

# Resonance structure counts in contorted and flat hexabenzocoronenes

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**Abstract** In several articles we have reported algorithms to count resonance structures for convex cyclofusenes and parallelogram-like benzenoids with and without holes using a combinatorial/geometric approach. In this article, using the same approach we report algorithms that facilitate resonance structure counts in both contorted and flat hexabenzocoronene.

**Keywords** Parallelogram-like benzenoid · Combinatorial/geometric approach · Hexabenzocoronene · Aromatic sextets

## 1 Introduction

We recently employed an algorithm to analyze the number of configuration of  $\pi$ -bonds (Kekulé or resonance structures) for parallelogram-like benzenoids with no holes [1]. In another article, we described an algorithm for counting the number of configuration of  $\pi$ -bonds for parallelogram-like benzenoids with parallelogram-like holes by counting descending paths in a corresponding rectangular mesh with rectangular holes [2]. Using a combinatorial/geometric approach, we reported an algorithm to count resonance structures for convex cyclofusenes [3].

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The number of resonance structures in the coronoid hydrocarbons which we termed cyclofusene [4] has long been established [5–7]. Gordon and Davison's algorithm graphically illustrated the Kekulé structures for catacondensed polycyclic benzenoids and coronoids [8]. Further refinement of Gordon and Davison's algorithm to include enumeration of Kekulé structures in conjugated hydrocarbons was achieved by Randić [9]. Using a combinatorial/geometric approach, similar to the method employed by Balaban and Randić [10] and us [3], we devise an algorithm to enumerate Kekulé structures for contorted and flat HBCs.

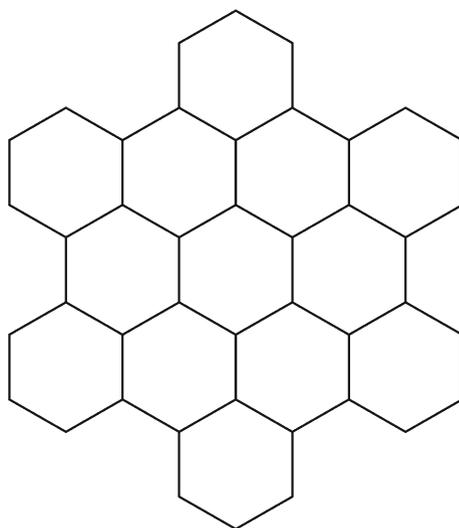
The synthesis of contorted HBC was achieved by Clar [11]. Some of the derivatives of HBC show that the material organizes into molecular stacks which further organize to cables and fibers [12]. The conjugated circuit currents in HBC and its derivatives [13] as well as a graph-theoretical analysis of large benzenoid hydrocarbons have been reported by Randić [14]. An efficient synthesis of flat HBC was reported by Müllen [15–21]. This molecule and its derivatives exhibit self-assembly due to  $\pi$ -stacking and serve as promising organic-based semiconductors in electronics [22,23]. Resonance energies and total resonance structure counts for both molecules described in this article have been noted by Randić [24]. Using our combinatorial approach, we achieve the same numbers of resonance structures for the two molecules mentioned.

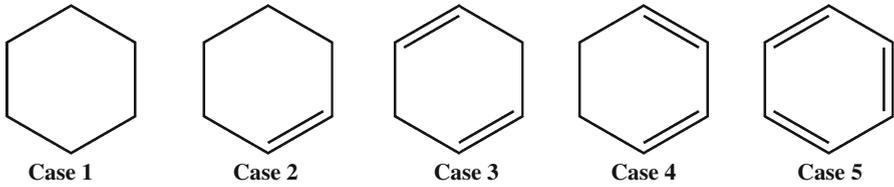
## 2 Flat HBC (FHBC)

We begin counting the resonance structures in FHBC (Fig. 1) by considering the five mutually exclusive and jointly exhaustive cases based on the number of  $\pi$ -bonds in the middle hexacycle, heretofore called the *center cycle* (Fig. 2).

