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Perimeter Ring Currents in Benzenoids from Pauling Bond Orders

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Abstract

It is shown that the ring currents in perimeter hexagonal rings of Kekulean benzenoids, as estimated within the Randić conjugated-circuit model, can be calculated directly without tedious pairwise comparison of Kekulé structures or Kekulé counting for cycle-deleted subgraphs. Required are only the Pauling bond orders of perimeter bonds and the number of Kekulé structures of the benzenoid, both readily available from the adjacency matrix of the carbon skeleton. This approach provides easy calculation of complete current maps for benzenoids in which every face has at least one bond on the perimeter (as in the example of cata-condensed benzenoids), and allows qualitative evaluation of the main ring-current contributions to ^{1}H chemical shifts in general benzenoids. A combined Randić-Pauling model for correlation of ring current and bond length through bond order is derived and shown to be consistent with resilience of current under bond alternation.

1. Introduction

Aromaticity is widely held to be synonymous with the ability of a (polycyclic) conjugated π system to sustain a diatropic ring current induced by an external magnetic field.[1-4] Other definitions based on relative energetics, geometry and reactivity[5,6] lack the decisive yes/no character of the criterion from current. Maps of induced current density can be calculated efficiently[7-9] in full ab initio approaches[9-15] for moderately sized benzenoids (nanographenes), polycyclic aromatic hydrocarbons and related carbon and heterocyclic networks. In the ipsocentric formulation,[9] molecular orbital (MO)-based methods offer interpretation of current maps in terms of orbital-orbital[16] and band-band[17] excitations induced in the magnetic field, diagnosing aromaticity and anti-aromaticity in terms of selection rules based on symmetry, energy and nodal character of frontier orbitals, and inspiring simplified models (e.g. the pseudo-π method[18]).

Another perspective is offered by models of ring current based on qualitative valence-bond (VB) concepts: the conjugated-circuit (CC) models.[19-24] These give distinctive insight into global patterns of current in (Kekulean) benzenoids. In models of this type, current in bonds is calculated combinatorially by considering pairings of perfect matchings (Kekulé structures) of the molecular graph. The present paper shows that there is a much more efficient way to calculate perimeter currents for the Randić model, and that this allows easy computation and rationalisation of the entire current

map for cases where every face of the benzenoid has at least one edge in the perimeter, and the most important part of the map for other cases..

2. Conjugated circuits and currents

A circuit C in a graph G is a conjugated circuit if both C and G-C (the graph with vertices of the cycle C deleted) have perfect matchings. In CC models it is assumed, consistently with the MO model for annulenes,[16] that conjugated circuits of length 4N+2 support diatropic ring currents and those of length 4N support paratropic ring currents. Models published by various authors[20-23] differ in how they assign weights to the conjugated circuits (see Ref. 24). In all of them, bond currents are calculated by vector addition of conjugated-circuit currents. As Figure 1 shows, the direction of the contribution of a CC to the current in a particular bond depends on the size of the circuit and on whether the circuit lies locally to the right or left of the bond. Any set of bond currents can be uniquely decomposed into ring currents for a more compact representation.

This paper considers the simplest of the conjugated-circuit models.[19,20] For a graph with $m(G)$ perfect matchings, the algorithm that Randić proposed to estimate current first finds an unscaled current for each edge by considering all pairs of perfect matchings. For each pair, a current of one unit is routed clockwise around each 4N cycle and anticlockwise around each 4N+2 cycle. In later accounts of the model,[25] a scaled (normalised) current is used. To obtain the scaled current, the current on each edge is divided by $m(G)[m(G) - 1]$. In passing, we note that this scaling is probably too severe in that it leads to drastic reduction in current for larger molecules, whilst other methods show a general tendency for absolute current to increase with molecular area (see e.g., Refs. 17, 18 and 24). In what follows, we will use $\tilde{J}$ for a scaled Randić current, and use J for its unscaled equivalent.

The union of two perfect matchings gives a spanning subgraph that consists of disjoint conjugated circuits and isolated double bonds. If a matching is paired with itself, there are no cycles (and hence no contribution to the current). The Randić current can be computed a little more efficiently by observing that the current from an ordered pair of matchings (M_1, M_2) is the same as that from the pair (M_2, M_1), so it suffices to consider unordered pairs only, and then multiply the current by two.

Analysis of the Randić model yields a more efficient approach for current computation. It can be shown[24] that the unscaled current contribution for each cycle C of a Kekulean benzenoid is equal to

$$|J| = 2\, m(G - C)^2, \tag{1}$$

for each bond in C, with direction determined as in Figure 1. In (1), $m(G - C)$ is the number of matchings of the graph G with cycle C deleted.

Both original and cycle-based approaches to the computation are exponential and soon outstrip the capacity of pencil-and-paper calculation for systems of chemical interest. Numbers of cycles and perfect matchings in graphs of interest can be very large: there are families of benzenoids in which the Kekulé count soon exceeds a billion.[26] Implementation requires efficient programming.

In what follows, it will be shown that perimeter currents in benzenoids within the Randić model can be found efficiently (in polynomial time) by a different approach that uses tools from the standard

repertoire of qualitative theoretical chemistry (finding the determinant and the inverse of the adjacency matrix of a graph) without special programming.

3. Matching Numbers and Pauling Bond Order

In 1935, Pauling, Brockway and Beach[27] proposed a simple criterion for bond order in carbon networks. The π bond order of a carbon-carbon link was taken to be the fraction of Kekulé structures of the whole molecule in which that link appears as a double bond. The number of Kekulé structures (perfect matchings) in which a given edge of the graph carries a double bond (is matched) is the matching number of that edge. If the matching number of the edge e connecting vertices u and v is $m(e)$, and the graph as a whole has $m(G)$ perfect matchings, the Pauling Bond Order (PBO) is

$$p_{uv} = m(e)/m(G). \tag{2}$$

Clearly, the sum of Pauling bond orders at any carbon atom of a conjugated structure, i.e., at any vertex of the molecular graph, is one, as the sum of the matching numbers of all edges incident on a common vertex is equal to the number of perfect matchings of the graph.

Pauling and co-workers made explicit calculations where they listed all Kekulé structures by hand and checked each bond within them. This is not a strategy with good scaling properties. It was soon realised that for benzenoids (and for other molecular graphs with every face of size 4N+2)[28] the Pauling bond orders of edges can be calculated from the corresponding entry in the inverse of the adjacency matrix.[29,30]

In matrix terms, for a Kekulean benzenoid and for the edge between vertices u and v,

$$p_{uv} = (A^{-1})_{uv} = (\text{adj } A)_{uv}/(\det A), \tag{3}$$

where $\mathbf{A}$ is the adjacency matrix of the molecular graph, and A^{-1}, adj $\mathbf{A}$ and det $\mathbf{A}$ are the inverse, adjugate and determinant of $\mathbf{A}$, respectively. For a benzenoid with n vertices, the determinant of $\mathbf{A}$ is linked to the number of perfect matchings by

$$\det A = (-1)^{n/2} m(G)^2, \tag{4}$$

and, if $m(G) \neq 0$, we have

$$p_{uv} = (-1)^{n/2} (\text{adj } A)_{uv}/m(G)^2, \tag{5}$$

and

$$m(e) = (-1)^{n/2} (\text{adj } A)_{uv}/m(G). \tag{6}$$

As det $\boldsymbol{A}$ is the product of eigenvalues of $\mathbf{A}$, m(G) for a benzenoid is the product of the non-negative eigenvalues. The matrix of Pauling bond orders (entries p_{uv} for neighbours uv, and zero otherwise) for a benzenoid is the Hadamard product of A^{-1} and $\mathbf{A}$.[31,32]

