

## A combinatorial/geometric analysis of convex cyclofusene

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**Abstract** Previously, we presented an algorithm for counting Kekulé structures for parallelogram-like benzenoids with holes by counting descending paths using rectangular meshes with holes. In this article, we describe an algorithm to count Kekulé structures for convex cyclofusenes using a combinatorial/geometric approach.

**Keywords** Kekulé structures · Convex cyclofusene · Combinatorial/geometric

We defined a *convex cyclofusene* as a special type of coronafusene [1] in which each hexacycle shares exactly two non-adjacent edges with its neighboring hexacycles [2–4]. We also defined multiply-connected *monolayered* cyclofusene (*MMC*) as a fused hexacyclic system with at least two interior regions called holes [5], and multiply-connected *bilayered* cyclofusene (*MBC*) as a structure derived from an *MMC* by replacing each layer of hexacycles by two layers [6]. We recently presented an algorithm for counting the number of configuration of  $\pi$ -bonds (Kekulé structures) for parallelogram-like benzenoids with parallelogram-like holes by counting descending paths in a corresponding rectangular mesh with rectangular holes [7].

The number of resonance structures in the coronoid hydrocarbons which we termed cyclofusene [2] is well established [8–10]. Kekulé structures for catacondensed polycyclic benzenoids and coronoids can be obtained graphically by the use of Gordon and Davison's algorithm [11]. Further refinement of the Gordon and Davison's algorithm

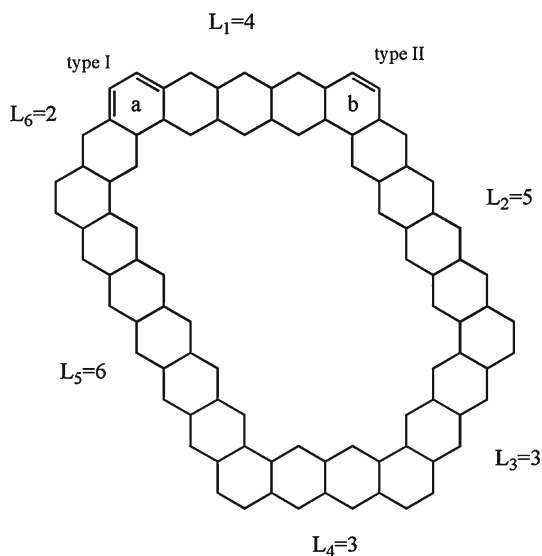
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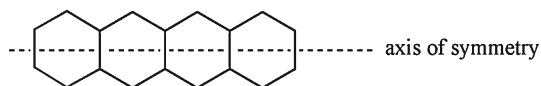
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**Fig. 1** Pivot cycle  $a$  is type I, while pivot cycle  $b$  is type II



**Fig. 2** A chain of four hexacycles with five rungs crossing its axis of symmetry



to include enumeration of Kekulé structures in conjugated hydrocarbons was achieved by Randić [12]. Although there are many algorithms available for counting Kekulé structures in polycyclic benzenoids, our analysis most closely resembles the work of Balaban and Randić on partitioning of  $\pi$ -electrons in rings of polycyclic benzenoid hydrocarbons [13].

A *pivot cycle* in a convex cyclofusene has three edges on the outer boundary and, therefore, exactly one edge on the inner boundary. There are six pivot cycles provided the molecule is convex [2–4]. Let  $L_i$ ,  $i = 1, 2, \dots, 6$ , be one less than the number of hexacycles in the  $i$ -th linear chain (Fig. 1).

Given a distribution of  $\pi$ -bonds, a pivot cycle is classified as follows (Fig. 1)

1. A type I pivot cycle (see cycle  $a$ ) has two  $\pi$ -bonds on the outer boundary.
2. A type II pivot cycle (see cycle  $b$ ) has exactly one  $\pi$ -bond (the middle edge) on the outer boundary.