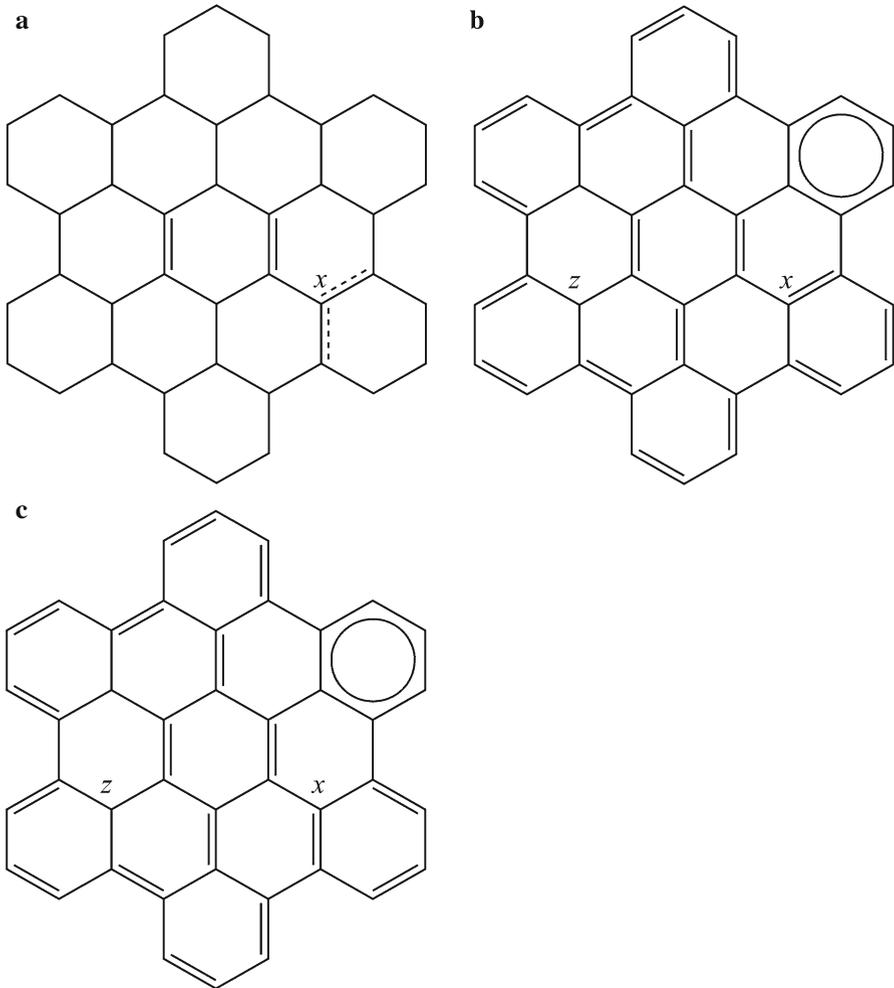
Case 3, involving two non-conjugated  $\pi$ -bonds in the center cycle, yields no resonance structures, which can be seen as follows. The atom  $x$  in Fig. 3a has exactly two

