Competition Between Sextet Aromaticity and Cyclobutadiene Antiaromaticity within the Same Molecule: Location is Important

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Dedicated to the memory of Professor Nenad Trinajstić who passed away on August 27, 2021 and was a world leader in chemical graph theory and topological indices

Abstract: The interplay between aromaticity and antiaromaticity is maximized in \(n\)-phenylenes. In their smaller isomer sets, some isomers can be aromatic while others can be antiaromatic. The sum of the superimposed constituent circuits contributes to the individual ring aromaticity. Both cyclic conjugated energy (CCE) of Bosanac and Gutman and Aihara’s topological bond resonance energy (t-BRE) are good measures of relative degree of ring aromatic/antiaromatic character. Topological resonance energy (TRE) is a reliable measure of global molecular aromaticity/antiaromaticity because it is independent of selection of frame-of-reference molecules for calibration.

Keywords: ring resonance energy, topological resonance energy, aromaticity/antiaromaticity, \([n]\)phenylenes.

INTRODUCTION

A N EXPLANATION for the exceptional stability of benzene is conventionally attributed to Robert Robinson, who was apparently the first to coin the term aromatic sextet as a group of six electrons that resists disruption.[1] In 1931, Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties.[2–4] His rule states that if a cyclic, planar molecule has \((4n+2)\)π electrons, it is considered aromatic. This rule would come to be known as Hückel’s Rule. Clar’s π-sextet rule was formulated in 1972 in his book “The Aromatic Sextet”.[5] This model expanded the initial work of Robinson and Hückel from a single monocyclic system to polycyclic systems. Clar’s π-sextet rule states that the Kekulé resonance structure with the largest number of disjoint aromatic π-sextets, i.e., benzene-like moieties, is the most important for characterization of properties of polycyclic aromatic hydrocarbons (PAHs). Aromatic π-sextets are defined as six π-electrons localized in a single benzene-like ring separated from adjacent rings by formal CC single bonds. The term ‘antiaromaticity’ was first proposed by Ronald Breslow in 1967 as “a situation in which a cyclic delocalization of electrons is destabilizing”.[6]

An important measure of molecular aromaticity is topological resonance energy (TRE) proposed by two research groups.[7,8] A fundamental premise of TRE is that all conjugated circuits contribute to aromaticity. Benzene is the prototype of aromaticity (TRE = 0.2726 \(\beta\)) and cyclobutadiene (TRE = –1.2263 \(\beta\)) is the prototype of antiaromaticity. Molecules with positive and negative TRE values are considered as aromatic and antiaromatic, respectively.[9,10] By most indices that measure aromaticity/antiaromaticity like Hess and Schaad resonance energy per electron method,[11] homodesmotic reactions that minimize the influence of strain,[12] and nucleus-independent chemical shifts,[13] antiaromaticity is stronger than aromaticity, i.e, antiaromaticity is a more destabilizing conjugated cyclic system than aromaticity is stabilizing a conjugated cyclic system.

The effect of antiaromatic cyclobutadiene rings on hexagonal polycyclic conjugated π-systems has been studied by conjugated circuit theory and higher level quantum theory which led to opposite conclusions.[14,15] This current study evaluates this issue from a different
theory using topological resonance energy (TRE). [13,14] TRE has the advantage that its values are derived without the ambiguities or arbitrary calibration with a selected reference molecule. Instead, a hypothetical reference without conjugated cyclic components is always selected in the same manner and has the same graph theoretical edge and vertex weights, the same geometry, the same number of π-electrons, the same degree of strain as the actual π-system.

Alhara showed that his circuit resonance energy (CRE) for each circuit i and the cyclic conjugated energy (CCE) of Bosanac and Gutman are strongly correlated for polycyclic aromatic hydrocarbons (PAHs) composed of only six membered rings. [15-17] Subsequently, Alhara showed his two different bond resonance energy (BRE) indices are strongly correlated, namely magnetic-BRE (m-BRE = ΣCRE) strongly correlates with topological-BRE (t-BRE). [18] m-BRE is determined from the sum of circuit resonance energy (ΣCRE) that corresponds to the ring currents determined by the graph theoretical version of the Hückel-London model. [19] Thus, it is of interest to compare the consequence of competition between the benzene sextet aromaticity moiety versus the cyclobutadiene antiaromaticity moiety within the same molecule using indices that measure global aromaticity (topological resonance energy, TRE) and ring aromaticity while comparing the agreement between Σef and t-BRE.