4. Matching Numbers and Conjugated Circuits

Given the set of matching numbers, it is straightforward to count the conjugated circuits that pass through a given edge e of a Kekulean graph. Let the total number of matchings of the graph be m(G). There are m(G)^2 ordered pairs of perfect matchings. Suppose that the given edge e is a double bond in $m(e)$ perfect matchings, and hence a single bond in the remaining $[m(G)–m(e)]$. Edge e will appear as an edge of a conjugated circuit if it is a double bond in one of the paired matchings and single in the other (Figure 2). Therefore, $2m(e)[m(G) - m(e)]$ ordered pairs of perfect matchings correspond to conjugated circuits passing through edge e. This formula is general for all chemical graphs.

5. Matching Numbers, Bond Orders and Current

Now we investigate the current arising from these $2m(e)[m(G) - m(e)]$ conjugated circuits. In a benzenoid, all conjugated circuits are of size 4N+2 and therefore in a CC model of current all contribute diatropic circulations. In general, traversing an edge in the direction u-v keeps the interior of the circuit either on the left or the right, and accordingly contributions to the current in edge e may have different directions. However, if e happens to be a perimeter edge, all CC in which e is included lie on the same side of that edge, all current contributions reinforce, and the bond current follows from simple counting.

Hence we have our result: in a Kekulean benzenoid, the unscaled Randić ring current in a perimeter hexagon (a hexagon with at least one edge in the perimeter) is diatropic and is of strength

$$|J| = 2m(e)[m(G) - m(e)] = 2m(G)^2 p_{uv}(1 - p_{uv}), \tag{7}$$

where $e = (u, v)$ is any perimeter edge of the hexagon, m(e) is its matching number, u and v are the vertices of e, p_{uv} is the Pauling bond order of the edge, and m(G) is the number of perfect matchings of the graph. The scaled Randić ring current in the perimeter hexagon is

$$\tilde{J} = 2m(G)p_{uv}(1 - p_{uv})/(m(G) - 1). \tag{8}$$

When $m(G) \gg 1$, as is often the case for large benzenoids, the scaled current is well approximated by a function of bond order alone:

$$\tilde{J} \approx 2p_{uv}(1 - p_{uv}). \tag{9}$$

Formulas (7) and (8) allow efficient calculation of the Randić current on the perimeter of a benzenoid using only the determinant and inverse of the adjacency matrix. Matrix inversion and evaluation of determinants are standard operations for which plug-in subroutines are readily available.[33]

Perimeter current is sufficient to determine the entire current map for benzenoids in which all vertices lie on the perimeter (i.e., for cata-condensed benzenoids) and for all sufficiently thin benzenoids (benzenoids in which every hexagon has at least one edge in the perimeter). For general Kekulean benzenoids, (7) and (8) still predict a main feature of the map: the strength of the diatropic circulation on the molecular perimeter, which is significant for ^{1}H chemical shifts (see below).

The presence of the factor $p_{uv}(1 - p_{uv})$ in these equations points to the importance of delocalisation for ring current. A perimeter edge of fixed single-bond ($p_{uv} = 0$) or double-bond ($p_{uv} = 1$) character kills ring current in the local hexagon. Conversely, a perimeter bond with $p_{uv} = ½$ leads to the highest

possible ring current for the total number of matchings. In what follows, it will often be convenient to compare currents to this theoretical maximum scaled current of $\tilde{J}_{max} = \frac{1}{2}m(G)/[m(G)-1]$, corresponding to (8) with $p_{uv} = \frac{1}{2}$.

6. Another definition of bond order

Although Pauling Bond Order is a concept associated with a localised valence-bond picture, there is a direct connection with the delocalised molecular-orbital picture through another definition of bond order. The Ruedenberg bond order p_{uv}^R is defined as[34]

$$p_{uv}^R = \sum_i g_i \, c_u^{(i)} c_v^{(i)} / \lambda_i \tag{10}$$

where the sum runs over all eigenvectors of $\mathbf{A}$, $c_u^{(i)}$ and $c_v^{(i)}$ are entries for atoms u and v in the eigenvector i corresponding to adjacency eigenvalue λ_i , and g_i is the occupation number of the orbital described by the eigenvector. For directly bonded neighbours in Kekulean benzenoids, Ruedenberg and Pauling bond orders are equal.[29] Randić perimeter currents in these systems could therefore in principle be calculated entirely from eigenvectors and eigenvalues derived from the standard Hückel procedure of diagonalisation of $\mathbf{A}$ as, $\hat{J}$ the scaled current in units of the theoretical maximum $\tilde{J}_{max}$, is

$$\hat{J} = |\tilde{J}/\tilde{J}_{max}| = 4p_{uv}^R(1 - p_{uv}^R) = 4\left(\sum_i g_i \, c_u^{(i)} c_v^{(i)} / \lambda_i\right)\left(1 - \sum_i g_i \, c_u^{(i)} c_v^{(i)} / \lambda_i\right). \tag{11}$$

7. Examples and applications

(i) Comparison of approaches

We now have three algorithms for calculating the perimeter ring currents in the Randić CC model. Figure 3 illustrates the way the three different calculations for the entire current map proceed in the case of phenanthrene. This benzenoid has m(G) = 5, and the ten distinct pairings of perfect matchings yield the CC, which contribute a current of 2 to each edge that they contain, for each time that they are produced by a pairing. Alternatively, formula (1), based on matching numbers of the graph G – C, can be used to attribute unscaled weights to the edges of conjugated cycles C of G. Finally, and most directly, the same pattern of current follows from (7) by noting that perimeter edges of the terminal hexagonal rings are present in either 2 or 3 Kekulé structures, whereas perimeter edges of the central hexagon are present in 1 or 4.

(ii) Linear polyacenes

The bond-order formula gives easy derivations of general formulas for some classes of benzenoids. For example, a linear polyacene with h hexagonal rings indexed with k = 1, … h starting from a terminal ring (Figure 4) has m(G) = h+1. A ring H_k has a perimeter edge with matching number h +1 – k and hence has a scaled ring current $2k(h + 1 - k)/[h(h + 1)]$, in agreement with the result previously derived by counting conjugated circuits.[24] The result is mathematically correct for all h, but any results from a pure CC model will be of physical significance only insofar as these molecules

remain in states that are well described by Kekulé structures; there is ongoing debate about the ground-state electronic structures of higher members of the linear-polyacene series.[35-38]

(iii) Starphenes

Similarly, a catafusene in which three linear branches (containing a, b and c hexagons, respectively) are fused to a central hexagon (a starphene[39]) is predicted to have minimum current in the central ring for all $a, b, c \geq 0$. These benzenoids have $m(G) = (a + 1)(b + 1)(c + 1) + 1$, and the perimeter edges of the central ring have matching number 1, and hence the central hexagon has unscaled ring current $2(a + 1)(b + 1)(c + 1)$. As no edges in a catafusene have matching number zero, this must be the minimum. In general, hexagon H_k of the arm of length a (counting out from the first ring glued to the central hexagon) contains a perimeter edge with matching number $(a + 1 - k)(b + 1)(c + 1)$ and has an unscaled ring current $2(a + 1 - k)(b + 1)(c + 1)[k(a + 1)(b + 1)(c + 1) + 1]$, which is larger than the central ring current for all k, so the minimum is unique.

