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 TRINAISTIĆ 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$_i$ = ef_i) 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

AN 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 β) and cyclobutadiene (TRE = −1.2263 β) 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).[7,8] 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.

Aihara showed that his circuit resonance energy (CRE$_i$) for each circuit i and the cyclic conjugated energy (CCE$_i$) of Bosanac and Gutman are strongly correlated for polycyclic aromatic hydrocarbons (PAHs) composed of only six membered rings.[16–18] Subsequently, Aihara showed his two different bond resonance energy (BRE) indices are strongly correlated, namely *magnetic*-BRE (*m*-BRE = $\sum$CRE$_i$) strongly correlates with *topological*-BRE (*t*-BRE).[19] *m*-BRE is determined from the sum of circuit resonance energy ($\sum$CRE$_i$) that corresponds to the ring currents determined by the graph theoretical version of the Hückel-London model.[20,21] 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 $\sum ef_i$ and *t*-BRE$_i$.

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 σ-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 $G-e_{rs}$ be the molecular graph of G with edge C$_r$–C$_s$ = r-s deleted and $G-(e_{rs})$ be the molecular graph of G with edge r-s and its corresponding vertices r and s deleted. $P_G(X)$ is the characteristic polynomial of molecular graph of G.[10]

The programs of Balasubramanian are used to obtain the characteristic and matching polynomials of a molecular graph.[22,23] The internet is used to obtain the roots of these polynomials (https://www.mathportal.org/calculators/polynomials-solvers/polynomial-roots-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.[20,21,24] 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 C$_p$–C$_q$ π-bond be blocked. In this hypothetical π-system, no circulation of π-electrons are expected along all the circuits sharing the C$_p$–C$_q$ bond in common.[25] The *t*-BRE (*t* stands for topological) for the C$_p$–C$_q$ 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 [$P(G_{ref};X)$] of this hypothetical reference π-system (G_{ref}) associated with a given actual system (G):

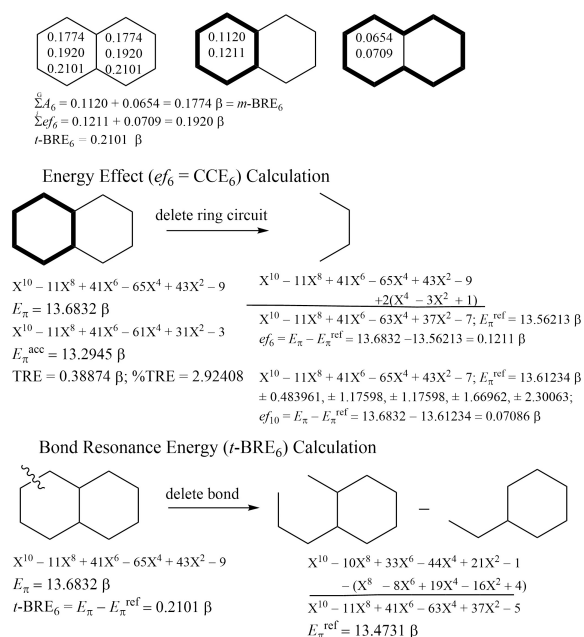$$P(G_{ref};X) = P(G-e;X) - P(G-(e);X)$$

where $G-e$ is the molecular graph of G with edge C$_p$–C$_q$ deleted and $G-(e)$ is the molecular graph of G with edge C$_p$–C$_q$ and its corresponding vertices deleted.[26] As an example, consider the C6 ring circuit of the molecular graph G_{ref} for naphthalene (Figure 1):

$$P(G_{ref};X) = P(\text{5-allylidene-6-methylenecyclohexa-1,3-diene};X) - P(\text{styrene};X)$$

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-methylenecyclohexa-1,3-diene ($G-e$) and styrene ($G-(e)$). For naphthalene $P(G_{ref};X) = X^{10}-11X^8+41X^6-63X^4+37X^2-5$ which gives the π-electronic energy for the hypothetical reference as E_π^{ref} = 13.4731 β. Per Aihara, *t*-BRE is given by

$$t\text{-BRE} = E(G)_\pi - E(G_{ref})_\pi = E_\pi - E_\pi^{ref}$$
$$= 13.6832 - 13.4731 = 0.2101 \text{ β.}$$

where $E(G)_\pi$ and $E(G_{ref})_\pi$ 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