RESULTS AND DISCUSSION

Terminology and Method of Calculations with Examples

Bond resonance energy (BRE) and topological resonance energy (TRE) are indices denoting degree of ring aromaticity and global aromaticity of a polycyclic conjugated polyene molecule, respectively. A molecular graph of a conjugated hydrocarbon (G) will be represented by its π-bonding skeleton where graph vertices and edges correspond to π-carbon atoms and bonds, respectively. Let a molecular graph (vertex-line depiction of a conjugated molecule) of a hydrocarbon be denoted by G. Let G–es be the molecular graph of G with edge Cp–Cq deleted and G–(e) be the molecular graph of G with edge Cp–Cq and its corresponding vertices deleted. P0(X) is the characteristic polynomial of a molecular graph of G. [10]

The programs of Balasubramanian are used to obtain the characteristic and matching polynomials of a molecular graph. [20,21] The internet is used to obtain the roots of these polynomials (https://www.mathportal.org/calculators/polynomial-root-calculator.php).

BRE and TRE are given here in units of β, where β is the standard resonance integral in Hückel theory. Throughout this paper where HMO numerical values are given the unit of β and often will be implied when it is obvious from the content. Ring current (RC = i) strength herein has been obtained using the graph theoretical version of the Hückel-London model and are given in benzene units. [20,21,22] The BRE and TRE indices are defined graph-theoretically within the framework of simple Hückel molecular orbital (HMO) theory. Bond length alternation is not taken into consideration. Larger BRE and TRE values indicate a more pronounced aromatic character. TRE and t-BRE require one to calculate the characteristic polynomials of the hypothetical reference molecule, the π-energy of which when subtracted from the π-energy of the actual molecule gives a measure of aromaticity.

Bond Resonance Energy (t-BRE)

To determine the hypothetical reference for calculation of t-BRE, let the HMO cyclic conjugation through a given Cp–Cq π-bond be blocked. In this hypothetical π-system, no circulation of π-electrons are expected along all the circuits sharing the Cp–Cq bond in common. [23] The t-BRE (t stands for topological) for the Cp–Cq bond is then defined as the destabilization energy of this hypothetical π-system relative to the actual one. We use the following graph-theoretical method to determine the characteristic polynomial [P(Gref;X)] of this hypothetical reference π-system (Gref) associated with a given actual system (G):

\[ P(G_{\text{ref}};X) = P(G-e;X) - P(G-e;X) \]

where \( G-e \) is the molecular graph of G with edge Cp–Cq deleted and \( G-e \) is the molecular graph of G with edge Cp–Cq and its corresponding vertices deleted. [24] As an example, consider the C6 ring circuit of the molecular graph Gref for naphthalene (Figure 1):

\[ P(G_{\text{ref}};X) = P(5\text{-allylidene-6-methylene cyclohexa-1,3-diene};X) - P(\text{styrene};X) \]

for the molecular graphs of 5-allylidene-6-methylene cyclohexa-1,3-diene and styrene (bottom of Figure 1), respectively. The squiggly line in Figure 1 denotes the edge of naphthalene (G) operated on to give 5-allylidene-6-methylene cyclohexa-1,3-diene (G–e) and styrene (G–(e)). For naphthalene \( P(G_{\text{ref}};X) = X^{10} - 11X^8 + 41X^6 - 63X^4 + 37X^2 - 5 \) which gives the π-electronic energy for the hypothetical reference as \( E_e^{\text{ref}} = 13.4731 \beta \). Per Alhara, t-BRE is given by

\[ t\text{-BRE} = E(G);X - E(G_{\text{ref}});X = E_e - E_e^{\text{ref}} = 13.6832 - 13.4731 = 0.2101 \beta \]

where \( E(G);X \) and \( E(G_{\text{ref}});X \) are the π-electronic energies of the actual and hypothetical reference molecular graphs, respectively. This means that π-electronic energy of naphthalene is more stable by 0.2101 β compared to its hypothetical reference which blocks conjugation through the selected π-bond. We use the above graph-theoretical
The t-BRE ring aromaticity index is only of interest for benzene. The passing through a given ring edge must surround the ring applicable to peripheral PAH bonds because all circuits of the hypothetical reference πpolyene reference (E_{\text{acc}}) polyene reference molecule have the same graph theoretical weights of their edges and vertices. Thus, they have the same geometry including bond length alternation and atomic hybridization, the same number of π-electrons, and the same degree of strain.

