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Number of *Kekulé* Structures for Circumkekulene and Its Homologs

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The symmetry-adapted method of fragmentation is used to derive for the first time the number of *Kekulé* structures for a class of pericondensed coronoids. The systems are regular hexagonal (D_{6h}) and consist of circumkekulene and its homologs.

(Keywords: Kekulé structures, enumeration of; Circumkekulene)

Die Anzahl möglicher Kekulé-Strukturen für Circumkekulen und seine Homologen

Es wurde die symmetrieadaptierte Fragmentierungsmethode benutzt, um erstmals die Anzahl möglicher *Kekulé*-Strukturen für eine Klasse von perikondensierten Coronoiden abzuleiten. Die untersuchten Systeme sind regelmäßig hexagonal (D_{6h}) und stellen Circumkekulen und seine Homologen dar.

Introduction

A coronoid is defined as a planar system of identical hexagons with a hole of at least two hexagons. The systems have obvious counterparts in polycyclic aromatic hydrocarbons. As a remarkable achievement one of these molecules, viz. kekulene $C_{48}H_{24}$, has been synthesized [1, 2]. Very recently the synthesis of a second member, $C_{40}H_{20}$, has been reported [3]. Also in other contexts a great interest in coronoid systems and the corresponding hydrocarbons is noted during the last years; cf., e.g. the theoretical work of *Vogler* [4] and the graph enumerations [5, 6]. In the present work the numbers of *Kekulé* structures (K) for some coronoid systems are considered.

We wish to demonstrate the virtue of the K enumeration method due to *Randić* [7] and referred to as the method of fragmentation. This method is the basis of some enumeration techniques described and employed previously [8–10]. In the present work the very useful method of fragmentation is exploited in a different direction. It is modified into the so-called symmetry-adapted method of fragmentation, which has been applied to regular hexagonal [11] and regular trigonal [12] benzenoids previously. Here we show an advanced application of this method to a class of regular hexagonal coronoids. The result is the first combinatorial formula of the number of *Kekulé* structures for a class of pericondensed coronoids.

Results and Discussion

Two Classes of Regular Hexagonal Coronoids

Figure 1 shows two classes of regular hexagonal coronoids: C_1 starts with kekulene and consists of catacondensed systems; C_2 starts with circumkekulene and consists of pericondensed systems. Catacondensed and pericondensed systems (coronoids as well as benzenoids) are defined by the absence and presence of a vertex belonging to three hexagons, respectively.

For the former class (C_1) the enumeration problem for *Kekulé* structures has been solved previously [13, 14]. The combinatorial formula in terms of the parameter α defined in Fig. 1 reads

$$K\{C_1(\alpha)\} = (\alpha^2 + 2\alpha + 2)^2(\alpha^2 + 2\alpha + 5) \tag{1}$$

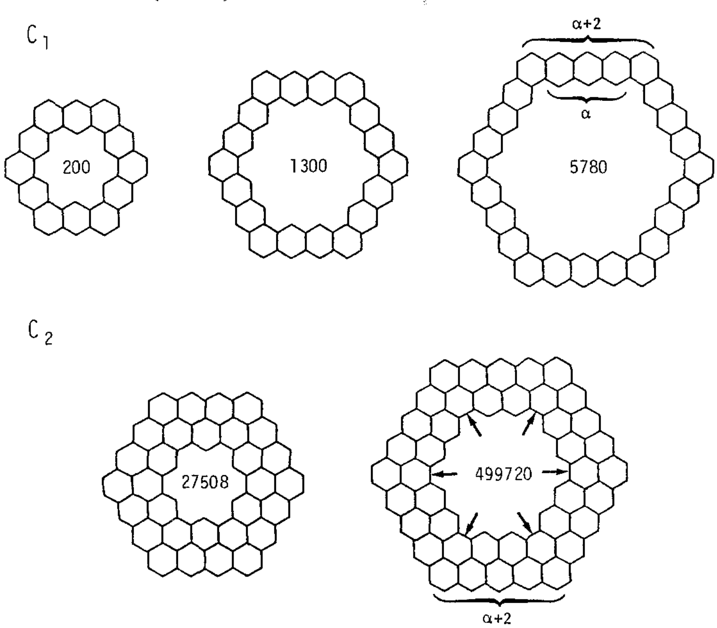


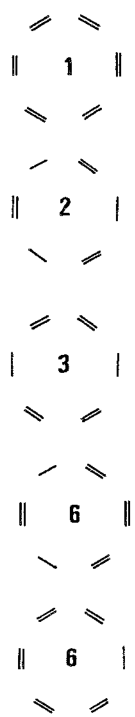
Fig. 1. Two classes of regular hexagonal coronoids. *K* numbers are inscribed. They were determined by means of a computer program