$\overset{ci}{\Sigma}A_6 = 0.1120 + 0.0654 = 0.1774\ \beta = m\text{-}BRE_6$

$\overset{ci}{\Sigma}ef_6 = 0.1211 + 0.0709 = 0.1920\ \beta$

$t\text{-}BRE_6 = 0.2101\ \beta$

Energy Effect ($ef_6 = CCE_6$) Calculation

delete ring circuit

$X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9$

$E_\pi = 13.6832\ \beta$

$X^{10} - 11X^8 + 41X^6 - 61X^4 + 31X^2 - 3$

$E_\pi^{acc} = 13.2945\ \beta$

TRE = 0.38874 β; %TRE = 2.92408

$X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9$
$\qquad\qquad\qquad +2(X^4 - 3X^2 + 1)$
$\overline{X^{10} - 11X^8 + 41X^6 - 63X^4 + 37X^2 - 7};\ E_\pi^{ref} = 13.56213\ \beta$

$ef_6 = E_\pi - E_\pi^{ref} = 13.6832 - 13.56213 = 0.1211\ \beta$

$X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 7;\ E_\pi^{ref} = 13.61234\ \beta$
$\pm 0.483961, \pm 1.17598, \pm 1.17598, \pm 1.66962, \pm 2.30063;$

$ef_{10} = E_\pi - E_\pi^{ref} = 13.6832 - 13.61234 = 0.07086\ \beta$

Bond Resonance Energy ($t\text{-}BRE_6$) Calculation

delete bond

$X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9$

$E_\pi = 13.6832\ \beta$

$t\text{-}BRE_6 = E_\pi - E_\pi^{ref} = 0.2101\ \beta$

$X^{10} - 10X^8 + 33X^6 - 44X^4 + 21X^2 - 1$
$\qquad\quad - (X^8 - 8X^6 + 19X^4 - 16X^2 + 4)$
$\overline{X^{10} - 11X^8 + 41X^6 - 63X^4 + 37X^2 - 5}$

$E_\pi^{ref} = 13.4731\ \beta$

Figure 1. Demonstrating the calculation of circuit conjugation energy ($ef_6 = CCE_6$) and bond resonance energy ($t\text{-}BRE_6$ and $m\text{-}BRE_6$) for the benzene rings of naphthalene. See Figure 2 and Table 1 for the detail calculation of $m\text{-}BRE_6$.

method to determine the characteristic polynomial [$P(G_{ref};X)$] of the hypothetical reference π-system (G_{ref}) associated with a given actual system (G), a proof of which is given.[26] Note in this example, one of two C6 circuits and the only C10 are simultaneously broken leaving one remaining C6 circuit which explains why the numerical value of 0.2101 β for the t-BRE of naphthalene is close to the t-BRE = 0.2726 β for benzene. The t-BRE ring aromaticity index is only applicable to peripheral PAH bonds because all circuits passing through a given ring edge must surround the ring of interest.

Topological Resonance Energy (TRE)

While BRE measures local aromaticity of individual peripheral rings, topological resonance energy (TRE) measures global aromaticity of the whole molecule. For monocyclic conjugated systems, BRE = TRE. TRE results from a delocalization of π-electrons in the entire polycyclic conjugated π-system. The total π-binding energy of the actual polycyclic π-system (E_π) and the polycyclic acyclic (acc) polyene reference (E_π^{acc}) are obtained by summing twice the orbital energies determined from the zeros of the characteristic polynomial over the occupied π-MOs of the actual π-system and the hypothetical polyene reference determined from the zeros of the matching polynomial over its occupied π-MOs, respectively. The matching polynomial omits all the cyclic Sachs graphs whereas the characteristic polynomial does not. The energy difference

between the actual molecule and its hypothetical polyene reference gives the extra stabilization of the actual molecule due to cyclic conjugation of all its circuits which corresponds to its aromaticity. To determine TRE, the characteristic polynomial gives the total π-binding energy of the actual π-system (E_π) and the matching polynomial gives the total binding energy for the hypothetical reference structure (E_π^{acc}).[22,23] In both the BRE and TRE calculations, the actual molecule and its hypothetical polycyclic acyclic 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_π^{acc}) of the hypothetical polyene reference. Trinajstić normalized TRE by dividing it by the corresponding number of π-electrons (N_c).[10] The % TRE of benzene is 100 % [($E_\pi - E_\pi^{acc}$) / E_π^{acc}] = 100 % (8.0 − 7.72741) / 7.72741 = 100 % × 0.2726 / 7.72741 = 3.528 and for cyclobutadiene % TRE = − 23.463. The TRE / N_c for benzene is 0.04543 β and for cyclobutadiene it is −0.3066 β. Using conjugated circuit theory, Randić defined degree of aromaticity as A = [RE(4n + 2) + RE(4n)] / RE(4n + 2).[14] Per Randić, the degree of aromaticity plus the degree of antiaromaticity equals 100 %.