(iv) Fibonacenes

Fibonacenes are zig-zag, unbranched cata-condensed benzenoids. All fibonacene isomers with h hexagonal rings have identical palindromic sequences of ring currents within any given CC model.[40] Each has F_{h+2} perfect matchings, where $F_0 = 1$, $F_1 = 1$, …, $F_i = F_{i-1}+F_{i-2}$ are the Fibonacci numbers, and the unscaled Randić ring current in ring H_k, counting from k = 1 at a terminal ring, has been found to be the product[40] $2\, F_k\, F_{k+1}\, F_{h+1-k}\, F_{h+2-k}$. The present approach gives an easy alternative derivation from the Pauling bond orders of fibonacenes. Matching numbers of corresponding edges are independent of fibonacene isomer. On the perimeter of hexagon H_k there are always[41] at least three edges that share matching number $F_k\, F_{h+1-k}$. Hence (7) gives the unscaled ring current in hexagon H_k of the [h]fibonacene as $2F_kF_{h+1-k}\,(F_{h+2} - F_kF_{h+1-k})$. Use of the easily proved identity $F_kF_{h+1-k} + F_{k+1}F_{h+2-k} = F_{h+2}$, yields exactly the previous formula for ring current.[40]

(v) Giant benzenoids

An extreme application is to the large benzenoids of maximum Kekulé count for a given number h of hexagons, which were characterised by Balaban, Liu, Cyvin and Klein.[26] These molecules are catafused, with maximum branching, and a number of Kekulé structures that rises extremely rapidly with h.

Catafusenes are series-parallel graphs and hence there is a linear-time algorithm for computing the number of perfect matchings (which uses only integer arithmetic). Using a series-parallel graph algorithm also to compute m(e) for each edge leads to an $O(n^2)$ algorithm for these quantities. In the approach proposed here, the matrix inversion used to find the Pauling Bond Orders takes $O(n^3)$ time, but is of wider applicability, as it can deliver the perimeter part of the current map for any Kekulean benzenoid. The graph algorithm gives each computed Randić ring current as a rational number, typically with many-digit integers in numerator and denominator. However, such precision is unnecessary from the physical point of view even if the Randić model is exact, which clearly it is not. The present method based on matrix inversion uses floating-point arithmetic, but in practice can supply precision adequate for any likely physical application, and does not require special coding. It also gives perimeter currents for non-catafusenes.

Figure 5 shows a schematic structure for a benzenoid with almost twenty billion perfect matchings ($m(G) = 17\,012\,572\,857$) taken from Ref. 26. Inversion of the adjacency matrix in double precision real arithmetic recovers $m(G)$ and edge matching numbers with absolute errors $< 10^{-5}$ (and hence exactly when rounded to integers.)

The illustrated benzenoid is totally resonant, i.e., its graph has an independent set of hexagons that covers each vertex once, or in more chemical terms, every carbon centre belongs to a hexagon that carries a Clar sextet. The alternation in ring current strength along the hexagon sequence A, B, C, D, E, F (see caption of Figure 5) is consistent with the chemical intuition that current should be strong in Clar hexagons.

(vi) Non-perimeter hexagons

An example of what perimeter bond orders do not tell us is given by coronene, the only benzenoid with $h \leq 7$ rings with a non-perimeter hexagon (Figure 6). Consider a perimeter edge that joins two vertices of degree two. This edge appears in 14 of the 20 perfect matchings of coronene. Therefore, of the $(14 + 6)(14 + 6) = 400$ pairs of perfect matchings, 168 ($=14 \times 6 + 6 \times 14$) have this edge in exactly one member of the pair. As all circuits contribute reinforcing diatropic (anticlockwise) currents on this edge, bond current and hence the unscaled ring current J in the perimeter hexagon is given immediately as 168. By similar reasoning, an edge on the interior hexagon, in 6 of the 20 perfect matchings, also belongs to 168 conjugated circuits, but the count alone tells us nothing about the sense of their contributions.

For conjugated circuits containing at least one edge of the internal hexagon, one picture from each isomorphism class of circuit is shown in Figure 6. Rotating the picture gives six different conjugated circuits in most cases, with the exception of D_{6h}-symmetric **6**, for which there is only one, and D_{3h}-symmetric **9**, for which there are two. From the set of pictures, we can calculate the current that flows in edge e, the top edge of the central hexagon. The contribution of a given isomorphism class to this current is the product of three numbers: the number of CC in the class that contain edge e, the number of ways of choosing a matching of the CC, and the square of the number of perfect matchings of $G - C$. From pictures **1** to **5**, the contribution is a current from u to v (total 128), and for the remainder it is a current from v to u (total 40). Hence, the bond current in e is 88 and flowing in the paratropic, clockwise sense, considered with respect to the central hexagon) even though the ring current in the central hexagon is actually diatropic.

This information is not available from pure CC counting: the perimeter ring currents would be compatible with any diatropic central ring current strength up to 168. As the central ring current is in fact weaker than the ring current in the perimeter hexagons, the total map has the characteristic appearance of a cartwheel with opposed 'rim' and 'hub' circulations, as found in ab initio calculation.[42]

8. Currents and Bond Length

Our premise here is that aromaticity is defined by the magnetic criterion of existence of ring current, but geometric measures have also been proposed from time to time (For a recent comprehensive review, see Ref. 43). Given that Pauling bond orders correlate reasonably well with bond lengths in benzenoids,[44] it seems natural to explore whether the present link between current and bond order in formula (7) has an implication for the limits of geometric variability of aromatic ring systems. Ab initio calculations indicate that ring currents, both diatropic and paratropic, can persist in the presence of considerable distortion of the carbon skeleton in clamped systems,[45,46,47] if the geometric distortion results from a pure σ effect that leaves the π frontier-orbital structure intact. Vibrational dependence of current in aromatic and anti-aromatic systems,[48] and geometric resilience of different indicators of aromaticity of benzene have also been explored in various theoretical studies.[49,50]