**Fig. 1** Carbon skeleton of flat HBC (FHBC)



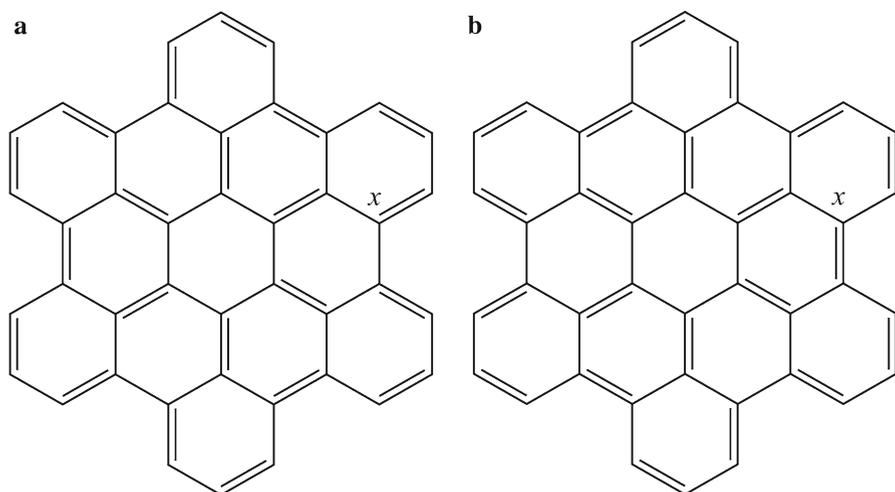


**Fig. 2** Position of  $\pi$ -bonds in the center cycle



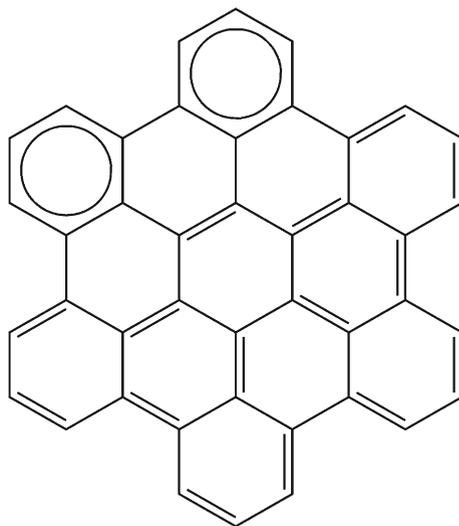
**Fig. 3** a Atom  $x$  has two available edges that can be  $\pi$ -bonds. b One possibility for the atom  $x$ . c The other possibility for the atom  $x$

available edges that can be  $\pi$ -bonds, as shown in Fig. 3b, c. In both cases, we add all the  $\pi$ -bonds that are necessary consequences of these two choices, finally reaching an atom  $z$  that has no  $\pi$ -bonds. This eliminates Case 3.



**Fig. 4** **a** One possibility for atom  $x$ . **b** The other possibility for the atom  $x$

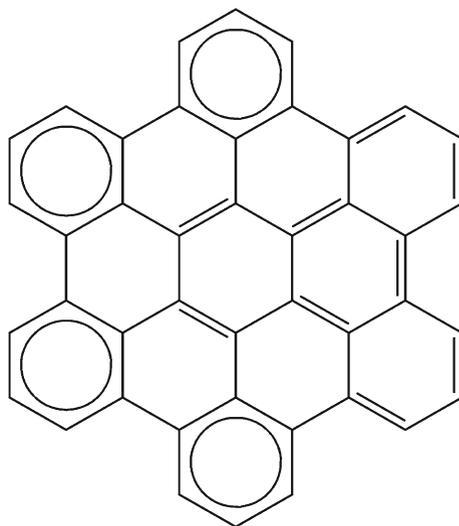
**Fig. 5** Two aromatic sextets in FHBC (One  $\pi$ -bond in the center cycle)



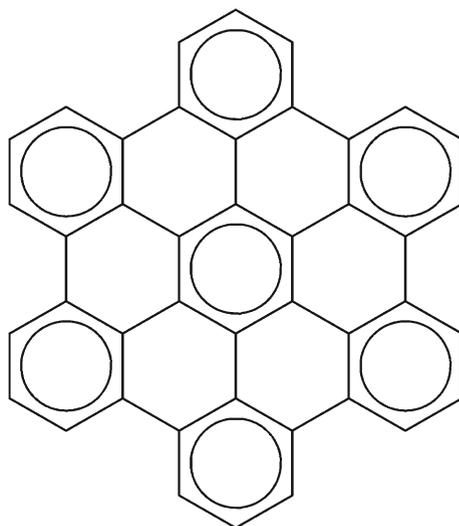
The two subcases for Case 1 are depicted in Fig. 4a, b, each depending on the choice of  $\pi$ -bond involving the atom labeled  $x$ . In both subcases, the remainder of the  $\pi$ -bond distributions is fully determined. Thus Case 1 yields two resonance structures.