Cyclic Conjugation Energy (CCE) and Benzene Ring Energy Effect (*ef*)

In 1977 Bosanac and Gutman proposed a measure of a kind of conjugated circuit energy (CCE$_i$ = ef_i) for polycyclic π-conjugated systems which is closely related to Aihara's CRE$_i$ = A_i.[17–19] 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/anti-aromaticity trend in the even carbon monocyclic polyenes.

Per Gutman and Bosanac, CCE$_z$ is also called energy effect (*ef*). In general, the Bosanac and Gutman circuit conjugation energy (*ef* = CCE) is given by

$$ef = CCE = E(G)_\pi - E(G_{ref})_\pi$$

where $E(G_{ref})_\pi$ is the π-energy of the hypothetical reference. The characteristic polynomial [$P(G-c_i;X)$] of the Bosanac and Gutman hypothetical reference system $G-c_i$ is determined as follows. Here $G-c_i$ has the same topology as G but is assumed to have no ith circuit, i.e., the

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contributions of the ith circuit to the coefficients of $P(G-c_i;X)$ are ignored when using the Sachs theorem.[27] The characteristic polynomial of $G-c_i$ is determined by

$$P(G-c_i;X) = P(G;X) + 2P(G-r_i;X) = P(G_{ref};X)$$

where $G-r_i$ is the molecular graph of G in which the ith ring (r_i) or circuit is deleted.[17,28] For the naphthalene molecular graph, this gives $P(G-c_i;X) = P(naphthalene;X) + 2P(butadiene;X) = (X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9) + 2(X^4 - 3X^2 + 1) = X^{10} - 11X^8 + 41X^6 - 63X^4 + 37X^2 - 7$ for the C6 ring circuit (Figure 1). This gives the reference binding energy $E_\pi^{ref} =$ 13.56213 β which when subtracted from the binding energy (E_π = 13.6832 β) of the original molecule gives $ef_6 =$ 0.1211 β. For the naphthalene case, the C10 circuit must be similarly calculated giving ef_{10}= 0.07086 β. These two different circuits are superimposed and must be added to finally give $\sum ef_6$ = 0.1920 β in order to compare it to Aihara's m-BRE and t-BRE values (0.1774 β and 0.2101 β, respectively) for naphthalene (Figure 1). In general, for all benzenoids studied the slight increase in m-BRE, $\sum ef_6$ and t-BRE magnitudes follow this order.[16,19] We now briefly review Aihara's graph theoretical method for calculating CRE.

Circuit Resonance Energy (CRE)

The graph-theoretical quantity A_i (CRE_i) for the ith circuit in a closed-shell polycyclic π-system G for the nondegenerate eigenvalues is given by the following equation

$$A_i = 4 \sum_{j=1}^{occ} \frac{P_{(G-ri)}(X_j)}{P'_G(X_j)} \tag{1}$$

where $G-r_i$ is the subsystem of G, obtained by deleting all carbon atoms in G that constitute the ith circuit; $P_G(X)$ and $P_{G-ri}(X)$ are the characteristic polynomials for G and $G-r_i$, respectively; $P'_G(X)$ is the derivative of the characteristic polynomial; X_j is the jth positive root of $P_G(X) = 0$; and j runs over all the π occupied orbitals. Aihara defines circuit resonance energy (CRE) for the ith circuit as $CRE_i = A_i$[9,16] Positive and negative A_i values indicate diatropic (counterclockwise) and paratropic (clockwise) currents, respectively.

For degenerate π MOs, the above equation must be replaced by others.[29–34] Note Eq. (1) is in units of β.

To understand the units used in CRE (β), CCE (β), m-BRE (β), t-BRE (β), and ring current I_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 β. For benzene CCE = t-BRE = 0.2726 β and CRE = $\sum A_i = m$-BRE where $\sum A_i = \sum CRE_i =$ 4[1/36 + 1/36] = 0.2222 β and $I = 4.5(I_o/β)\sum CRE_i(S_i/S_o) =$ 4.5$(I_o/β)$(0.2222 β)(S_o/S_o) = 1.0 I_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 β. Note that 1/0.2222 = 4.5 which is the origin of this constant above for ring current I. Equations for treating various eigenvalue degeneracy have been reviewed by Dias.[34]

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_6), ring ef_6, and ring current I_6 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_6 and ef_6 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$_6$ = 0.1774 β, $\sum ef_6$ = 0.1920 β, and t-BRE$_6$ = 0.2101 β is the result of somewhat more emphasis of six-circuits. In determining $\sum ef_6$ = 0.1920 β deletion of the six-circuit also disrupts the ten-circuit and in determining t-BRE$_6$ = 0.2101 β (indicated by the squiggly line) both the six-circuit and the

