

A combinatorial/geometric analysis of parallelogram-like benzenoids

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Abstract We recently reported an algorithm to count Kekulé (resonance) structures for convex cyclofusenes using a combinatorial/geometric approach. Previously, we presented an algorithm for counting resonance structures for parallelogram-like benzenoids with holes by counting descending paths using rectangular meshes with holes. In this article, we employ a similar combinatorial/geometric approach to determine algorithms that will facilitate counting of the resonance structures in parallelogram-like benzenoids with no holes.

Keywords Kekulé structures · Parallelogram-like benzenoid · Combinatorial/geometric approach

1 Introduction

We discuss a class of polycyclic aromatic hydrocarbons termed *parallelogram-like benzenoids*. Figure 1 depicts a parallelogram-like benzenoid.

We have previously described an algorithm for counting the number of configurations of π -bonds (Kekulé or resonance structures) for parallelogram-like benzenoids with parallelogram-like holes by counting descending paths in a corresponding rectangular mesh with rectangular holes [1]. Using a combinatorial/geometric approach, we

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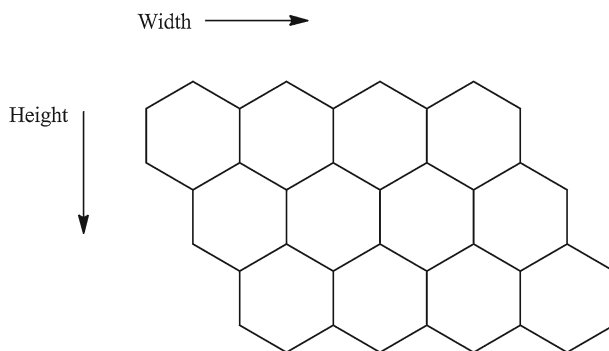


Fig. 1 A parallelogram-like benzenoid

recently reported an algorithm to count resonance structures for convex cyclofusenes [2]. We defined a *convex cyclofusene* as a special type of coronafusene [3] in which each hexacycle shares exactly two non-adjacent edges with its neighboring hexacycles [4–6]. We also defined multiply-connected *monolayered* cyclofusene (MMC) as a fused hexacyclic system with at least two interior regions called holes [7], and multiply-connected *bilayered* cyclofusene (MBC) as a structure derived from an MMC by replacing each layer of hexacycles by two layers [8].

The number of resonance structures in the coronoid hydrocarbons which we termed cyclofusene [4] has long been established [9–11]. Gordon and Davison's algorithm graphically illustrated the Kekulé structures for catacondensed polycyclic benzenoids and coronoids [12]. Further refinement of Gordon and Davison's algorithm to include enumeration of Kekulé structures in conjugated hydrocarbons was achieved by Randić [13]. Although there are many algorithms available for counting Kekulé structures in polycyclic benzenoids, our analysis using the combinatorial approach [2] most closely resembled the work of Balaban and Randić on partitioning of π -electrons in rings of polycyclic benzenoid hydrocarbons [14]. Rispoli solved the parallelogram with a clever induction argument [15]. Induction proofs do not shed light on the methods of reasoning employed in obtaining the results. We address this issue with a combinatorial approach that leads to the solution.

In this article, we use a combinatorial/geometric approach similar to that of Balaban and Randić [14] in order to determine algorithms that will facilitate counting of the resonance structures in parallelogram-like benzenoid with no holes such as Fig. 1.

2 Parallelogram-like benzenoids

We turn our attention to a class of polycyclic aromatic hydrocarbons termed *parallelogram-like benzenoids*. Figure 1 depicts such a molecule. Each row has the same number of hexacycles, and the same goes for the columns. For each parallelogram-like benzenoid, the height of the molecule is the number of hexacycles in each column and the width of the molecule is one more than the number of hexacycles in each row. For the parallelogram-like benzenoid in Fig. 1, the height is three and the width is five.