Figure 5 depicts the  $2^2$  configurations in Case 2, for each of the six choices of the lone,  $\pi$ -bond in the center cycle. Each such choice creates two “aromatic sextets,” denoted in the figure by circles inside them, to indicate the presence of both Kekulé structures of benzene, bringing the number of resonance structures to  $6 \times 2^2 = 24$ .

**Fig. 6** Four aromatic sextets in FHBC (Two conjugated  $\pi$ -bonds in the center cycle)



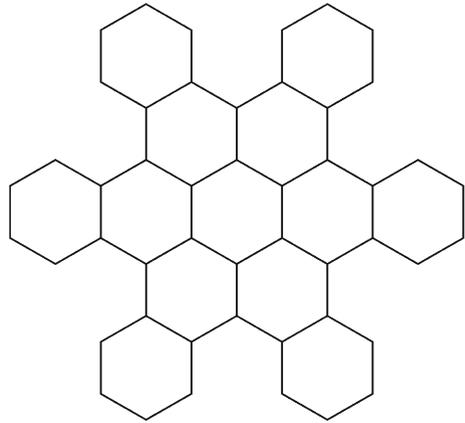
**Fig. 7** Seven aromatic sextets counting the center and peripheral cycles in FHBC



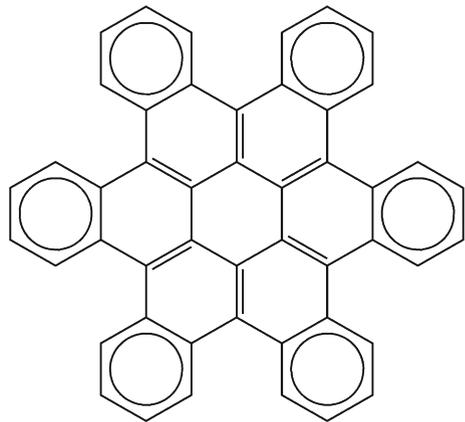
The analysis of Case 4 is similar to that of Case 2 and yields  $6 \times 2^4 = 96$  resonance structures. There are six possibilities for the location of the two conjugated  $\pi$ -bonds in the center cycle (Fig. 6).

Finally, Case 5 depicted in Fig. 7, yields  $2^7 = 128$  resonance structures since there are seven “aromatic sextets”. It follows that flat HBC has  $2 + 24 + 96 + 128 = 250$  resonance structures, in agreement with Randić [24].

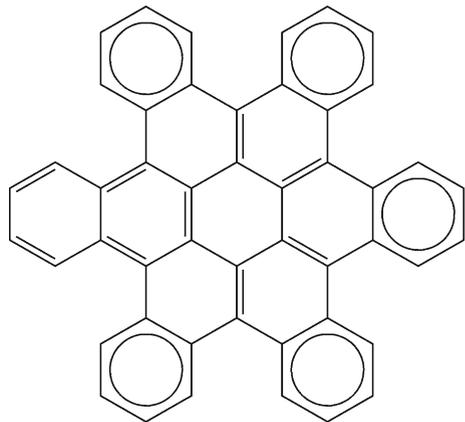
**Fig. 8** Carbon skeleton of contorted HBC (CHBC)