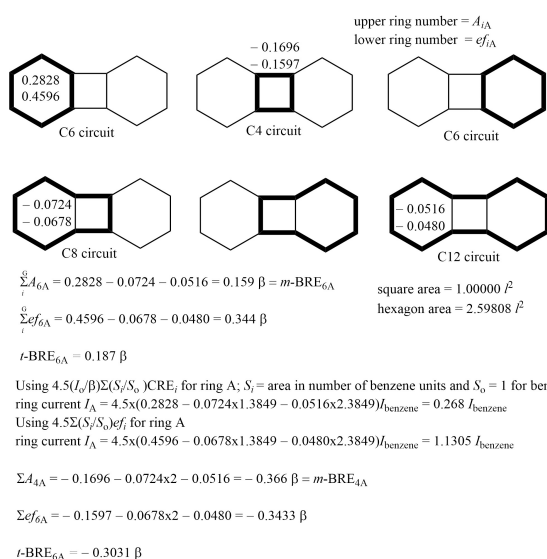**Table 1.** Data for Calculation of Circuit Resonance Energy and Currents in Naphthalene.

X_j, β	$P_{G-C6A}(X_j)/P'_G(X_j)$	$P_{G-C6B}(X_j)/P'_G(X_j)$	$P_{G-C10}(X_j)/P'_G(X_j)$	$P'_G(X_j)$
2.30278	0.013995	0.013995	0.00105935	943.97573
1.61803	0.0	0.0	−0.0345508	−28.942871
1.30278	−0.1526669	−0.1526669	0.12605659	7.9329448
1.0	0.1666667	0.1666667	−0.16666667	−6.0
0.61803	0.0	0.0	0.09044873	11.055987
$CRE_i = A_i = 4\sum$	0.11198	0.11198	0.06538871	

$P_G(X_j) = X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9$; $P'_G(X_j) = 10X^9 - 88X^7 + 246X^5 - 260X^3 + 86X$; $P_{G-C6A}(X_j) = P_{G-C6B}(X_j) = X^4 - 3X^2 + 1$; $P_{G-C10}(X_j) = 1$; $I = 4.5(I_o/β)\sum CRE_i(S_i/S_o)$
$I_{C6A} = 4.5A_{C6A} I_o = 4.5 \times 0.11198 I_o = 0.50391 I_o$ and $I_{C10} = 4.5 \times 2A_{C10} I_o = 4.5 \times 2 \times 0.06538871 I_o = 2 \times 0.29425 I_o = 0.5885 I_o$; $I = 0.50391 I_o + 0.5885 I_o = 1.0924 I_o$ which is the total C6 ring current.

ten-circuit are disrupted leaving a remaining six-circuit. Thus, explaining this sight increase in these values of m-BRE$_6$ < $\sum ef_6$ < t-BRE$_6$ for naphthalene.

Lack of correlation between CRE$_6$ and ef_6 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 (CRE$_4$ and ef_4, CRE$_8$ and ef_8, CRE$_{12}$ and ef_{12} 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 A_{6A} and ef_{6A} circuit values appear to be too large compared to the antiaromatic circuit values. In the study of energy effects of larger circuits in cyclobutadienylpolybiphenylene, Gutman noted violation of Hückel's 4n +2 aromatic rule.[35]

Herein, we will use TRE as a measure of global aromaticity and t-BRE$_6$ and $\sum ef_6$ as a measure of distribution of local ring aromaticity with special emphasis on alternating sextet and cyclobutadiene rings within the same polycyclic conjugated hydrocarbon molecule. Since for all benzenoid PAHs, t-BRE$_6$ turns out to be slightly larger than $\sum ef_6$ whereas for biphenylene $\sum ef_6$ is significantly larger than t-BRE$_6$, we will use these indices to study the polycyclic conjugated hydrocarbon molecules having both sextet and cyclobutadiene rings. The total number of circuits for nonbranching polycyclic conjugated systems with no internal 3rd degree vertices and r rings is given by number circuits = ½(r^2 + r). Polycyclic conjugated systems with internal 3rd degree vertices have even more circuits. Thus, t-BRE$_6$ has an advantage over m-BRE$_6$ and $\sum ef_6$ in that enumeration of many circuits present in large polycyclic conjugated systems is not necessary.