The edges of a linear chain that cross its axis of symmetry shall be called *rungs* (Fig. 2). Since a linear chain of hexacycles has exactly one  $\pi$ -bond rung [2], we have the following lemma:

**Lemma 1** *The neighboring pivot cycles of a type I pivot cycle must be type II.*

*Proof* The two “outer”  $\pi$ -bond edges on the type I pivot cycle are rungs of the two linear chains to which the given type I pivot cycle belongs. Since a linear chain has

exactly one  $\pi$ -bond rung, the neighboring pivot cycles of these chains must be type II.  $\square$

In light of Lemma 1, the distribution of type I and II pivot cycles must fall into exactly one of the following four cases:

Case 1: There are three type I and three type II pivot cycles.

Case 2: There are two type I and four type II pivot cycles.

Case 3: There is one type I and five type II pivot cycles.

Case 4: All six of the pivot cycles are type II pivot cycles.

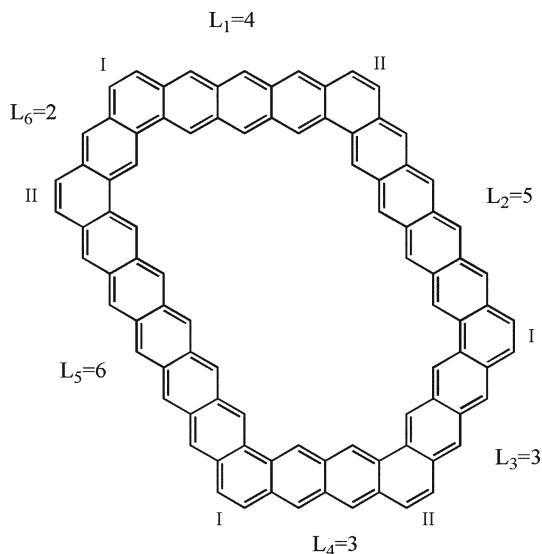
One deduces further that each case may have subcases.

Case 1 has two subcases, depending on the locations of the alternating type I/type II pivot cycles. By Lemma 1, each linear chain has exactly one  $\pi$ -bond rung in its type I pivot cycle (Fig. 3), from which it follows that there are no shared  $\pi$ -bonds (that is,  $\pi$ -bonds shared by two hexacycles). Then for each of the two there are two valid alternating sequences of  $\pi$ -bonds for the interior cycle of the molecule, thereby yielding a total of four configurations for Case 1.

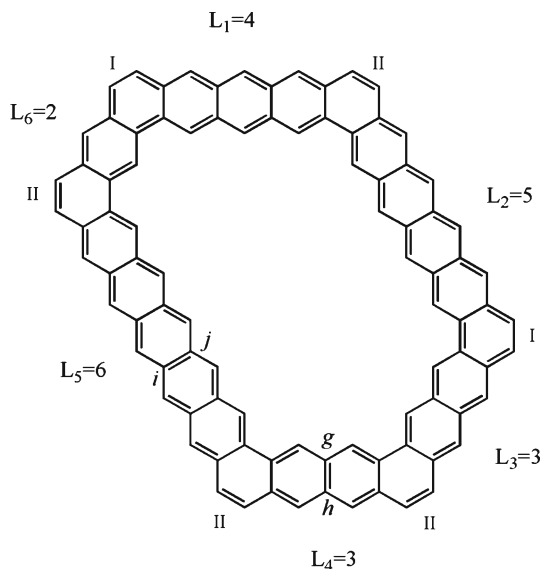
Case 2 has two subcases and a total of nine kinds of configurations, each of which must be counted using the  $L_i$ 's. (This counting using the  $L_i$ 's will occur in all remaining cases due to the possible locations of shared  $\pi$ -bond rungs.)

Case 2a: The two type I pivot cycles share a common type II pivot cycle neighbor. This enables six configurations, depending on the six different possible locations for the common type II pivot cycle. Focusing on the configuration of Fig. 4, there are  $L_5 = 6$  choices for the shared  $\pi$ -bond rung  $ij$  and  $L_4 = 3$  choices for the shared  $\pi$ -bond rung  $gh$ , yielding a total of  $L_5 L_4 = 18$  configurations for the molecule in that figure. Adding this kind of product for all six configurations for Case 2a yields  $\sum_{i=1}^6 L_i L_{i+1}$ , where the indices belong to the complete set of residues  $\{1, 2, 3, 4, 5, 6\} \pmod 6$ . (We adhere to this set of residues in the remaining cases.)