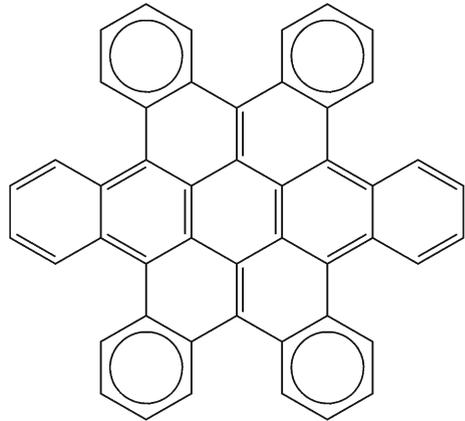
**Fig. 9** Six aromatic sextets in CHBC



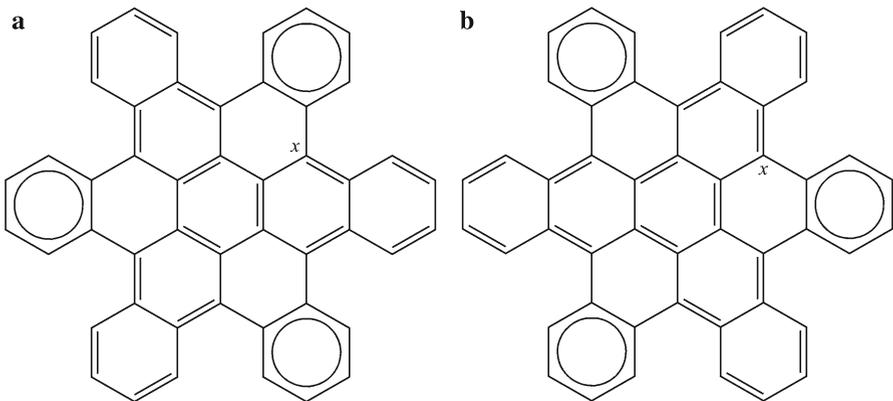
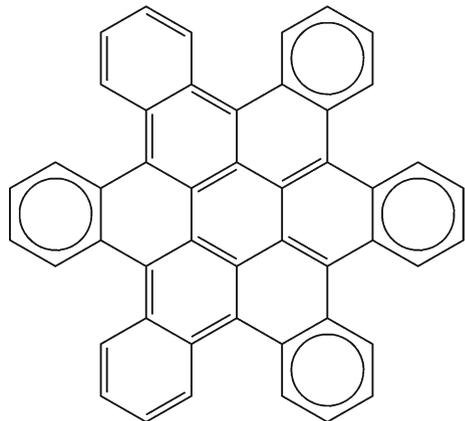
**Fig. 10** Five aromatic sextets in CHBC (One  $\pi$ -bond in the center cycle)



**Fig. 11** Four aromatic sextets in CHBC (Two non-conjugated  $\pi$ -bonds in the center cycle)



**Fig. 12** Four aromatic sextets in CHBC (Two conjugated  $\pi$ -bonds in the center cycle)



**Fig. 13** **a** One possibility for the atom *x*. **b** The other possibility for the atom *x*

### 3 Contorted HBC (CHBC)

To count resonance structures of CHBC depicted in Fig. 8, an analogous procedure is employed. The five cases illustrated in Figs. 9, 10, 11, 12, and 13, depending on the number of  $\pi$ -bonds in the center cycle, are mutually exclusive and jointly exhaustive:

- Case (a): No  $\pi$ -bonds. This yields  $2^6 = 64$  resonance structures (Fig. 9).  
Case (b): One  $\pi$ -bond. This yields  $6 \times 2^5 = 192$  resonance structures (Fig. 10).  
Case (c): Two non-conjugated  $\pi$ -bonds. This yields  $3 \times 2^4 = 48$  resonance structures (Fig. 11).  
Case (d): Two conjugated  $\pi$ -bonds. This yields  $6 \times 2^4 = 96$  resonance structures (Fig. 12).  
Case (e): Having three  $\pi$ -bonds in the center cycle follows the procedure employed in Sect. 2, Case 1. This produces two possibilities for the  $\pi$ -bond involving the atom  $x$ . Each choice implies  $2^3$  configurations for a total of  $2 \times 2^3$ . Since the center cycle has an “aromatic sextet”, this last quantity is doubled, yielding  $2 \times 2^4 = 32$  resonance structures (Fig. 13a, b).

Thus the number of resonance structures of CHBC is 432, once again in agreement with Randić [24].

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