Aromaticity of Benzene and Antiaromaticity of Cyclobutadiene

The m-BRE = CRE, ef, t-BRE, %TRE, I (ring current) and HOMA values for benzene and cyclobutadiene, respectively, are 0.2222 (m-BRE$_6$), 0.2726 (ef_6), 0.2726 (t-BRE$_6$), 3.528 (%TRE), 1.0 I_0 (I), 0.996 (HOMA), and $-\infty$ (m-BRE$_4$), $-$1.2263 (ef_4), $-$1.2263 (t-BRE$_4$), $-$23.463 (%TRE), $-\infty$ (I), $-$2.570 (HOMA).[12] 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$_6$ = 0.04934 β and t-BRE$_6$ = 0.05064 β (Figure 3) agree well with each other but like with biphenylene $\sum ef_6$ = 0.16141 β appears too large. The cyclobutadiene ring in benzocyclobutadiene has about 60 % the antiaromaticity of cyclobutadiene 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 benzocyclobutadiene. A complete eigenvalue/eigenvector solution of benzocyclobutadiene was featured in a 1996 paper by Dias.[36]

$\sum_i^G A_{6A} = 0.2828 - 0.0724 - 0.0516 = 0.159\ \beta = m\text{-BRE}_{6A}$

$\sum_i^G ef_{6A} = 0.4596 - 0.0678 - 0.0480 = 0.344\ \beta$

$t\text{-BRE}_{6A} = 0.187\ \beta$

square area = 1.00000 l^2
hexagon area = 2.59808 l^2

Using 4.5(I_o/β)Σ(S_i/S_o)CRE$_i$ for ring A; S_i = area in number of benzene units and S_o = 1 for benzene.
ring current I_A = 4.5x(0.2828 $-$ 0.0724x1.3849 $-$ 0.0516x2.3849)$I_{benzene}$ = 0.268 $I_{benzene}$
Using 4.5Σ(S_i/S_o)ef_i for ring A
ring current I_A = 4.5x(0.4596 $-$ 0.0678x1.3849 $-$ 0.0480x2.3849)$I_{benzene}$ = 1.1305 $I_{benzene}$

$\sum A_{4A} = -0.1696 - 0.0724x2 - 0.0516 = -0.366\ \beta = m\text{-BRE}_{4A}$

$\sum ef_{6A} = -0.1597 - 0.0678x2 - 0.0480 = -0.3433\ \beta$

$t\text{-BRE}_{4A} = -0.3031\ \beta$

Figure 2. m-BRE$_{6A}$ and $\sum ef_{6A}$ in units of β for the sum of the superimposed constituent circuits of i = C6A, C8A, and C12. The value for the ef_{6A} = 0.4596 is unexpectedly large.

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

X_j, β	$P_{G\text{-}C4}(X_j) / P'_G(X_j)$	$P'_G(X_j)$
2.0	1/16	16
0 & 0	1/0	0
CRE$_i$ =A$_i$ = 4$\sum$	¼ (dication), $-\infty$	

$P_G(X) = X^4 - 4X^2$; $P'_G(X) = 4X^3 - 8X$; $P_{G\text{-}C4}(X) = 1$; $I = 4.5(I_o/\beta)\sum CRE_i(S_i/S_o)$

CREc_4= A_{C4} = 4[1/16] = ¼ for dication.

For doubly degenerate eigenvalues use Aj/4 = [$U(X_j) P'_{G\text{-}ri}(X_j) - U'(X_j) P_{G\text{-}ri}(X_j)$]/ $U(X_j)^2$ once for the two occupied orbitals where $(X-0)^2 U(X) = P_G(X) = 0×0 = 0$ for $X = X_j = 0$, Thus, $U(0) = 0$ and A$_0$/4 = [0×0−0×0]/0 = $-\infty$ for diradical cyclobutadiene.

$I_{C4} = 4.5A_{C4}\ I_o = 4.5x(-\infty)\ I_o = -\infty\ I_o$ which is the total ring current.

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

| X_j, β	$P_{G\text{-}C6}(X_j)\,/\,P'_G(X_j)$	$P_{G\text{-}C4}(X_j)\,/\,P'_G(X_j)$	$P_{G\text{-}C8}(X_j)\,/\,P'_G(X_j)$	$P'_G(X_j)$
2.35567	0.0120315	0.0400571	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
$CRE_i = A_i = 4\sum$	0.43658	−0.59064	−0.387241	

$P_G(X_j) = X^8 - 9X^6 + 22X^4 - 16X^2 + 1$; $P'_G(X_j) = 8X^7 - 54X^5 + 88X^3 - 32X$; $P_{G\text{-}C6}(X_j) = X^2 - 1$; $P_{G\text{-}C4}(X_j) = X^4 - 3X^2 + 1$; $P_{G\text{-}C8}(X_j) = 1$; $I = 4.5(I_o/\beta)\sum CRE_i(S_i/S_o)$

