sum_{i=1}^{6}(R_0 - R_i)^2, \tag{1}$$

where $\alpha = 257.7$ and $R_0 = 1.388\,\text{Å}$, both of which are the constants characteristic of C–C bonds in a hydrocarbon $\pi$-system, $R_i$ is the realistic length of the $i$th C–C bond in a given benzene ring, and the summation is made over six bonds that form the benzene ring. On the other hand, the BOIA value for each benzene ring in a PAH molecule is defined as:[22,24]

$$\mathrm{BOIA} = 1 - \frac{1}{6}\sum_{i=1}^{6}(B_0 - B_i)^2, \tag{2}$$

where $B_i$ is the bond order (two-center bond index) between a pair of adjacent carbon atoms in the benzene ring, $B_0$ is that in benzene, and the summation is made over six bonds that form the benzene ring.

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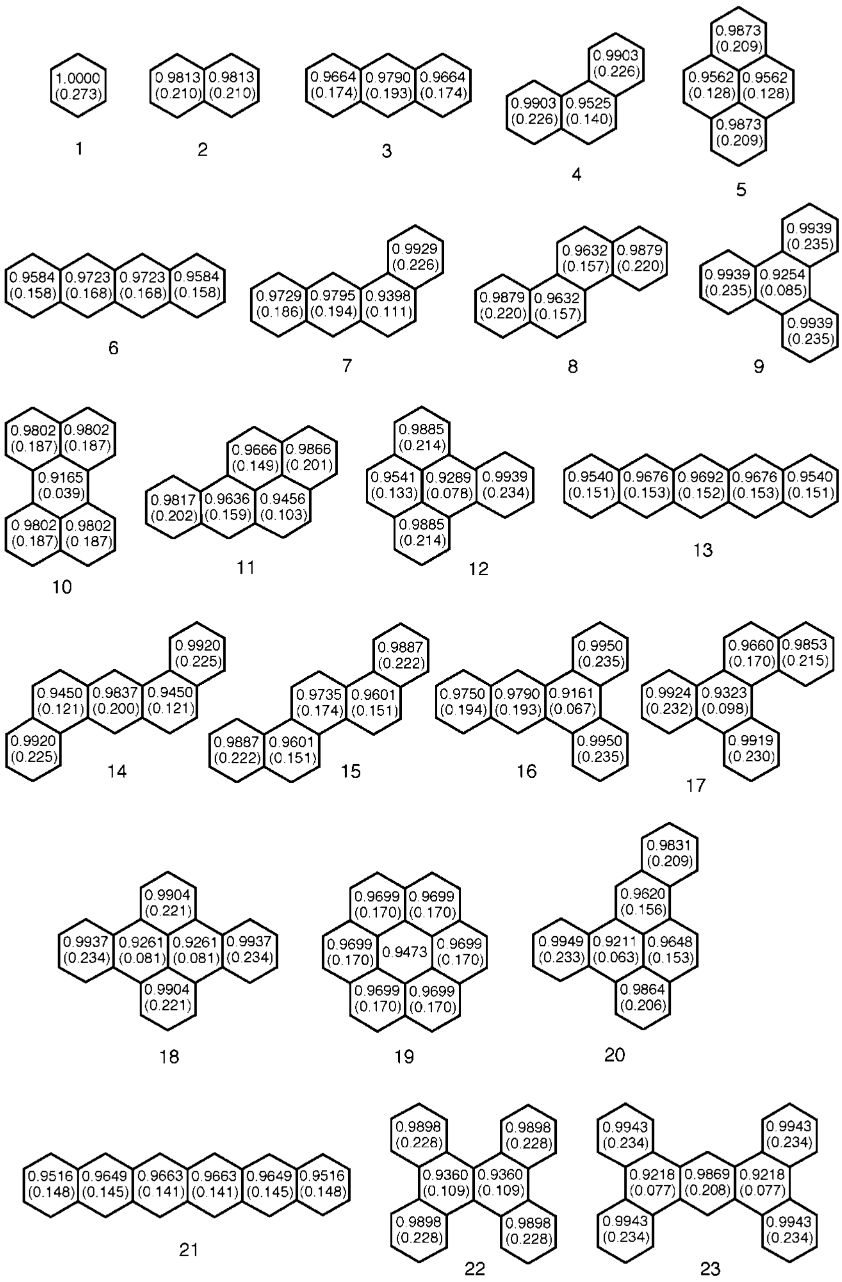

Fig. 1. BOIA values for individual rings in PAHs. Values in parentheses are the peripheral BREs in units of $|\beta|$. BOIA values were taken from Refs. 22 and 24.