Several linear and non-linear formulas for correlating bond length with Pauling bond order have been investigated.[44,51] The standard formula due to Pauling[52] gives bond length as a function of bond order as

$$\text{(Pauling)} \qquad R = R_1 - (R_1 - R_2)Kp/(Kp + 1 - p), \qquad (12)$$

where R is the predicted bond length of a bond with Pauling bond order p, R_1 and R_2 are lengths of single and double bonds between sp^2 carbon centres, respectively, and K is a parameter that accounts for the larger force constant of the double bond. The values used by Pauling changed over time, but by the 1960 edition of his book they are $R_1 = 1.504$ Å and $R_2 = 1.332$ Å, with K = 1.84. Inversion of (12) to give p as a function of bond length, and setting $r = (R_1 - R)/(R_1 - R_2)$ gives

$$\text{(Pauling)} \qquad p = r/[K(1 - r) + r], \qquad (13)$$

Note that as $R_1 \geq R \geq R_2$ for $0 \leq p \leq 1$, the ratio obeys $0 \leq r \leq 0$. If we combine Pauling and Randić approaches, a perimeter bond of length R in a benzenoid is predicted to carry a current of

$$\text{(Pauling)} \quad \hat{J} = \left|\tilde{J}/\tilde{J}_{\max}\right| = 4p(1 - p) = \frac{4Kr(1 - r)}{[K(1 - r) + r]^2} = \frac{4K(R_1 - R)(R - R_2)}{[K(R - R_2) + (R_1 - R)]^2}, \qquad (14)$$

where $\hat{J}$ is the scaled Randić current in units of $\tilde{J}_{\max}$, the maximum scaled current for the given m(G). A value of $\hat{J} = 1$ is predicted for the bond length R that corresponds to p = ½, r = K/(K + 1) and R = $(R_1 + KR_2)$ /(K + 1) i.e., for R ≈ 1.4 Å. Not surprisingly, the ideal structure for carrying delocalised perimeter ring current in this hybrid Randić/Pauling model (14) has benzene-like bonds all around that perimeter.

Resilience of the current to bond alternation can also be estimated. Suppose a given perimeter vertex of degree two lies at the junction of bonds with Pauling bond orders p_a and $p_b = 1 - p_a$, and bond lengths R_a and R_b, respectively. If the correlation (12) is taken as exact, the bond lengths for the two bonds are related by:

$$\text{(Pauling)} \qquad\qquad R_a = R_1 - \frac{(R_b - R_2)(R_1 - R_2)}{(R_b - R_2) + K^{-2}(R_1 - R_b)} \qquad (15)$$

and the scaled Randić current passing through the vertex, again in units of $\tilde{J}_{\max}$, can be written as a function of the two lengths:

(Pauling) $\qquad \hat{J} = |\tilde{J}/\tilde{J}_{\max}| == \dfrac{4(R_1 - R_a)(R_1 - R_b)}{[K(R_a - R_2) + (R_1 - R_a)][K(R_b - R_2) + (R_1 - R_b)]}$. (16)

Figure 7 shows the dependence of this fractional current $\hat{J}$ on order, length and length difference for the two bonds incident on the degree-two vertex. The maximum in each curve corresponds to a pair of benzenoid bonds, as before, but the curves also illustrate a surprising resilience of the current to disparity between bond orders, and hence bond lengths, in the pair. When bond orders deviate from the ideal value, a difference $|p_a - p_b| = \frac{1}{10}\sqrt{\delta}$ leads to a fall-off of $\delta\%$, in $\hat{J}$ and is associated with a predicted difference in bond length of

(Pauling) $\quad \Delta R \;=\; |R_a - R_b| \;=\; \dfrac{1}{10}\sqrt{\delta}(R_1 - R_2)/[1 + (100 - \delta)(K - 1)^2/400K]$ (17)

which implies bond alternation of $\Delta R \;=\; 0.035,\; 0.080,\; 0.116\,\text{Å}$ for $5\%, 25\%$ and 50% reductions in current. These differences, although considerably over-estimated, are qualitatively compatible with the above-mentioned evidence from ab initio calculations on clamped benzene systems.

An even simpler correlation of bond length and bond order is given by linear regression for a curated set of geometric data for 22 benzenoids (223 symmetry inequivalent bond lengths).[44,51]

(Linear) $\quad R = D_1 - (D_1 - D_2)p$ (18)

with $D_1 = 1.467$ Å and $D_2 = 1.320$ Å. This equation does not perform significantly worse than the non-linear Pauling equation. If (18) is taken as exact, we can calculate $\hat{J}$ for our degree-two vertex, from analytical functions of bond order, bond length or bond alternation (limits of analogous Pauling relations for $K \to 1$):

(Linear) $\hat{J} = 4p_a(1 - p_a) = \dfrac{4(D_1 - R_a)(R_a - D_2)}{(D_1 - D_2)^2} = \dfrac{4(D_1 - R_a)(D_1 - R_b)}{(D_1 - D_2)^2} = 1 - \dfrac{(R_a - R_b)^2}{(D_1 - D_2)^2}$ (19)

Like (12), linear correlation is forgiving of bond alternation, with reductions of $5\%, 25\%$ and 50% in current corresponding to differences of $\Delta R \;=\; 0.033,\; 0.074,\; 0.104$ Å, respectively.

9. Conclusion

Connections between bond order and aromaticity have of course been discussed before, as represented in the classic work of Jug,[53] where the aromaticity of a ring is determined by its weakest link. Explicit connections between aromaticity and bond order in the Coulson definition have also been made for a variety of MO-based delocalisation indices.[54] There is also a long tradition of empirical MO calculations of current based on the Hückel-London model. (For a review see Ref. 55.) One recent application of this MO method in the formulation developed by Aihara[56] discusses current maps of benzenoids that have factorisable Kekulé structures (i.e., of regions of fixed single and double bonds). These are natural subjects for comparison of MO and CC methods; in a pure CC model, any fixed bond in a perimeter ring kills the local current; MO approaches may predict more complicated behaviour.[56,57]

The present work started from an observation that the method of calculation of currents in the CC model could be greatly simplified. As we have shown, bond orders and ring currents on the perimeter of a benzenoid, as calculated within Pauling and Randić models, are related by a closed formula, and both sets of quantities can be obtained by inversion of the adjacency matrix.

The formulas given in Equations (7) to (9) allow us to reproduce the results of the Randić CC model from bond orders, but for perimeter hexagons only. This is certainly a theoretical limitation, but in practice the main experimental probe of ring currents is a perimeter effect: induced diatropic currents cause downfield changes in the chemical shifts of protons in external CH bonds. In typical cases, these changes are dominated by nearby currents, which on the perimeter tend to be large. The ring currents with most influence on chemical shifts of external protons are therefore accessible by inversion of the adjacency matrix of the molecular graph. A model that predicts perimeter currents can be expected to capture the main effects of ring current on the ^{1}H NMR spectra of the stable (Kekulean) benzenoids.

Another implication of the reformulation is a link between perimeter current and bond lengths, via the Pauling bond order/bond length correlation. This gives results that are compatible with the known resilience of ring current aromaticity to bond alternation. In addition, as Ruedenberg and Pauling bond orders are identical for benzenoids, the required bond orders are themselves formal functions of π-MO quantities. As a result, the new formulation in terms of the $p(1 - p)$ function of Pauling bond order p gives an explicit linkage between three criteria of aromaticity: π-energetic, geometric and magnetic.