To compare the degrees of aromaticity in different molecules, every TRE value must be normalized with respect to the size of the π-system. The normalized index employed by Aihara is a percentage TRE (% TRE) given by 100 times TRE divided by the total π-binding energy (E_{\text{\pi-ef}}) of the most polar conjugated polyene reference. Triajnić normalized TRE by dividing it by the corresponding number of π-electrons (N_{\pi}). The % TRE of benzene is 100% \[\frac{(E_{\pi,\text{exc}}) - E_{\pi,\text{ref}}}{E_{\pi,\text{\text{\pi-ef}}}}\] and the % TRE of cyclobutadiene it is \(-0.3066\) %. Using conjugated circuit theory, Randić defined degree of aromaticity as \[\text{A} = \frac{\text{RE}(4\text{\text{n+2}}) + \text{RE}(4\text{\text{n}})}{\text{RE}(4\text{\text{n+2}})}\]. Per Randić, the degree of aromaticity plus the degree of antiaromaticity equals 100 %.

**Cyclic Conjugation Energy (CCE) and Benzene Ring Energy Effect (\text{ef})**

In 1977 Bosanac and Gutman proposed a measure of a kind of conjugated circuit energy (CCE, = \text{ef}) for polycyclic π-conjugated systems which is closely related to Aihara’s CRE = \text{A}_{\pi,\text{\text{\pi-ef}}}^{\text{\text{\pi-ef}}}. The difference between these measures is the hypothetical reference system used. The t-BRE index includes all circuits passing through the selected bond, the smallest circuits are the most important because aromaticity/antiaromaticity rapidly diminishes with increasing circuit size. This can be seen by the aromaticity/antiaromaticity trend in the even carbon monocyclic polyenes.

Per Gutman and Bosanac, CCE, is also called energy effect (\text{ef}). In general, the Bosanac and Gutman circuit conjugation energy (\text{ef} \text{CCE}) is given by \[\text{ef} = \text{CCE} = E(G_{\text{1}}) - E(G_{\text{2}})\text{h}\]

where \(E(G_{\text{1}})\) is the π-energy of the hypothetical reference. The characteristic polynomial \(P(G_{\text{2}} - c; X)\) of the Bosanac and Gutman hypothetical reference system G−c, is determined as follows. Here G−c has the same topology as G but is assumed to have no ith circuit, i.e., the
contributions of the \(i\)th circuit to the coefficients of \(P(G-c;\pi)\) are ignored when using the Sachs theorem.\[^{27}\] The characteristic polynomial of \(G-c\) is determined by
\[
P(G-c;\pi) = P(G;\pi) + 2P(G-r;\pi) = P(G_{ref};\pi)
\]
where \(G-r\) is the molecular graph of \(G\) in which the \(i\)th ring \((r_i)\) or circuit is deleted.[\(^{17,28}\)] For the naphthalene molecular graph, this gives \(P(G-c;\pi) = P(\text{naphthalene};\pi) + 2P(\text{butadiene};\pi) = (X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9) + 2(4X^4 - 3X^2 + 1) = X^{10} - 11X^8 + 41X^6 - 63X^4 + 37X^2 - 7\) for the C6 ring circuit (Figure 1). This gives the reference binding energy \(E_{\text{ref}} = 13.56213\) \(\beta\) which when subtracted from the binding energy \((E_n = 13.6832\) \(\beta\)) of the original molecule gives \(e_{\text{f}} = 0.1211\) \(\beta\). For the naphthalene case, the C10 circuit must be similarly calculated giving \(e_{\text{f}} = 0.07086\) \(\beta\). These two different circuits are superimposed and must be added to finally give \(\Sigma e_{\text{f}} = 0.1920\) \(\beta\) in order to compare it to Aihara’s \(m\)-BRE and \(t\)-BRE values (0.1774 \(\beta\) and 0.2101 \(\beta\), respectively) for naphthalene (Figure 1). In general, for all benzenoids studied the slight increase in \(m\)-BRE, \(\Sigma e_{\text{f}}\) and \(t\)-BRE magnitudes follow this order.[\(^{16,18}\)] We now briefly review Aihara’s graph theoretical method for calculating CRE.