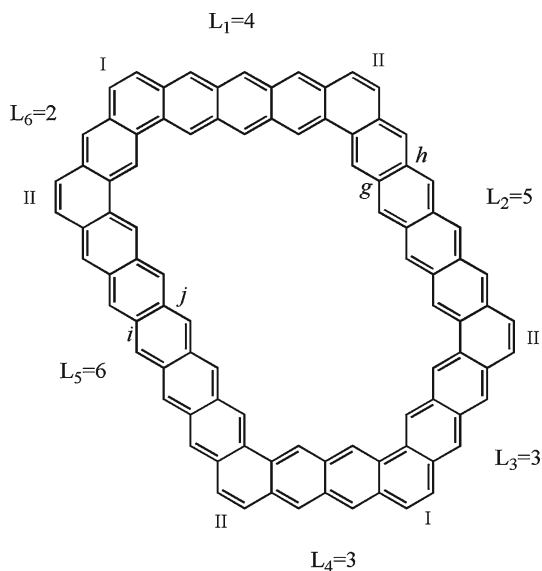
**Fig. 3** Case 1: There are no shared  $\pi$ -bonds



**Fig. 4** Case 2A:  $\pi$ -bonds  $gh$  and  $ij$  are the chosen  $\pi$ -bond rungs in their respective linear chains

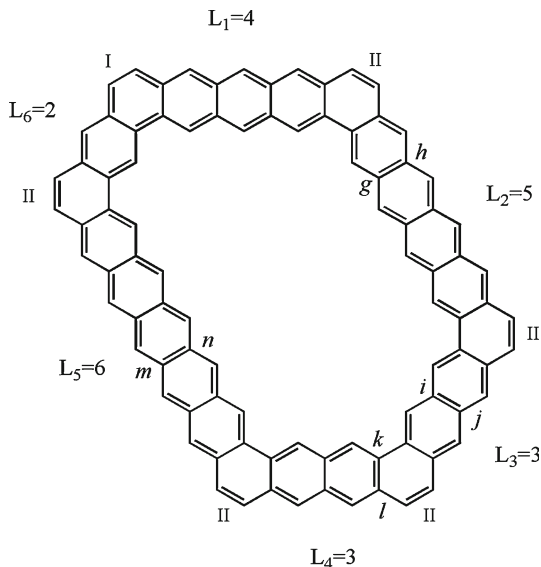


**Fig. 5** Case 2b:  $\pi$ -bonds  $gh$  and  $ij$  are the chosen  $\pi$ -bond rungs in their respective linear chains



Case 2b: The two type I pivot cycles are antipodal. This clearly enables three configurations, depending on the three different possible locations of the pair of antipodal type I cycles. Focusing on the configuration of Fig. 5, there are  $L_2 = 5$  choices for the shared  $\pi$ -bond rung  $gh$  and  $L_5 = 6$  choices for the shared  $\pi$ -bond rung  $ij$ , yielding a total of  $L_2 L_5 = 30$  configurations for molecule in that figure. Adding this kind of product for all three configurations for Case 2b yields  $\sum_{i=1}^3 L_i L_{i+3}$ .

**Fig. 6** Case 3:  $\pi$ -bonds  $gh$ ,  $ij$ ,  $kl$ , and  $mn$  are the chosen  $\pi$ -bond rungs in their respective linear chains



Case 3: There are six configurations depending on the placement of the sole type I pivot cycle. Focusing on the configuration of Fig. 6, there are  $L_2 = 5$  choices for the shared  $\pi$ -bond rung  $gh$ ,  $L_3 = 3$  choices for the shared  $\pi$ -bond rung  $ij$ ,  $L_4 = 3$  choices for the shared  $\pi$ -bond rung  $kl$ ,  $L_5 = 6$  choices for the shared  $\pi$ -bond rung  $mn$ , yielding a total of  $L_2L_3L_4L_5 = 270$  configurations for molecule in that figure. Adding this kind of product for all six configurations for Case 3 yields  $\sum_{i=1}^6 L_i L_{i+1} L_{i+2} L_{i+3}$ .