10. Acknowledgements

References

1. P. von Ragué Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, J. Am. Chem. Soc., 1996, **118**, 6317.
2. L. Pauling, J. Chem. Phys., 193 **4**, 673.
3. F. London, J. Phys. Radium, 1937, **8**, 397.
4. J.A. Pople, J. Chem. Phys., 1956, **24**, 1111.
5. M. B. Smith and J. March, March's Advanced Organic Chemistry, Wiley, New York, 2007.
6. V. Minkin, M. Glukhovtsev and B. Simkin, Aromaticity and Antiaromaticity, Wiley Interscience, New York, 1994.
7. T. A. Keith and R. F. W. Bader, Chem. Phys. Lett., 1993, **210**, 223.
8. S. Coriani, P. Lazzeretti, M. Malagoli and R. Zanasi, Theoret. Chim. Acta, 1994, **89**, 181.
9. E. Steiner and P.W. Fowler, J. Phys. Chem., 2001, **105**, 9553.
10. E. Steiner, P. W. Fowler and R. W.A. Havenith, J. Phys. Chem. A, 2002. **106**. 7048.
11. A. Soncini and P. W. Fowler, Chem. Phys. Lett., 2008, **450**, 431.
12. R.W. A. Havenith and P. W. Fowler, Chem. Phys. Lett., 2007, **449**, 347.
13. J. Jusélius, D. Sundholm and J. Gauss, J. Chem. Phys., 2004, **121**, 3952.
14. H. Fliegl, S. Taubert, O. Lehtonen and D. Sundholm, Phys. Chem. Chem. Phys., 2011, **13**, 20500.
15. A. Soncini, A. M. Teale, T. Helgaker, F. De Proft and D. J. Tozer, J. Chem. Phys., 2008, **129,** 074101.

16. E. Steiner and P. W. Fowler, Chem. Comm. 2001, 2220.

17. E. Steiner, P. W. Fowler, A. Soncini and L.W. Jenneskens, Faraday Discussions, 2007, **135**, 309.

18. P. W. Fowler and E. Steiner, Chem. Phys. Lett., 2002, **364**, 259.

19. M. Randić, Chem. Rev., 2003, **103**, 3449.

20. M. Randić, Chem. Phys. Lett., 2010, **500**, 123.

21. A. Ciesielski, T. M. Krygowski, M. K. Cyrański, M. A. Dobrowolski and J. Aihara, Phys. Chem. Chem. Phys., 2009, **11**, 11447.

22. M. Mandado, J. Chem. Theory Comput., 2009, **5**, 2009, 2694.

23. J. A. N. F. Gomes and R. B. Mallion, Revista Portuguesa de Química, 1979, **21**, 82.

24. P. W. Fowler and W. Myrvold, J. Phys. Chem. A, 2011, **115**, 13191.

25. M. Randić, D. Vukičević, A. T. Balaban, M. Vračko and D. Plavšić, J. Comp. Chem., 2012, **33**, 1111.

26. A. T. Balaban, X. Liu, S. J. Cyvin, and D. J. Klein, J. Chem. Inf. Comput. Sci., 1993, **33**, 429.

27. L. Pauling, L. O. Brockway, J. Y. Beach, J. Am. Chem. Soc., 1935, **57**, 2705.

28. H. Sachs, *Algebra und Graphentheorie: Beiträge der Jahrestagung 'Algebra und Grenzgebiete'* Siebenlehn, Oktober 1985, pp 65-70.

29. N. S. Ham, J. Chem. Phys., 1958, **29**, 1229.

30. I. Samuel, Comp. Rend. Acad. Sci. Paris, 1961, **252**, 1795.

31. A. Ciesielski, T. M. Krygowski and M. K. Cyránski, Symmetry, 2010, **2**, 1390.

32. P. W. Fowler, W. Myrvold and W. H. Bird, J. Math. Chem., 2012, **50**, 2408.

33. W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, Numerical Recipes. The Art of Scientific Computing, University Press: Cambridge, U.K., 1986.

34. K. Ruedenberg, J. Chem. Phys. 1954, **22**, 1878.

35. M. Bendikov , H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter and F. Wudl, J. Am. Chem. Soc., 2004, **126**, 7416; erratum, J. Am. Chem. Soc. 2004, **126**, 10493.

36. G. Portella, J. Poater, J. M. Bofill, P. Alemany and M. Solà, J. Org. Chem., 2005, **70**, 2509; erratum, J. Org.Chem., 2005, **70**, 4560.

37. J. Poater, J. M. Bofill, P. Alemany and M. Solà, J. Phys. Chem. A, 2005, **109**, 10629.

38. B. Hajgató, M. Huzak, and M. S. Deleuze, J. Phys. Chem. A, 2011, **115**, 9282.

39. I. Gutman, T. Morikawa and S. Narita, Z. Naturforsch., 2004, **59a**, 295.

40. P. W. Fowler, S. Cotton, D. Jenkinson, W. Myrvold and W. H. Bird, Chem. Phys. Lett., 2014, **597**, 30.

41. I. Gutman, A. T. Balaban, M. Randić, and C. Kiss-Tóth, Z. Naturforsch., 2005, **60a**, 171.

42. E. Steiner, P. W. Fowler and L. W. Jenneskens, Angew. Chemie Int. Edn., 2001, **40**, 362.

43. T. M. Krygowski, H. Szatylowicz, O. A. Stasyuk, J. Dominikowska, and M. Palusiak, Chem. Rev., 2014, **114**, 6383.

44. R. Kiralj and M. M. C. Ferreira, J. Chem. Inf. Comput. Sci., 2002, **42**, 508.

45. A. Soncini, R. W. A. Havenith, P. W. Fowler L. W. Jenneskens and E. Steiner, J. Org. Chem., 2002, **67**, 4753.

46. P. W. Fowler, R. W. A. Havenith, L. W. Jenneskens, A. Soncini and E. Steiner, Angew. Chemie Int. Edit., 2002, **41**, 1558.

47. R. W. A. Havenith, P. W. Fowler and L. W. Jenneskens Org. Lett., 2006, **8**, 1255.

48. D. E. Bean and P. W. Fowler, J. Phys. Chem. A, 2011, **115**, 13649.

49. M. K. Cyránski and T. M. Krygowski, Tetrahedron, 1999, **55**, 6205.

50. F. Feixas, E. Matito, J. Poater and M. Solà, J. Phys. Chem. A, 2007, **111**, 4513.

51. R. Kiralj and M. M. C. Ferreira, Hemijski Pregled (Chem. Rev.), 2002, **44**, 82 (In Serbian).

52. L. Pauling, Nature of the Chemical Bond, Cornell University Press, Ithaca N.Y., 2nd Edition (1945), 3rd edition (1960).