**Circuit Resonance Energy (CRE)**

The graph-theoretical quantity \(A_i\) (CRE) for the \(i\)th circuit in a closed-shell polycyclic \(\pi\)-system \(G\) for the nondegenerate eigenvalues is given by the following equation
\[
A_i = \sum_{j=1}^{\text{occ}} \frac{P_{\text{circ}}(X)}{P_{G}(X)}
\]
where \(G-r_i\) is the subsystem of \(G\), obtained by deleting all carbon atoms in \(G\) that constitute the \(i\)th circuit; \(P_{G}(X)\) and \(P_{\text{circ}}(X)\) are the characteristic polynomials for \(G\) and \(G-r_i\), respectively; \(P_{\text{circ}}(X)\) is the derivative of the characteristic polynomial; \(X_j\) is the \(i\)th positive root of \(P_{\text{circ}}(X) = 0\); and \(j\) runs over all the \(\pi\) occupied orbitals. Aihara defines circuit resonance energy (CRE) for the \(i\)th circuit as \(\text{CRE}_i = A_i^{1,16}\)

Positive and negative \(A_i\) values indicate diatropic (counterclockwise) and paratropic (clockwise) currents, respectively.

For degenerate \(\pi\) MOs, the above equation must be replaced by others.[\(^{29-34}\)] Note Eq. (1) is in units of \(\beta\).

To understand the units used in CRE (\(\beta\)), CCE (\(\beta\)), \(m\)-BRE (\(\beta\)), \(t\)-BRE (\(\beta\)), and ring current \(l_o\), we will use these solutions on benzene. Accordingly, it turns out that CCE = \(t\)-BRE for all monocyclic polyenes, benzene, biphenyl, \(p\)-triphenyl, and so on in units of \(\beta\). For benzene CCE = \(t\)-BRE = 0.2726 \(\beta\) and CRE = \(\Sigma e_{\text{f}}/m\)-BRE where \(\Sigma e_{\text{f}} = \Sigma \text{CRE}_i = 4[1/36 + 1/36] = 0.2222\) \(\beta\) and \(l = 4.5(l_o/\beta)\Sigma \text{CRE}_i/S_i = 4.5(l_o/\beta)(0.2222\beta)S_o/S_i = 1.0\) \(l_o\) since cycle \(i\) corresponds to only one C6 circuit. For nondegenerate eigenvalue of 2.0, Eq. (1) is used directly and for the doubly degenerate eigenvalues of 1.0 the equation noted in reference must be used.[\(^{32,34}\)] For benzene this gives \(m\)-BRE = 0.2222 \(\beta\). Note that 1/0.2222 = 4.5 which is the origin of this constant above for ring current \(l\). Equations for treating various eigenvalue degeneracy have been reviewed by Dias.[\(^{14}\)] To clarify the relationships between aromaticity, ring resonance energy, ring ef, and ring BRE, and ring current, we demonstrate these parameters in naphthalene and show how they are calculated in Figure 1 and Table 1. Unlike benzene which has only one ring and one circuit, naphthalene with two rings has three distinct circuits, two C6 circuits and one C10 circuit. Three ring systems like anthracene and biphenylene have six distinct circuits. To determine ring resonance energy (CRE\(_R\)), ring ef\(_R\) and ring current \(l_o\) for a given benzene ring, all circuits that superimpose the given ring must be considered. Application of eq (1) on naphthalene gives the data in Table 1.