## Results and Discussion

Twenty-three PAHs (**1**–**23**) were selected for the present work. Peripheral BREs for these PAHs are graphically summarized in Fig. 1. There are 65 non-identical peripheral rings in all in these PAHs. Among these peripheral rings are rings in *cata*-condensed hydrocarbons and most rings in *peri*-condensed hydrocarbons. Only the central ring in coronene (**19**) is not a peripheral ring. All peripheral BREs for **1**–**23** were positive in sign and lie in the range 0.039–0.273$|\beta|$. Those for $\pi$-bonds shared by two rings were relatively large.[11] Thus, all $\pi$-bonds in PAHs were more or less aromatic with positive BREs, indicating that all rings are aromatic in nature.

Benzene (**1**) had the most aromatic $\pi$-bonds with the largest BREs. The least aromatic $\pi$-bonds in the PAHs studied were nearly single ones at the center of the perylene (**10**) molecule. Note that a six-membered conjugated circuit[36,37] cannot be chosen from the central benzene ring of **10**. Such a benzene ring is called an "empty" ring.[1–3] As pointed out previously,[11] the geometric distribution of BRE values in a PAH molecule conforms well to Clar's sextet formula,[1–3] strongly suggesting that the peripheral BRE can be used as a local aromaticity index. Peripheral $\pi$-bonds that belong to sextet rings in fully benzenoid hydrocarbons have BREs $> 0.221|\beta|$. All rings on which Clar's aromatic sextet cannot be placed exhibit relatively small BREs for the peripheral $\pi$-bonds. All of these observations are consistent with Clar's theory.[1–3]

Figure 2 shows a plot of the HOMA index against the

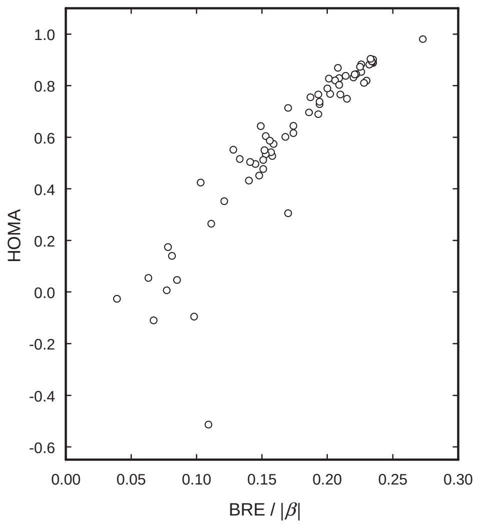

Fig. 2. Correlation between peripheral BREs and HOMA indices for peripheral rings in PAHs.

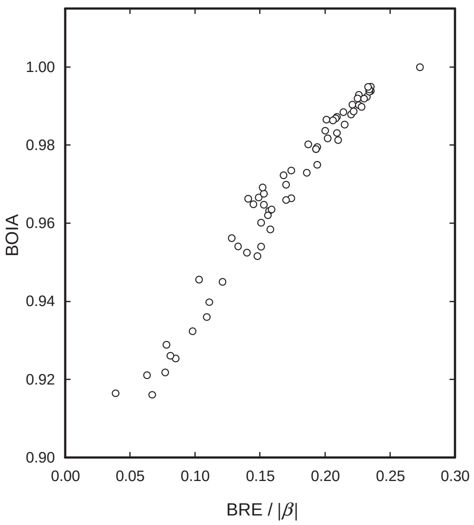

Fig. 4. Correlation between peripheral BREs and BOIA values for peripheral rings in PAHs.

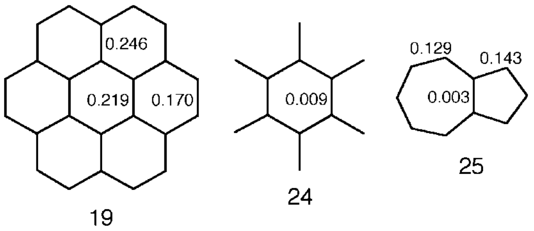

Fig. 3. BREs for **19**, **24**, and **25**.

peripheral BRE for all peripheral rings in **1**–**23**. HOMA indices employed are the ones calculated by Bultinck et al. at the B3LYP/6-31G* level of theory.[22,24] A fairly good correlation was found between the two quantities with a correlation coefficient of 0.909. However, there were several marked outliers in this figure, some of which are obviously associated with negative or small positive HOMA indices. As noted by Portella et al.,[14] negative HOMA values are probably not as meaningful as positive ones since HOMA = 0 must ideally correspond to non-aromatic $\pi$-systems. The extreme case is [6]radialene (**24**) in Fig. 3, which has a large negative HOMA index of $-2.41$,[20] although it is essentially non-aromatic with a very small BRE of $0.009|\beta|$.