53. K. Jug, J. Org. Chem., 1983, **48**, 1344.

54. E. Matito, F. Feixas and M. Sola, J. Mol. Struct.: THEOCHEM, 2007, **811**, 3.

55. J. A. N. F. Gomes and R. B. Mallion, Chem. Rev., 2001, **101**, 1349.
56. J-I. Aihara, R. Sekine and T. Ishida, J. Phys. Chem. A, 2011, **115**, 9314.
57. S. Radenković, P. Bultinck, I. Gutman and J. Đurđević, Chem. Phys. Lett., 2012, **552**, 151.
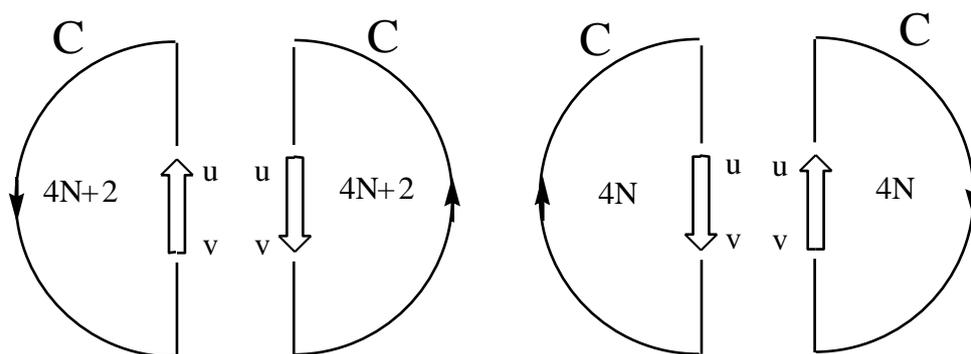
Figure 1. Contribution of an even cycle C to induced current in bond u v depends on whether the cycle size leaves remainder 2 or 0 on division by 4, and whether the interior of the cycle lies to left or right of the bond when travelling in the direction u to v. In the convention used here, diatropic (aromatic) circulations run anticlockwise in 4N+2 cycles C and paratropic (antiaromatic) circulations run clockwise in 4N cycles. The broad arrows show the resultant bond current.

(a)

$m(e)$

(b)

$m(G) \!-\! m(e)$

(c)

$2m(e)[m(G) \!-\! m(e)]$
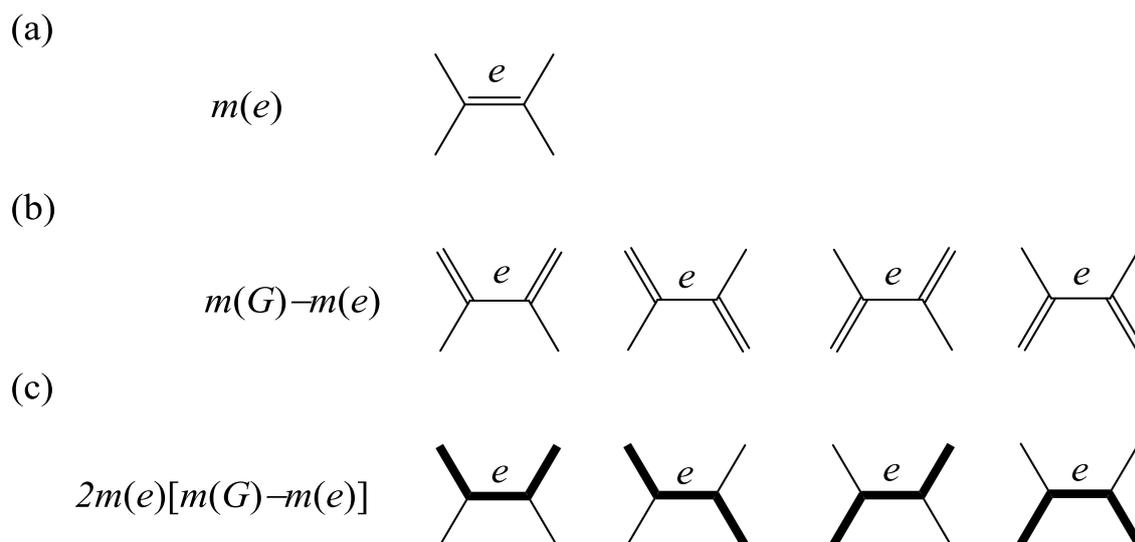
Figure 2. Counting the conjugated circuits passing through a given edge of a benzenoid. The fragment shown in (a) to (c) is of the edge in a local environment typical of a benzenoid. The edge e has matching number m(e). The m(G) perfect matchings of the graph include (a) m(e) in which edge e is a double bond and (b) the remainder, in which e is a single bond. Therefore, (c), the pairs of matchings in which one is taken from each set (allowing for both orderings of the pair) give the $2m(e) [m(G) - m(e)]$ conjugated circuits that pass through edge e, as illustrated here in bold.

(a)

A   B   C   D   E

(b)

AC   BD   AB   CD   DE

BE   CE   AE   AD   BC

(c)

2   2   1

1   1   1

(d)
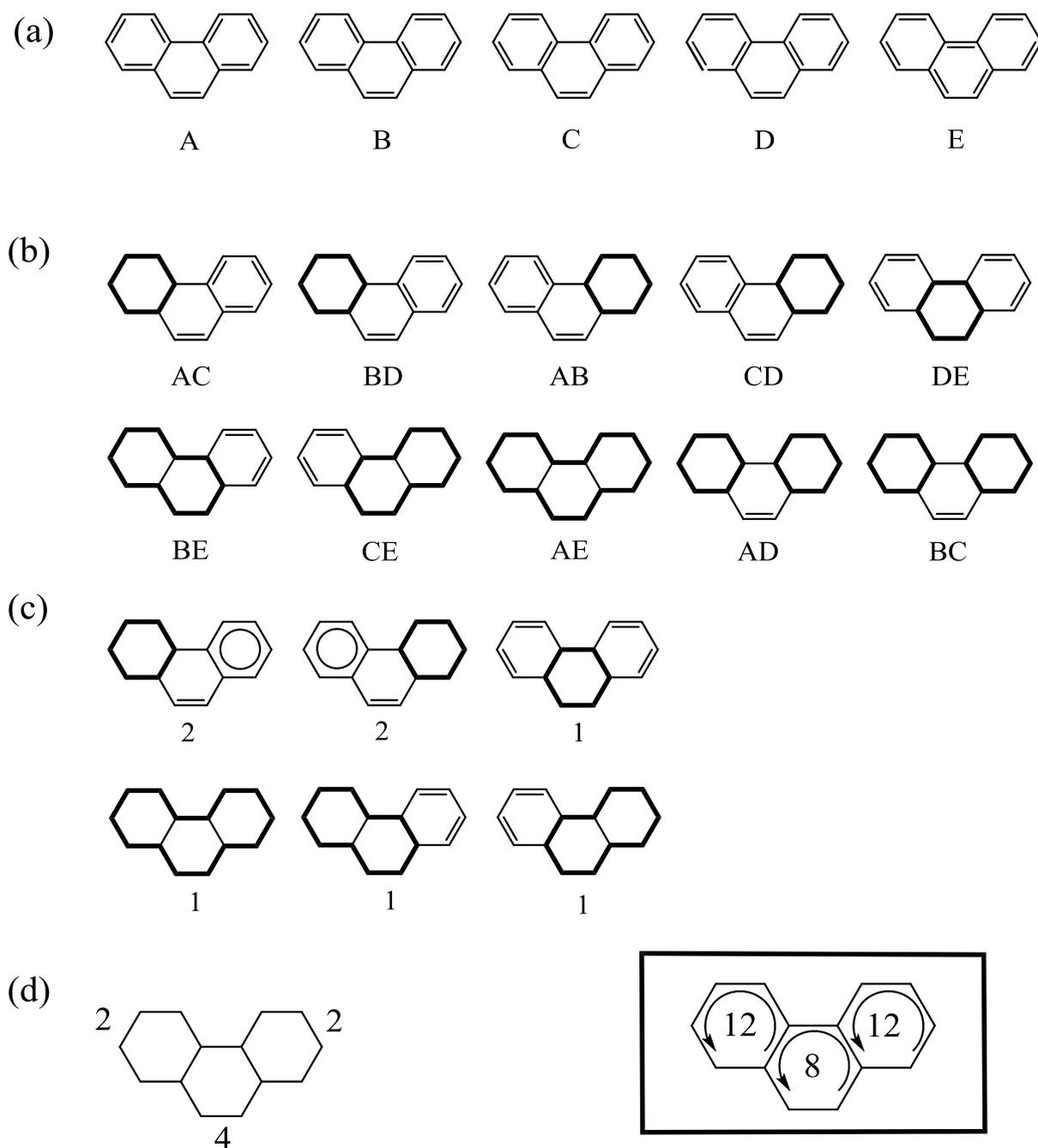
Figure 3. Three approaches to calculation of perimeter currents. (a) Phenanthrene has five perfect matchings: $m(G) = 5$; (b) Conjugated circuits (bold) are found by the ten distinct pairwise comparisons of the five matchings, each pairing contributing an unscaled current of 2 in each bold edge; (c) Values $m(G - C)$ are calculated for all conjugated cycles C, as shown in bold, and edge of C is given unscaled weight $2m(G - C)^2$; (d) Matching numbers, $m(e)$, are calculated for one perimeter edge e per perimeter hexagon, and are used to produce unscaled ring currents in perimeter hexagons according to the formula $2m(e)[m(G) - m(e)]$. All three approaches lead to the same set of unscaled ring-currents, shown inset. (Scaled ring currents are obtained on division by $m(G)[m(G) - 1] = 20$).