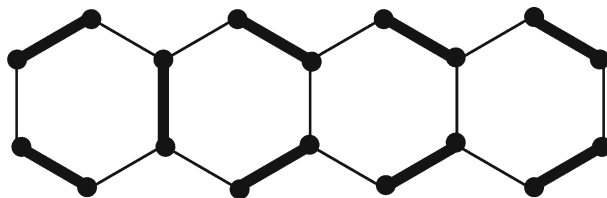


Fig. 2 One vertical π -bond per row

Fig. 3 Vertical π -bonds must descend to the right

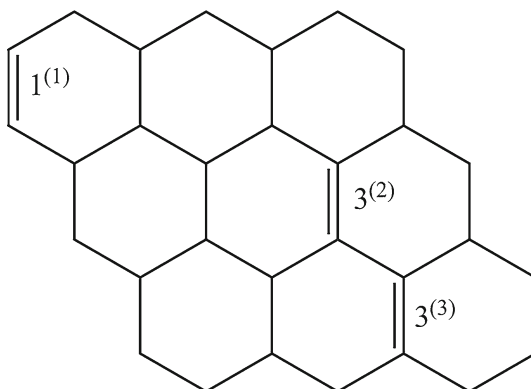
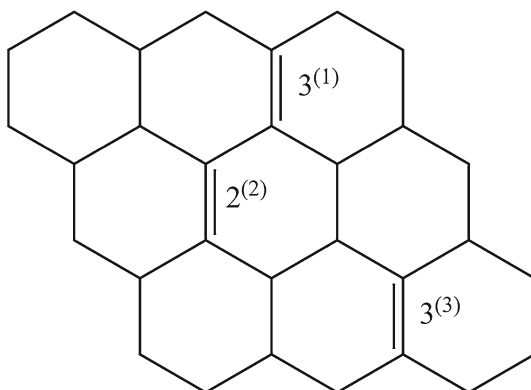


Fig. 4 Principle 2 is violated



We derive the equation for the number of viable resonance structures in a parallelogram-like benzenoid. There are three important principles.

1. Each row must contain exactly one vertical π -bond (Fig. 2).
2. The π -bond occupying the k th rung in the j th row is denoted $k^{(j)}$ as shown in Fig. 3. As we descend from any given row to the next, the vertical π -bonds must cascade to the right, that is, as j increases, k must be *non-decreasing*. On the other hand, Fig. 4 shows a non-viable resonance structure since it contains the π -bonds $3^{(1)}$ and $2^{(2)}$. If one were to attempt to complete the distribution of π -bonds in the molecule, the attempt would fail.

Fig. 5 Complete π -bond distribution for Fig. 4

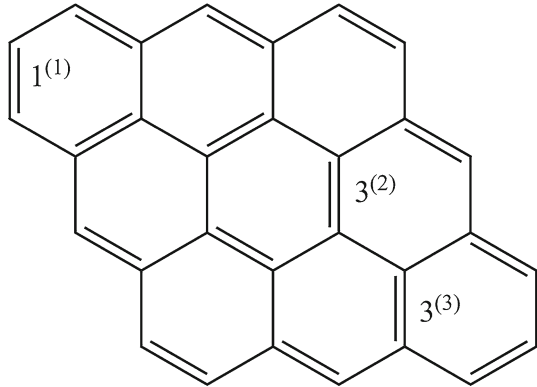
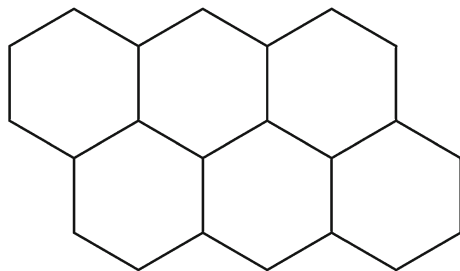


Fig. 6 A parallelogram-like benzenoid with $h = 2$ and $n = 4$



3. The positions of the vertical π -bonds in a parallelogram-like benzenoid determine the distribution of the remaining π -bonds, as illustrated by Fig. 5.

Parallelogram-like benzenoids of height one are *straight chains*. Since there is only one row, the number of resonance structures equals the number of rungs. In the general case, we denote the number of rungs per row, that is, the *width*, by n and the number of rows, that is, the *height*, by h .

The parallelogram-like benzenoid in Fig. 2 has five rungs, which leaves five possible places for the vertical π -bond. According to Principle 3, the placement of the vertical π -bond determines the remaining distribution of π -bonds. Since there are five rungs, the number of resonance structures in Fig. 2 is 5. More generally, the number of resonance structures of a parallelogram-like benzenoid with $h = 1$ is n .