These naphthalene results in Figure 1 and Table 1 illustrate the strong agreement between CRE\(_R\) and ef\(_R\) for PAHs composed of only hexagonal rings as Aihara demonstrated in 2006[\(^{16}\)] and between \(m\)-BRE and \(t\)-BRE in 2008.[\(^{19}\)] In Figure 1, the slight progression of values in \(m\)-BRE \(= 0.1774\) \(\beta\), \(\Sigma e_{\text{f}} = 0.1920\) \(\beta\), and \(t\)-BRE \(_6 = 0.2101\) \(\beta\) is the result of somewhat more emphasis of six-circuits. In determining \(\Sigma e_{\text{f}} = 0.1920\) \(\beta\) deletion of the six-circuit also disrupts the ten-circuit and in determining \(t\)-BRE \(_6 = 0.2101\) \(\beta\) (indicated by the squiggly line) both the six-circuit and the

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**Table 1.** Data for Calculation of Circuit Resonance Energy and Currents in Naphthalene.

| \(X_i\), \(\beta\) | \(P_{\text{circ}}(X)/P_{G}(X)\) | \(P_{\text{circ}}(X)/P_{G}(X)\) | \(P_{\text{circ}}(X)/P_{G}(X)\) | \(P_{\text{circ}}(X)/P_{G}(X)\) |
|-------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 2.30278           | -0.013995                     | -0.013995                     | -0.00105935                  | 943.97573                    |
| 1.61803           | 0.0                            | 0.0                            | 0.00345508                   | -28.942871                  |
| 1.30278           | -0.1526669                    | -0.1526669                    | 0.12605659                   | 7.9329448                   |
| 1.0               | 0.1666667                     | 0.1666667                     | 0.1666667                    | -6.0                        |
| 0.61803           | 0.0                            | 0.0                            | -0.09044873                  | 11.055987                   |
| CRE\(_R\) = \(A_i\) | 0.1198                        | 0.1198                        | 0.06538871                   | 0.06538871                  |

\(P_{G}(X) = X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9\); \(P_{\text{circ}}(X) = 10X^8 - 88X^6 + 246X^4 - 260X^2 + 86X\); \(P_{\text{circ}}(X) = 10X^8 - 34X^4 + 1\); \(P_{\text{circ}}(X) = 1\); \(l = 4.5(l_o/\beta)\Sigma \text{CRE}_i/S_i\); \(S_o = 4.5\Sigma \text{CRE}_i/S_i = 0.05391\); \(l_o = 0.05391\); \(l_o = l_o/\beta\); \(S_o = 4.5\Sigma \text{CRE}_i/S_i = 0.05391\); \(l_o = 0.05391\); \(l_o = l_o/\beta\); which is the total C6 ring current.

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ten-circuit are disrupted leaving a remaining six-circuit. Thus, explaining this sight increase in these values of m-BRE = Σef6 < t-BRE for naphthalene.

Lack of correlation between CRE6 and ef6 for biphenylene which possesses a cyclobutadiene ring in addition to hexagonal rings has been noted.[34] Figure 2 shows this apparent anomaly occurs only with the six-circuit whereas the other circuit sizes (CRE4 and ef6, CRE8 and ef6, CRE12 and ef12 values) seem to agree well. From Figure 2, it is seen that the general magnitude of the individual circuits in biphenylene agree well with Hückel’s 4n +2 aromatic rule and Breslow’s 4n antiaromatic rule and relative size, except the sextet A6 and ef6 circuit values appear to be too large compared to the antiaromatic circuit values.

In the study of energy effects of larger circuits in cyclobutadienypolybiphenylene, Gutman noticed violation of Hückel’s 4n +2 aromatic rule.[35] Figure 2, it is seen that the general magnitude of the relative size, except the sextet 6A and BRE6 turns out to be slightly larger than -BRE6A and -BRE6 for naphthalene. Thus, explaining this sight increase in these values of -BRE6 = 0.2222 (m-BRE6A), 0.2726 (ef6), 0.2726 (t-BRE6), 3.528 (%TRE), 1.0 I6 (l), 0.996 (HOMA), and -∞ (m-BRE6), -1.2263 (ef6), -1.2263 (t-BRE6), -23.463 (%TRE), -∞ (l), -5.70 (HOMA).[32] Thus, by these six different indices, the antiaromaticity of cyclobutadiene turns out to be more energetically destabilizing than the aromaticity of benzene is energetically stabilizing. Another thing of note here is that for cyclobutadiene m-BRE = CRE and I (ring current) are very large, i.e., Eq. (1) appears to break down for all conjugated antiaromatic monocyclic bond-equalized π-systems (Table 2) whereas the ef = t-BRE give to sensible values.[24]