Bultinck et al. have found that the correlation between the HOMA index and the BOIA value is rather satisfactory.[22,24] The correlation coefficient was 0.969 for the present set of PAHs. They have observed several outliers in the correlation diagram, most of which again correspond to negative HOMA values. The correlation between BOIA and HOMA is largely improved by removing negative HOMA values.[22,24] Scattered points in Fig. 2 may possibly be interpreted in a similar manner. It, however, seems that the HOMA index is very sensitive to the molecular geometry employed.[15,16,18] Krygowski et al. have reported a positive HOMA value for every ring in 32 PAHs.[15]

Next, BOIA values were then plotted against the BREs in Fig. 4, where the BOIA values were the ones calculated by Bultinck et al. at the B3LYP/6-31G* level of theory.[22,24] An excellent linear relationship was found between two quantities with a correlation coefficient of 0.982. This indeed is one of the best linear correlations found between two different types of local aromaticity indices.[22,24] This correlation is really remarkable considering that quite different levels of theory are used to calculate the two indices. Furthermore, one should note that bond-length alternation is taken into account in the BOIA values but not in the peripheral BREs.[22,24] We can now say that both peripheral BRE and BOIA are good indicators of local aromaticity, at least for polycyclic benzenoid hydrocarbons. Because of the excellent correlation with peripheral BREs, the BOIA values are cited in Fig. 1.

What is the essence of local aromaticity defined by BOIA and peripheral BRE? By definition, BRE for a given $\pi$-bond represents the sum of aromatic stabilization energies due to all of the circuits that share the $\pi$-bond.[25–27] Therefore, the BRE for a given peripheral $\pi$-bond represents the sum of aromatic stabilization energies due to all of the circuits that share the peripheral $\pi$-bond. In this case, all of the circuits enclose the ring concerned. High correlation between peripheral BRE and BOIA values suggests that the local aromaticity defined by BOIA and HOMA strongly reflects the sum of aromatic stabilization energies due to all of the circuits that share the peripheral $\pi$-bond. Krygowski et al. have noted that the HOMA value correlates to the sum of empirical bond energies of the benzene ring in question.[15] This fact also supports our interpretation of the peripheral BRE being an energetic criterion of local aromaticity.

As already mentioned, $\pi$-bonds shared by two benzene rings are more aromatic with larger BREs than peripheral ones but seem to be less influential on the local aromaticity.[11] At least for PAHs, kinetic stability and local aromaticity are determined primarily by the peripheral BREs. This aspect of local aromaticity is probably associated with the fact that the longest and/or shortest bonds in a PAH molecule are often located along the periphery of the $\pi$-system. These $\pi$-bonds necessarily make the largest contribution to the HOMA and BOIA values. Likewise, the smallest BRE in the ring, i.e., the BRE for a peripheral $\pi$-bond, primarily determines the degree of local aromaticity.

One should note that the present approach cannot be used to predict the local aromaticity of inner rings surrounded by six other rings. Such a situation is illustrated with **19**[11,32] in Fig. 3. Although BREs for $\pi$-bonds that form the inner benzene ring are appreciably larger than those for peripheral $\pi$-bonds, no one would agree that the central benzene ring in **19** is more aromatic than the peripheral ones.[21,22] The HOMA and BOIA values for the central ring are smaller than those for the peripheral rings.[22,24] If a given $\pi$-bond is shared by two benzene rings, at least the two benzene rings contribute to the BRE for the $\pi$-bond. Therefore, such BRE values are not easy to interpret in terms of local aromaticity.

As has been seen, the present approach could be applied safely to polycyclic benzenoid hydrocarbons. However, nonbenzenoid hydrocarbons did not always conform to this approach. BREs for all $\pi$-bonds in azulene (**25**),[11,33] a typical nonbenzenoid hydrocarbon, are given in Fig. 4. Peripheral BREs for **25** are fairly large; however, this never means that the two rings are fairly aromatic. The five- and seven-membered circuits in **25** are not conjugated ones in Randić's sense.[36,37] The aromaticity of **25** is presumed to arise primarily from the peripheral ten-membered circuit, because the BRE for the $\pi$-bond shared by the five- and seven-membered rings was negligibly small. A $\pi$-bond with the smallest BRE might again be a determinant of local aromaticity.

## Concluding Remarks

We showed that the peripheral BRE value calculated within the Hückel framework can be used satisfactorily as an energetic criterion of local aromaticity for polycyclic benzenoid hydrocarbons. An excellent linear relationship between peripheral BREs and BOIA values suggests that BOIA must be linearly related to the degree of local aromaticity, supporting the use of the benzene bond-order as a reference value in the formulation of BOIA.[22,24] Some other local aromaticity indices exhibit non-linear dependences on BOIA and BRE.[22,24] The geometric distribution of peripheral BREs in each PAH molecule conforms well to Clar's sextet formula.

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