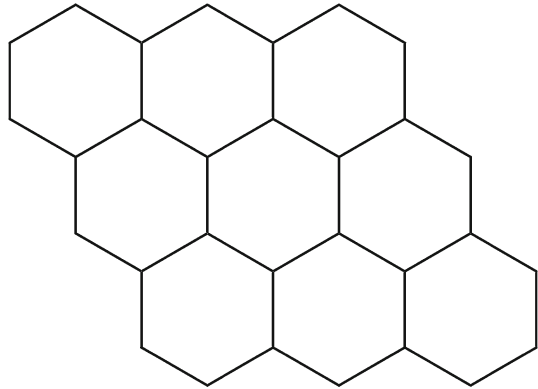
We denote the number of resonance structures of a parallelogram-like benzenoid with height h and width n by $f(n, h)$. Thus we have

$$f(n, 1) = n = \binom{n}{1}$$

Figure 6 shows a parallelogram-like benzenoid with $h = 2$ and $n = 4$. If one selects $1^{(1)}$ for the placement of a π -bond, there are four possible places for the π -bond in row 2. If one selects $2^{(1)}$, there are three choices for placement of the π -bond in row 2. Selecting $3^{(1)}$, yields two choices in row 2. Finally, if one selects $4^{(1)}$, there is only

Table 1 Values of $f(n, 2)$ as n increases from 2 to 8

n	$f(n, 2)$
2	3
3	6
4	10
5	15
6	21
7	28
8	36

Fig. 7 A parallelogram-like benzenoid with $h = 3$ and $n = 4$ **Table 2** Values of $f(n, 3)$ as n increases from 2 to 7

n	$f(n, 3)$
2	4
3	10
4	20
5	35
6	56
7	84

one choice in row 2. It follows that there are $4 + 3 + 2 + 1 = 10$ resonance structures for the parallelogram-like benzenoid shown in Fig. 6.

Table 1 lists $f(n, 2)$ as n increases from 2 to 8.

The numbers in the right column are the triangular numbers, so we have

$$f(n, 2) = \frac{n(n+1)}{2} = \binom{n+1}{2} \quad (1)$$

We move on to $h = 3$ (Fig. 7). Table 2 lists $f(n, 3)$ as n increases from 2 to 7.

The numbers in the right column are *pyramidal* (that is, sums of consecutive triangular numbers beginning with 1), so we have

$$f(n, 3) = \frac{n(n+1)(n+2)}{6} = \binom{n+2}{3} \quad (2)$$

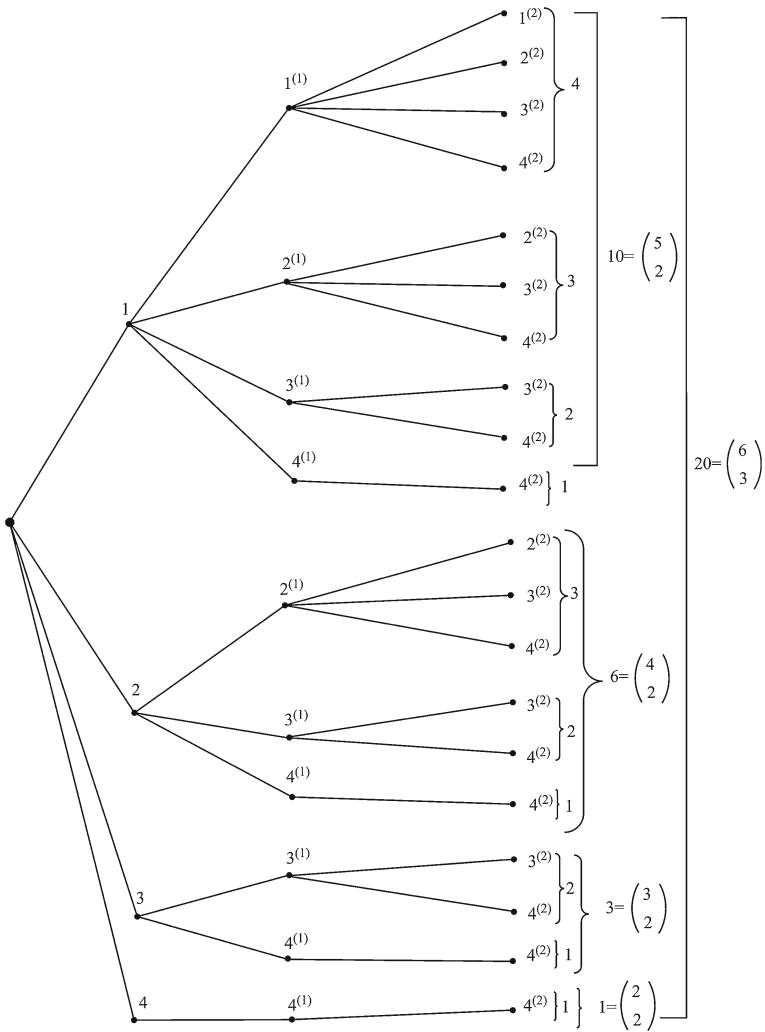


Fig. 8 Decision tree

The formulas for $f(n, h)$ for $h = 1, 2,$ and $3,$ suggest the following general formula