Fusion of benzene and cyclobutadiene gives benzocyclobutadiene (Figure 3) which allows one to examine the direct competition between the aromaticity of the benzene ring pitted against the antiaromaticity of the cyclobutadiene ring. Overall, the antiaromaticity of the cyclobutadiene ring dominates giving a global antiaromaticity for benzocyclobutadiene %TRE = -3.6469. The m-BRE = 0.04934 β and t-BRE = 0.05064 β (Figure 3) agree well with each other but like with biphenylene CRE6 = 0.16141 β appears too large. The cyclobutadiene ring in benzocyclobutadiene has about 60 % the antiaromaticity of benzocyclobutadiene itself and the benzene ring has about 20 % the aromaticity of benzene itself. Table 3 give the data and equations for determining m-BRE and ring current (I) of benzocyclodyiene. A complete eigenvalue/eigenvector solution of benzocyclobutadiene was featured in a 1996 paper by Dias.[36]

**Table 2.** Data for Calculation of Circuit Resonance Energy and Currents in Cyclobutadiene.

| Xo | β | P_{oc}(X)/P(X) | P(X) |
|----|---|----------------|------|
| 2.0 | 1/16 | 16 |
| 0 & 0 | 1/0 | 0 |
| CRE = A6 = 4Σ (diradical), -∞ |

P_{oc}(X) = X^2 - 4X; P(X) = 4X^2 - 8X; P_{oc}(X) = 1; |J| = 4.5β/[(β)ΣCRE/S] CRE = A6 = 4[1/16] = 1.5 % for diradical.

For doubly degenerate eigenvalues use A_{oc} = Σ[X_{oc} P_{oc}(X)]/U(X)^{12} once for the two occupied orbitals where (X_{oc} - U(X))P_{oc}(X) = 0 or X = X_{oc} = 0. Thus, U(X) = 0 and A_{oc} = 1/4 [0 or 0/0 or 0/0] = 0 for diradical cyclobutadiene.

I_{oc} = 4.5A_{oc} \; \beta = 4.5 \times 3 \times 10^{-3} \; \text{I_{oc}} \; \text{I_{oc}} = 3 \times 10^{-3} \; \text{I_{oc}} which is the total ring current.

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Table 3. Data for Calculation of Circuit Resonance Energy and Currents in Benzocyclobutadiene.

| X, β | P_c-i(X)/P_S(X) | P_c+o(X)/P_S(X) | P_c-o(X)/P_S(X) | P_c+o(X)/P_S(X) |
|------|-----------------|-----------------|-----------------|-----------------|
| 2.24133 | 0.012035 | 0.040057 | 0.00264475 | 378.107 |
| 1.47726 | −0.0572303 | 0.037973 | −0.048406 | −20.6586 |
| 1.095294 | 0.018859 | −0.109544 | 0.094451 | 10.5875 |
| 0.26236 | 0.135486 | −0.116145 | −0.14550 | −6.8728 |
| CRE = A = 0.43658 | −0.59064 | −0.387241 |

P_c+i(X) = X^2 – 5X^4 + 22X^6 – 16X^8 + 1; P_c−o(X) = 8X^7 – 54X^9 + 88X^11 – 32X^13; P_c-o(X) = X^3 – 3X^5 + 1; P_c+o(X) = X^3 – 3X^5 + 1; t = 4.5S_i(S_i) \sum_{CRE} S_i |

Location is Everything

Figure 3. Calculation of TRE, A, m-BRE, Σef, and t-BRE of benzocyclobutadiene. See Table 3 for data and calculation of A and m-BRE.

Figure 4. For small systems with a mix of cyclobutadiene and benzene rings, some isomers can be antiaromatic and others can be aromatic which emphasizes that location is everything.

[3]phenylene is overall aromatic. In passing, it should be noted that linear [3]phenylene can be embedded by antiaromatic benzocyclobutadiene and therefore must contain its eigenvalues among others. All the circuits are enumerated for [3]phenylene and [4]phenylene in Figures 5 and 6, respectively. Bent [3]phenylene is the first member of the helical [n]phenylene series. The synthesis and X-ray crystal structure of helical [4]phenylene, [6]phenylene, and [7]phenylene have been reported.