(a)

(b)
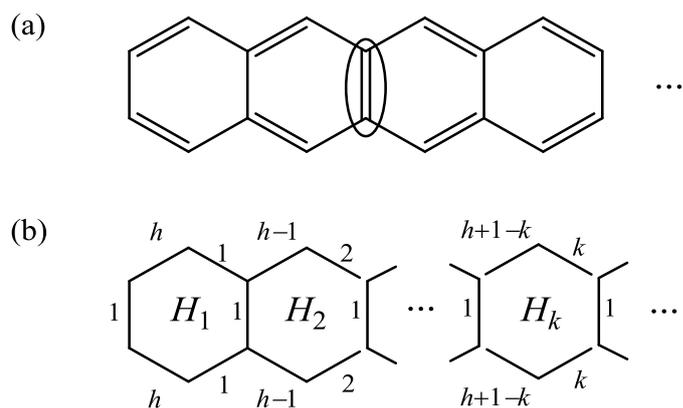
Figure 4. Matching-number calculation for Randić ring currents in linear polyacenes. Hexagonal rings H_k are indexed with $k = 1, 2, \ldots$, starting from the leftmost ring. (a) A double bond in any 'vertical' position (ringed) forces the whole perfect matching, implying matching number 1 for every vertical edge; (b) Matching numbers for all perimeter edges follow from the vertex sum rule, beginning from a terminal vertical edge.
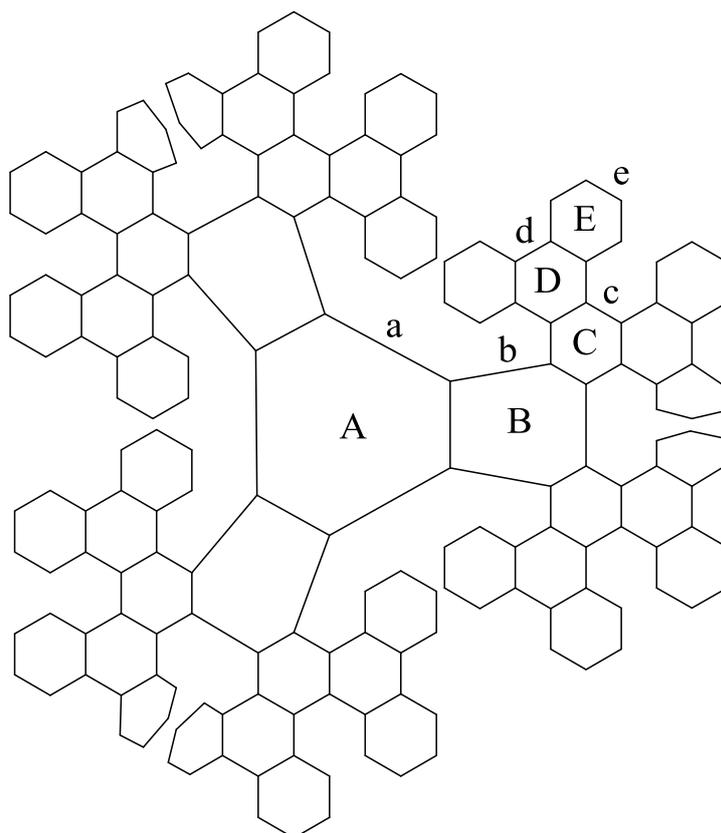
Figure 5. Schematic carbon skeleton of a benzenoid $C_{182}H_{96}$ with the maximum number of Kekulé structures for 46 hexagonal rings.[26] Matching numbers and Pauling bond orders for the perimeter edges a to e, are: (a) 4750104241, 0.2792113974, (b) 3323522500, 0.1953568416 (c) 5342068432, 0.3140070862; (d) 2334100885, 0.1371985828 (e) 7339235986, 0.4314007086. The derived scaled Randić ring currents for rings A to E are: (A) 0.402504786; (B) 0.314385092; (C) 0.430813272; (D) 0.236750263; (E) 0.490588274.