$$f(n, h) = \binom{n + h - 1}{h} \tag{3}$$

which a glance at the decision tree of Fig. 8 confirms. We simplify (3) by substituting m for $n - 1,$ m being the number of cycles in each row, obtaining

$$f(m, h) = \binom{m + h}{h} \tag{4}$$

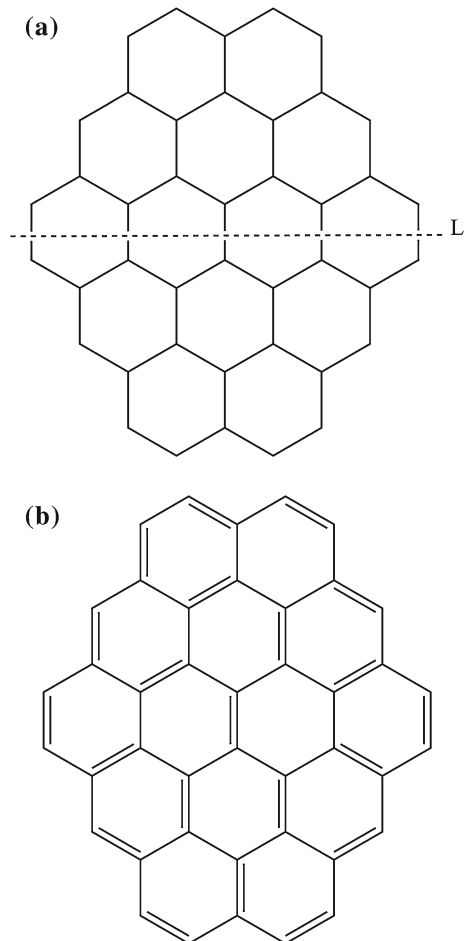
in accordance with Rispoli’s result [15].

3 Diminished parallelogram-like benzenoids

In a *diminished parallelogram-like benzenoid*, the first row has more than one hexacycle, and each successive row increases its length by one hexacycle until the middle (longest) row. The subsequent rows decrease by one hexacycle until the last row, which has as many hexacycles as the first row. Figure 9a yields an example of a diminished parallelogram-like benzenoid. Let k denote the number of vertical bonds in the first row, and let n denote the number of vertical bonds in the middle (longest) row. Note that k and n determine the entire molecule. In Fig. 9a, for example, $k = 3$ and $n = 5$.

Note the line of symmetry, L , bisecting the molecule into mirror images. The distribution of π -bonds in a benzenoid corresponds to a perfect matching in its graph, the latter being equitable bipartite. That is, one can color each vertex either black or white and adjacencies link vertices of opposite color. The “equitable” indicates that the two color sets have the same cardinality. The following theorem asserts this.

Fig. 9 **a** Diminished parallelogram-like benzenoid.
b A distribution of π -bonds for the molecule in Fig. 9a



Theorem Given a bipartite graph, G , such that there is a line of symmetry, L , which only intersects edges, then G is equitable.

Proof If one colors the vertices above the line of symmetry, L , the corresponding vertices below the line of symmetry will be oppositely colored, from which equitability follows.

The number of vertical π -bonds in each row of the molecule starts at 1 for the first (top) row and increments by 1 until we reach the middle row, after which the count decreases by one π -bond in each row until the final row is reached with one vertical π -bond. In Fig. 9b, for example, there is one vertical π -bond in the first row, two in the second, three in the third, two in the fourth, and one in the fifth row. \square

Theorem The number of vertical π -bonds in the molecule is the square of the number of vertical π -bonds in the middle row.

Proof The theorem follows by showing that

$$1 + 2 + 3 + \cdots + n + (n - 1) + (n - 2) + \cdots + 3 + 2 + 1 = n^2$$

Observe that

$$\begin{aligned} 1 + 2 + 3 + \cdots + n + (n - 1) + (n - 2) + \cdots + 3 + 2 + 1 &= \\ [1 + 2 + 3 + \cdots + n] + [(n - 1) + (n - 2) + \cdots + 3 + 2 + 1] &= \\ = \frac{n(n + 1)}{2} + \frac{n(n - 1)}{2} = n^2 \end{aligned}$$

Figure 9b, for example, yields $1 + 2 + 3 + 2 + 1 = 3^2 = 9$

In assigning the vertical π -bonds, the π -bond distribution in any row must interlace with the π -bond distribution(s) in the above and/or lower row. \square

The diminished parallelogram-like benzenoid depicted in Fig. 10a, for example, has $k = 3$ and $n = 4$. As the rows descend from the top the number of vertical π -bonds increases from one to two and then decreases back to one.