Case 4 requires no subcases as there is only one distribution of the six type II pivot cycles. As there is exactly one shared  $\pi$ -bond rung in each linear chain (Fig. 7), this can be done in  $\prod_{i=1}^6 L_i$  ways.

As a result of the above calculations, we have obtained a 6th degree polynomial in the  $L_i$ 's that yields the total number of distributions of  $\pi$ -bonds in a convex cyclofusene. We have proven the following theorem.

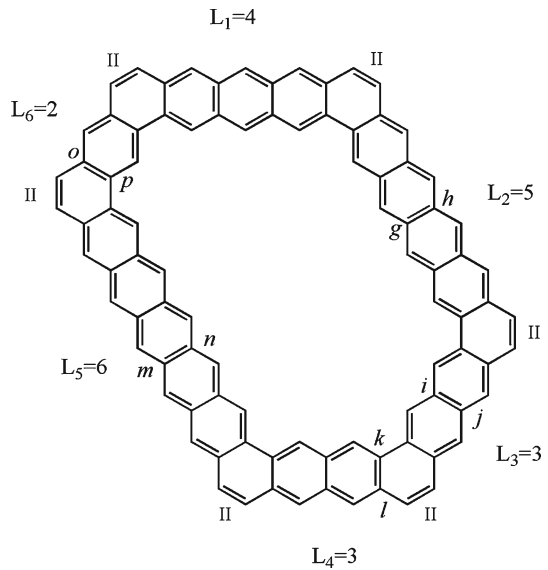
**Theorem 1** Given a convex cyclofusene whose linear chains are described as above by the vector  $(L_1, L_2, \dots, L_6)$ , the total number of distributions of  $\pi$ -bonds is given by:

$$4 + \sum_{i=1}^6 L_i L_{i+1} + \sum_{i=1}^3 L_i L_{i+3} + \sum_{i=1}^6 L_i L_{i+1} L_{i+2} L_{i+3} + \prod_{i=1}^6 L_i.$$

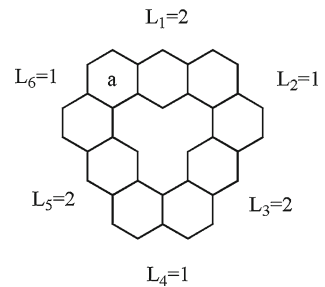
We illustrate the above theorem using the cyclofusene of Fig. 8 for which the  $L_i$ 's are 2, 1, 2, 1, 2, 1. The formula of the theorem yields  $4 + 6 \times 2 + 3 \times 2 + 6 \times 4 + 8 = 54$  which is in agreement with the result in [13] using the Randić algorithm.

For the special case in which the  $L_i$ 's are equal, that is,  $L_i = k$  for  $i = 1, 2, \dots, 6$ , and a given integer  $k$ , we obtain the 6th degree polynomial  $f(k) = k^6 + 6k^4 + 9k^2 + 4$ .

**Fig. 7** Case 4:  $\pi$ -bonds  $gh$ ,  $ij$ ,  $kl$ ,  $mn$ , and  $op$  are the chosen  $\pi$ -bond rungs in their respective linear chains



**Fig. 8** Cyclofusene for which the  $L_i$ 's are 2, 1, 2, 1, 2, 1



Thus, for example, the number of Kekulé structures for coronene [14, 15] is  $f(1) = 20$ , as can be confirmed using the Randić algorithm [13].

### Relations among the $L_i$

The following lemma is easily verified using hexacyclic graph paper. We state it without proof.

**Lemma 2** *Given a convex cyclofusene, the  $L_i$ ,  $i = 1, 2, \dots, 6$ , associated with it satisfy the three relationships  $L_i + L_{i+1} = L_{i+3} + L_{i+4}$ ,  $i = 1, 2$ , and 3, where the indices belong to the complete set of residues  $\{1, 2, 3, 4, 5, 6\} \bmod 6$ .*

Observe that the equation for the case  $i = 3$  may be obtained by taking the difference of the equations of the first two cases.

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