$I_{C6} = 4.5A_{C6}\,I_o = 4.5 \times 0.43658\,I_o = 1.9646\,I_o$; $I_{C4} = 4.5A_{C4}(S_i/S_o)I_o = 4.5 \times (-0.59064)0.3849\,I_o = -1.02302\,I_o$; and $I_{C8} = 4.5 \times A_{C8}(S_i/S_o)I_o = 4.5 \times (-0.387241)1.3849\,I_o = -2.24133\,I_o$; $I_6 = 1.9646\,I_o - 1.02302\,I_o = 0.9416\,I_o$ which is the total C6 ring current;
$I_4 = -1.02302\,I_o - 2.24133\,I_o = -3.26435\,I_o$ which is the total C4 ring current.
square area = 1.00000 l^2
hexagon area = 2.59808 l^2
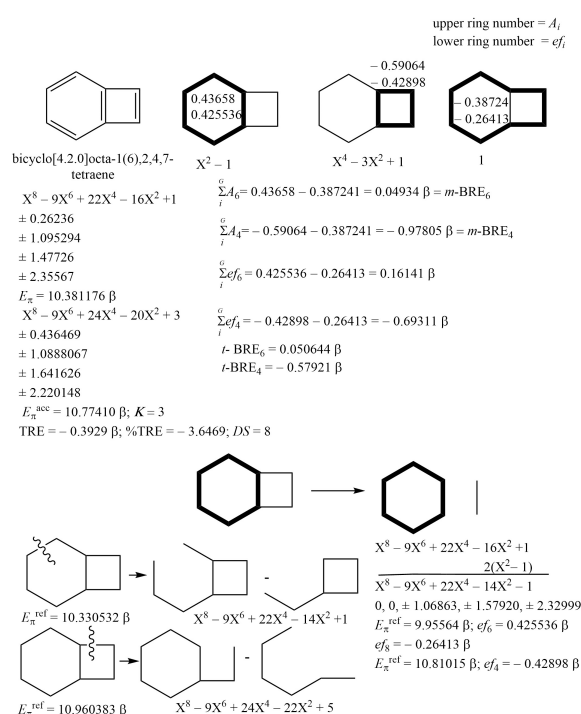
Figure 3. Calculation of TRE, A_i, m-BRE, $\sum ef$, and t-BRE of benzocyclobutadiene. See Table 3 for data and calculation of A_i and m-BRE.

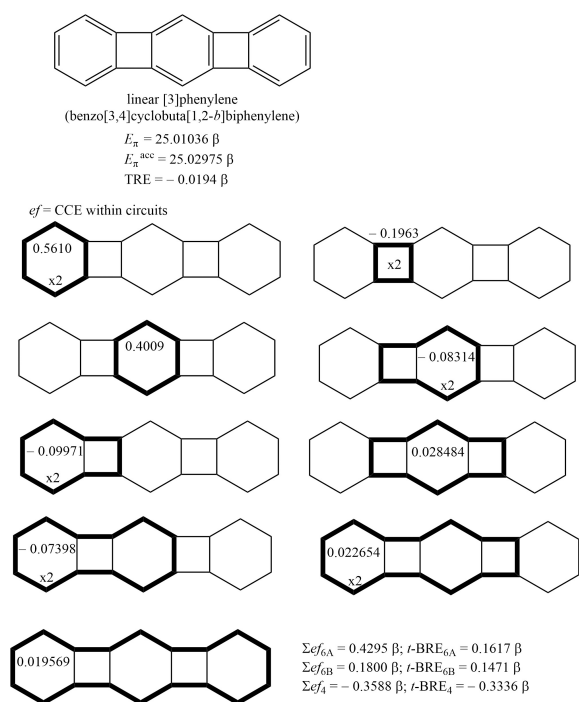## Location is Everything

Figure 4 demonstrates that depending on relative location of the cyclobutadiene and benzene rings, for small polycyclic conjugated hydrocarbon molecules, one can get some isomers that are overall antiaromatic and others that are aromatic. As postulated by Maksic and coworkers biphenylene and bent [3]phenylene become aromatic compared to their isomers because of a decrease in the antiaromaticity of the two 4-membered rings as indicated by the more positive values of t-BRE$_4$.[15] Thus, linear [3]phenylene is overall antiaromatic whereas bent
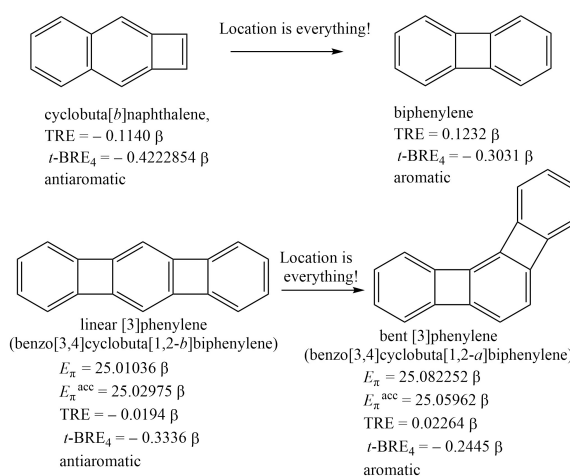

Figure 4. For small systems with a mix of cyclobutadiene and benzene rings, some isomers can be antiaromatic and others can be aromatic which emphasizes that location is everything.