This problem is initially solved by placing the vertical π -bonds in the middle row, and then the number of possible π -bond placements in the entire molecule is counted. In Fig. 10a, there are six ways to select exactly two vertical π -bonds in the middle row. The number of resonance structures for each of the six cases will be counted, and the sum of these numbers will yield the number of resonance structures for the molecule shown in Fig. 10a. Since Fig. 10a is symmetrical, there will be mirror images in two of the six cases for placement of the middle-row π -bonds. For simplicity, one of each mirror image is counted and the result is doubled. Figure 10b–e depict the four arrangements of the middle row π -bonds from which the final count is obtained. The remaining π -bonds in the molecule are omitted for simplicity.

Arrangements I and II (Fig. 10b, c) have mirror images. The number of total resonance structures is doubled.

A glance at arrangement I (Fig. 10b) shows that the vertical π -bonds in the middle row are consecutive. This leaves only one way to distribute the vertical π -bonds in the

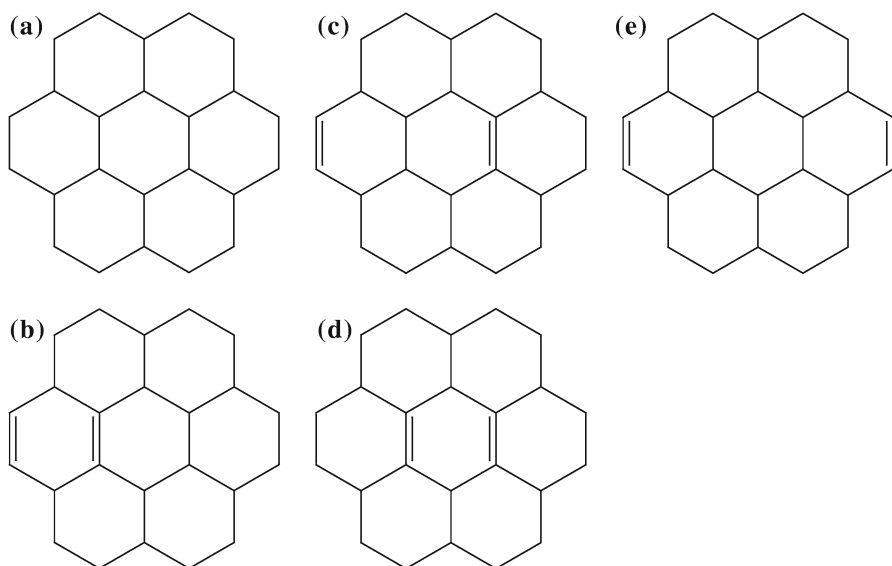


Fig. 10 **a** Diminished parallelogram-like benzenoid, $k = 3$ and $n = 2$. **b** Arrangement I. **c** Arrangement II. **d** Arrangement III. **e** Arrangement IV

top and bottom rows, in which case, the number of resonance structures is one. Since this has a mirror image for the molecule it is counted twice, yielding two.

Arrangement II (Fig. 10c) is more complicated because of the top and bottom rows. Since there are two choices for vertical π -bond placement in the top row, and two in the bottom row, there are four ways to place one vertical π -bond in the top row and one in the bottom. Since Arrangement II has a mirror image, the four is doubled, yielding eight possible resonance structures for Arrangement II.

Arrangement III (Fig. 10d) is much like Arrangement I since the two vertical π -bonds in the middle row are consecutive. This leaves only one choice for the vertical π -bonds in the top and bottom row. Arrangement III adds one to the total.

Arrangement IV (Fig. 10e) leaves us with the most options for π -bond placement. The vertical π -bonds in the middle row facilitate three choices for the top and bottom rows. Since one vertical rung out of three rungs in each of the top and bottom rows must be selected, nine possible configurations of π -bonds in Fig. 10e are obtained.

Addition of the subtotals yields the number of resonance structures for the molecule, that is, $2 + 8 + 1 + 9 = 20$.

4 Conclusion

As mentioned earlier, Rispoli used an induction argument to prove his resonance structure counts in parallelogram-like benzenoids [15]. We devised an algorithm that facilitates resonance structure counts for this type of molecule with a combinatorial approach. We extended this analysis to diminished parallelogram-like benzenoids.

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