Figure 7 summarizes the calculated antiaromatic/ aromatic parameters for the initial members of the polyphenylene series. By the TRE values in Figure 7, antiaromaticity increases as the length of the members of the linear polyphenylene series increases. Table 25 and Figure 66 in a review by Randic gives conjugated circuit data for [2]–[4]phenylenes. The degree of aromaticity of linear [2]–[4]phenylenes progressively decreases which means that their antiaromaticity proportionally increases.
The conjugated circuit antiaromaticity/aromaticity predictions for benzylocyclobutadiene and biphenylene agrees with our TRE predictions. As the \([n]\)phenylene series in Figure 7 increases in length, the ratio of the number of benzene rings to cyclobutadiene rings approach one, and we expect the %TRE to approach the %TRE value of benzylocyclobutadiene (%TRE = –3.6469, Figure 3). Both \(\Sigma ef\) and \(t\)-BRE\(_6\) predict that the outer benzene rings are more aromatic than the inner ones which is opposite to what is predicted for the linear polyacenes. This is because the inner benzene rings that are linearly bounded by cyclobutadiene rings on both sides cause a destabilization influence. This effect is emphasized by the three ring isomers of cyclobuta\([1,2-b:3,4-b]dibenzocyclobutadiene\) in Figure 8. In all examples examined, whenever benzene rings are linearly bounded by cyclobutadiene rings on both sides cause a destabilization influence. In agreement with conjugated circuit theory, as the circuit size in Figures 2, 6, and 7 increase, the absolute magnitude of the \(ef\) values decrease. Ignoring the three largest circuits in Figure 6 will only change the \(\Sigma ef\) values by –0.0006 \(\beta\).

In passing, extensive comment on \([n]\)phenylenes in regard to the paper by Kovaček and coworkers can be found in the review by Randić. This comment also applies...
to their subsequent paper.\textsuperscript{[15]} In TRE calculations, it is assumed that the hypothetical polycyclic polyene reference molecule has the same number of \(n\)-electrons, the same geometry including atomic hybridization, and the same degree of strain as in the actual molecule. Thus, these variables are cancelled out by the hypothetical polycyclic polyene reference molecule and there is no need to take them into account separately. The results in Figure 4 agree with the higher level quantum results of Maksić and coworkers\textsuperscript{[13]} who found that angular phenylene isomers are slightly more stable than their linear counterparts and explained this as being the result of decreased antiaromatic character of the planar four-membered rings. More recently Suresh and coworkers\textsuperscript{[42]} also found that angular \([3]\)phenylene was slightly more stable than its linear \([3]\)phenylene isomer. This was rationalized as being the result of adopting a configuration containing the least number of localized bonds over the antiaromatic cyclobutadiene moieties which is equivalent to being the result of decreased antiaromatic character of the planar four-membered rings. We ascertain this interpretation by calculating relative t-BRE\(_4\) values for these isomeric systems. Per the results in Figure 4, TRE = –0.0194 \(\beta\) and t-BRE\(_4\) = –0.3336 \(\beta\) for linear \([3]\)phenylene and TRE = 0.02264 \(\beta\) and t-BRE\(_4\) = –0.2445 \(\beta\) for bent \([3]\)phenylene. Thus, linear \([3]\)phenylene is aromatic and bent \([3]\)phenylene is aromatic as a result of decreased antiaromatic character in the four-membered rings in the bent isomer; also the latter has a larger HMO binding energy. In other words, the topological bond resonance energy of the 4-membered rings (t-BRE\(_4\)) is more positive for the bent isomer meaning it has decreased antiaromatic character relative to the linear isomer.\textsuperscript{[3]} Phenylene can be embedded by benzcyclobutadiene and therefore has its eigenvalues (listed in Figure 3); both have the same HOMO/LUMO = ±0.26236 \(\beta\).\textsuperscript{[36–38,40]} Thus, the greater antiaromatic character of the planar four-membered rings (\(\Sigma_{ef}\)) and t-BRE both give the same relative order of ring aromatic/antiaromatic predictions. TRE is a reliable measure of molecular global aromaticity/antiaromaticity and is independent of selection of frame-of-reference molecules for calibration. TRE predicts that bent \([3]\)phenylene is more aromatic than its linear \([3]\)phenylene isomer. While in principle, \(m\)-BRE; and \(\Sigma_{ef}\) require one to enumerate all superimposing circuits, truncating this enumeration at circuit sizes around C14 as done in conjugated circuit theory leads to reasonable prediction values.

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