[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.[37,38] 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.[39]

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 Randić gives conjugated circuit data for [2] − [4]phenylenes.[14] The degree of aromaticity of linear [2] − [4]phenylenes progressively decreases which means that their antiaromaticity proportionally increases.[14]

linear [3]phenylene
(benzo[3,4]cyclobuta[1,2-*b*]biphenylene)
$E_\pi = 25.01036\ \beta$
$E_\pi^{\text{acc}} = 25.02975\ \beta$
TRE = $-0.0194\ \beta$

ef = CCE within circuits

$\Sigma ef_{6A} = 0.4295\ \beta$; t-BRE$_{6A} = 0.1617\ \beta$
$\Sigma ef_{6B} = 0.1800\ \beta$; t-BRE$_{6B} = 0.1471\ \beta$
$\Sigma ef_4 = -0.3588\ \beta$; t-BRE$_4 = -0.3336\ \beta$

Figure 5. Overall the linear [3]phenylene is antiaromatic. By both Σef_6 and t-BRE$_6$ the outer sextet (benzene) ring being more aromatic than the inner sextet ring.
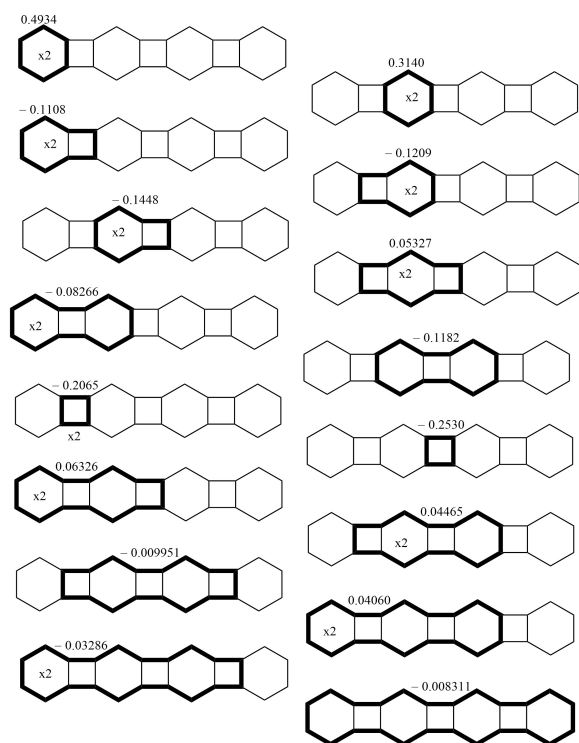
Figure 6. Circuits in cyclobuta[1,2-*b*:3,4-*b*]dibiphenylene with ef values listed.
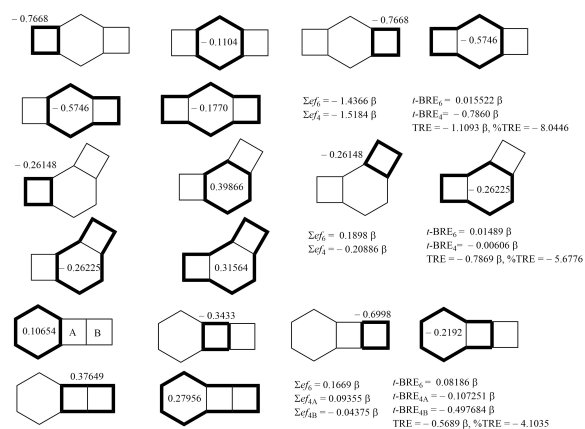

biphenylene or
[2]phenylene
$E_\pi = 16.5055\ \beta$
$E_\pi^{\text{acc}} = 16.3823\ \beta$
TRE = $0.1232\ \beta$
%TRE = 0.7523
t-BRE$_6 = 0.187\ \beta$
$\Sigma ef_6 = 0.344\ \beta$
t-BRE$_4 = -0.30308\ \beta$
$\Sigma ef_4 = -0.3433\ \beta$
$K = 5$; $a_{12} = 9$
$ef_6 = 0.4596\ \beta$
$DS = 30$