1: 1.2.25 = 50   **2**: 2.2.9 = 24   **3**: 3.2.4.= 24

4: 4.2.1 = 8   **5**: 5.2.1.= 10   **6**: 1.2.4 = 8

7: 5.2.1 = 10   **8**: 4.2.1 = 8   **9**: 1.2.1 = 2

10: 3.2.1 = 6   **11**: 2.2.1 = 4   **12**: 1.2.1 = 2
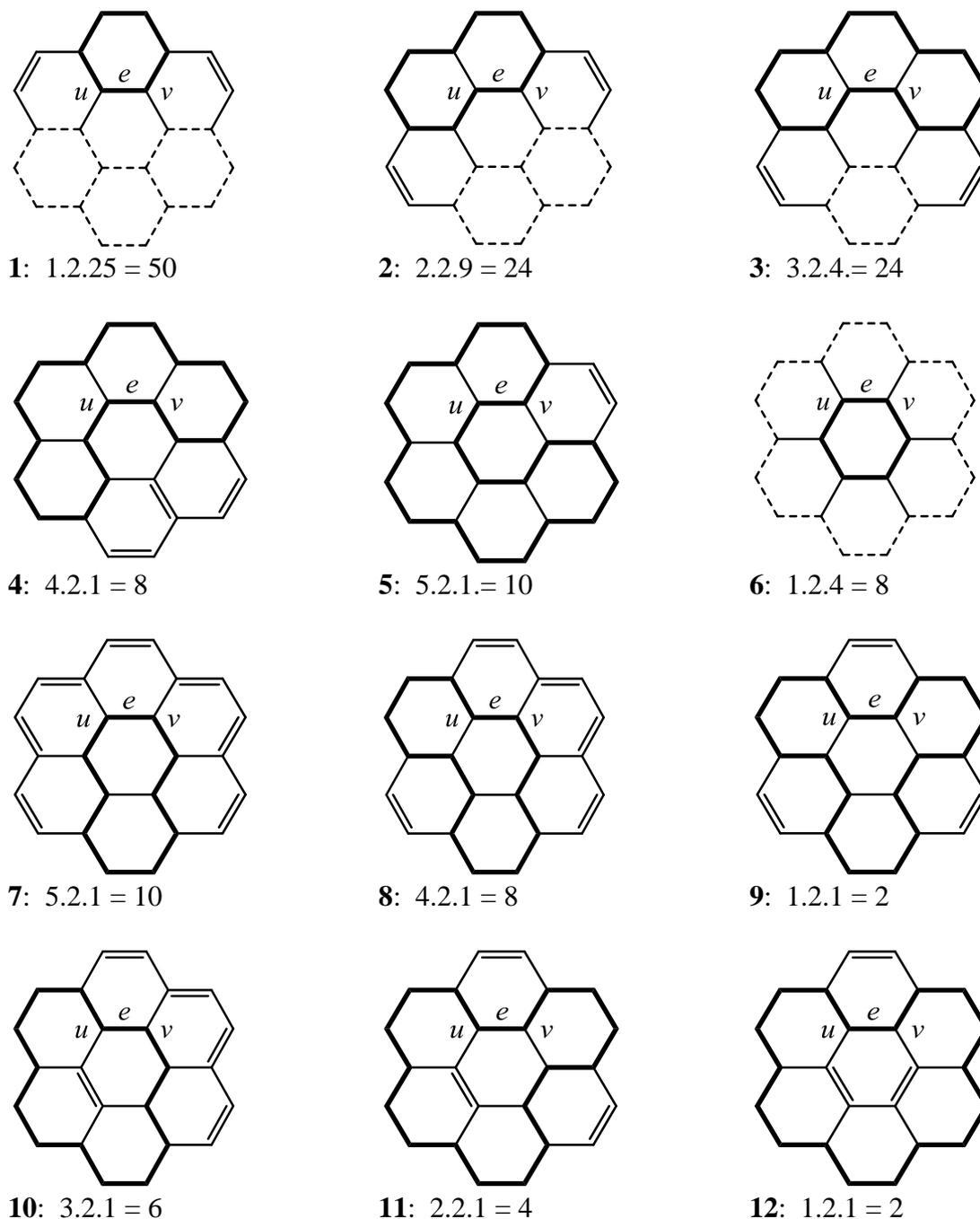
Figure 6. Calculation of the unscaled current map of coronene in the Randić CC model. Perimeter ring currents follow from bond orders and are diatropic of strength 168. Currents along edge e, the top edge of the central hexagon, are calculated using Eq. (1). For the representative cycle, shown in bold, the contribution to current along e is the product $\alpha\beta\gamma$, where α is the number of times e occurs in the set of isomorphic copies of the cycle, β is the number of perfect matchings of the cycle (= 2), and γ is the square of the number of perfect matchings of the remainder of the graph. Single and double lines indicate bonds fixed by the conjugated cycle; dotted lines indicate mobile bonds. Cycles 1 to 5 contribute left-right current in e, but 6 to 12 contribute right-left current. Net bond currents in the central ring flow clockwise u to v, but ring current in the central ring is diatropic (of strength 80).
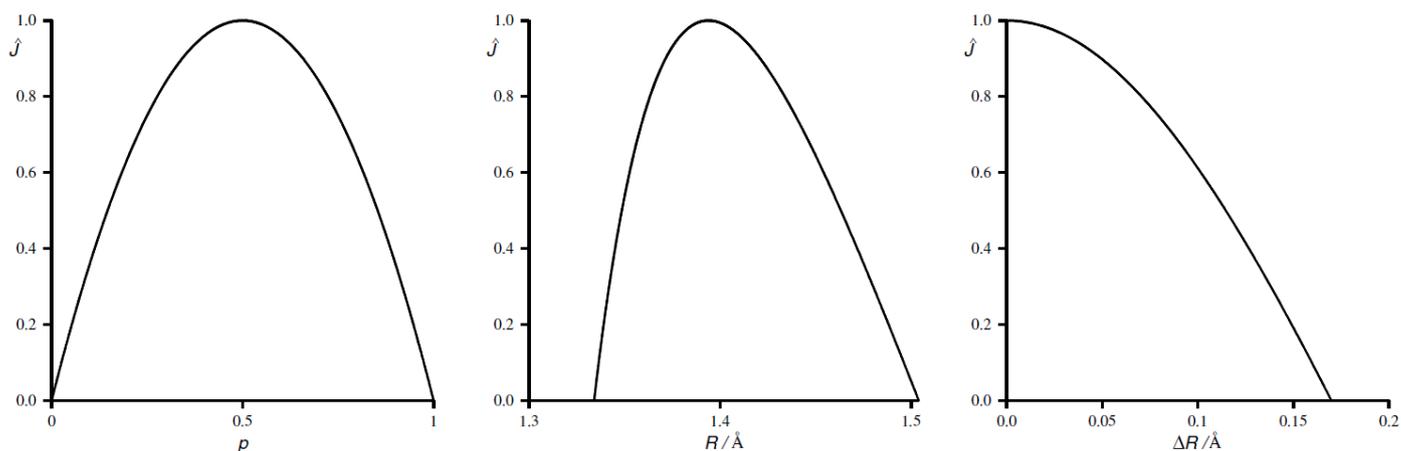
Figure 7. Perimeter current through a degree-two vertex in a benzenoid. All three plots show $\hat{J}$, the fraction of the maximum possible current for a given total number of Kekulé structures. In (a), $\hat{J}$ is shown as a function of Pauling Bond Order p and horizontal tie lines would connect the complementary bond orders $p_a = p$ and $p_b = 1 - p$ for the two bonds incident to the vertex, corresponding to a given current. In (b), $\hat{J}$ is transformed to a function of bond length R, and horizontal tie lines would connect the two bond lengths R_a and R_b predicted by the Pauling equation (12) for the given p_a and p_b. In (c), $\hat{J}$ is shown as a function of the difference $\Delta R = |R_a - R_b|$. All bond lengths are in Å units. Current is maximised for $p = 1/2$, $R \approx 1.4$ Å and $\Delta R = 0$.

Graphical Abstract
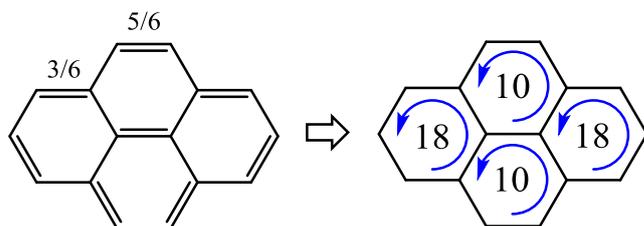
Benzenoid perimeter currents within the Randić
conjugated-circuit model follow directly from
a simple calculation of Pauling Bond Orders and
Kekulé count.