[3]phenylene
(benzo[3,4]cyclobuta[1,2-*b*]biphenylene)
$E_\pi = 25.01036\ \beta$
$E_\pi^{\text{acc}} = 25.02975\ \beta$
TRE = $-0.0194\ \beta$
%TRE = -0.0775
t-BRE$_{6A} = 0.1617\ \beta$, t-BRE$_{6B} = 0.1471\ \beta$
$\Sigma ef_{6A} = 0.4295\ \beta$, $\Sigma ef_{6B} = 0.1800\ \beta$
t-BRE$_4 = -0.33364\ \beta$
$\Sigma ef_4 = -0.3596\ \beta$
$K = 12$; $a_{18} = 16$
$ef_{6A} = 0.5610\ \beta$; $ef_{6B} = 0.4009\ \beta$
$DS = 145$

[4]phenylene
(cyclobuta[1,2-*b*:3,4-*b*]dibiphenylene)
$E_\pi = 33.514389\ \beta$
$E_\pi^{\text{acc}} = 33.679533\ \beta$
TRE = $-0.16514\ \beta$
%TRE = -0.49034
t-BRE$_{6A} = 0.1534\ \beta$, t-BRE$_{6B} = 0.1289\ \beta$
$\Sigma ef_{6A} = 0.3625\ \beta$; $\Sigma ef_{6B} = 0.05057$
t-BRE$_{4A} = -0.3400\ \beta$, t-BRE$_{4B} = -0.3738\ \beta$
$\Sigma ef_{4A} = -0.3703\ \beta$; $\Sigma ef_{4B} = -0.2800$
$K = 29$; $a_{24} = 25$
$ef_{6A} = 0.4934\ \beta$; $ef_{6B} = 0.3140\ \beta$
$DS = 540$

Figure 7. Linear polybiphenylene ([*n*]phenylene) series and their calculated antiaromatic/aromatic parameters.

The conjugated circuit antiaromaticity/aromaticity predictions for benzocyclobutadiene 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 benzocyclobutadiene (%TRE = -3.6469, Figure 3). Both Σef_6 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.[40] 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[*b*]benzocyclobutadiene in Figure 8. In all examples examined, whenever benzene rings are linearly bounded by cyclobutadiene rings, there is a significant reduction in their aromaticity. 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 Σef values by $-0.0006\ \beta$.

In passing, extensive comment on [n]phenylenes in regard to the paper by Kovaček and coworkers[41] can be found in the review by Randić.[14] This comment also applies

$\Sigma ef_6 = -1.4366\ \beta$ t-BRE$_6 = 0.015522\ \beta$
$\Sigma ef_4 = -1.5184\ \beta$ t-BRE$_4 = -0.7860\ \beta$
TRE = $-1.1093\ \beta$, %TRE = -8.0446

$\Sigma ef_6 = 0.1898\ \beta$ t-BRE$_6 = 0.01489\ \beta$
$\Sigma ef_4 = -0.20886\ \beta$ t-BRE$_4 = -0.00606\ \beta$
TRE = $-0.7869\ \beta$, %TRE = -5.6776

$\Sigma ef_6 = 0.1669\ \beta$ t-BRE$_6 = 0.08186\ \beta$
$\Sigma ef_{4A} = 0.09355\ \beta$ t-BRE$_{4A} = -0.107251\ \beta$
$\Sigma ef_{4B} = -0.04375\ \beta$ t-BRE$_{4B} = -0.497684\ \beta$
TRE = $-0.5689\ \beta$, %TRE = -4.1035

Figure 8. Antiaromaticity comparison of three C10 isomers. Only the linearly bounded benzene ring above is antiaromatic.

to their subsequent paper.[15] In TRE calculations, it is assumed that the hypothetical polycyclic polyene reference molecule has the same number of π-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[15] 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[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 β and t-BRE$_4$ = –0.3336 β for linear [3]phenylene and TRE = 0.02264 β and t-BRE$_4$ = –0.2445 β for bent [3]phenylene. Thus, linear [3]phenylene is antiaromatic 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.[3] Phenylene can be embedded by benzocyclobutadiene and therefore has its eigenvalues (listed in Figure 3); both have the same HOMO/LUMO = ±0.26236 β.[36–38,40] Thus, the greater antiaromatic character of the linear dicyclobutabenzene over the angular one in Figure 8 is also in full agreement with this interpretation.

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$_i$ and $\sum ef_i$ 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.

CONCLUSION

Since most molecules that exist have neither aromaticity nor antiaromaticity, molecules with antiaromaticity may still exist because there are other stabilizing factors. The existence of aromaticity or antiaromaticity is just additional stabilizing or destabilizing variables in a molecule. This study is only evaluating the degree of aromatic stabilization or antiaromatic destabilization present in [n]phenylenes and the possible influence this may have in determining their existence. Except for biphenylene, $\sum ef_i$ and t-BRE$_i$ both give the same relative order of ring aromatic/antiaromatic predictions. TRE is a reliable measure of molecular global

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