The corresponding combinatorial formula for the latter class (C_2) is the main result of the present work. It reads

$$K\{C_2(\alpha)\} = \frac{1}{32}(\alpha^2 + 4)(\alpha^2 + 2\alpha + 5)(\alpha^8 + 4\alpha^7 + 22\alpha^6 + 52\alpha^5 + 129\alpha^4 + 176\alpha^3 + 208\alpha^2 + 128\alpha + 64) \qquad (2)$$

Application of the Symmetry-Adapted Method of Fragmentation

Six symmetrically equivalent edges were selected as those of the bay regions inside the corona hole; they are marked by arrows on the bottom-right drawing of Fig. 1. The possible patterns of single and double bonds for these edges are the same as those of the central hexagon in a regular hexagonal benzenoid [11, 12]. In both cases one has the only restriction



$$k_1 = \frac{1}{32}\alpha^6(\alpha^6 + 2\alpha + 5)^3$$

$$k_2 = (\alpha^2 + 2\alpha + 2)^2(\alpha^2 + 2\alpha + 5)$$

$$k_3 = \frac{1}{2}\alpha^2(\alpha^2 + 2\alpha + 2)(\alpha^2 + 2\alpha + 5)$$

$$k_4 = \frac{1}{4}\alpha^2(\alpha^2 + 2\alpha + 2)(\alpha^2 + 2\alpha + 3)(\alpha^2 + 2\alpha + 5)$$

$$k_5 = \frac{1}{16}\alpha^4(\alpha^2 + 2\alpha + 3)(\alpha^2 + 2\alpha + 5)^2$$

Fig. 2. Patterns of single and double bonds for selected edges with multiplicities inscribed. Formulas for the numbers of *Kekulé* structures of the corresponding fragments (see Fig. 3)

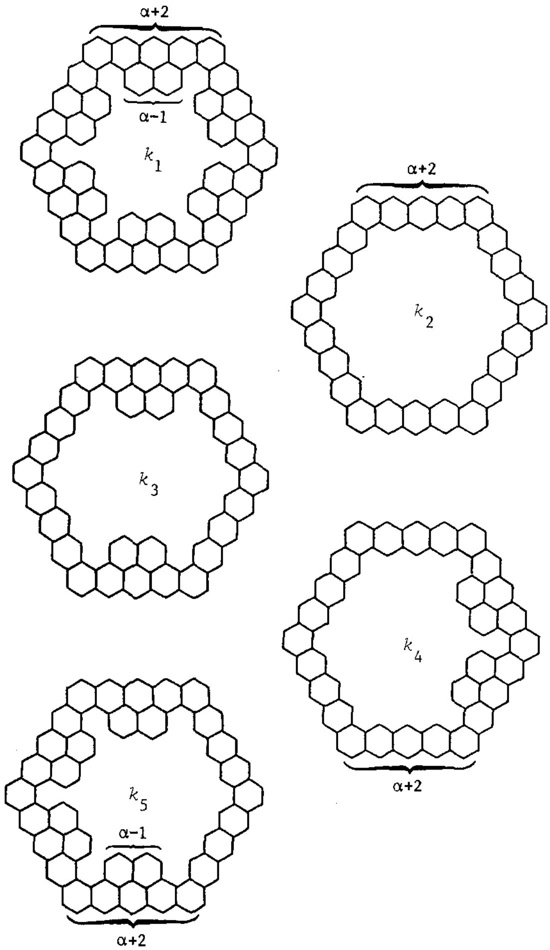


Fig. 3. Five fragments of a coronoid belonging to the class C_2

that two nearest neighbours of the edges never can both be double. These patterns, along with the multiplicities associated with them are depicted in Fig. 2. Figure 3 shows the five fragments obtained from the different patterns. Their numbers of *Kekulé* structures are designated $k_1, \ldots, k_5$. For each fragment this number was derived as a function (polynomial) of α. The results are collected in Fig. 2.

Now the final formula (2) is obtained as

$$K = k_1 + 2k_2 + 3k_3 + 6k_4 + 6k_5 \qquad (3)$$

Derivation of the Intermediate Results

In order to derive the formulas of Fig. 2 the symmetry-adapted method of fragmentation may be used in every case, but it must be adapted to different symmetries.

For the first fragment, for instance, which has the regular hexagonal symmetry of D_{6h}, a scheme with five fragments was deduced similarly to the one of Figs. 2 and 3. The individual numbers of *Kekulé* structures, viz.

$$\kappa_1 = \frac{1}{32}\alpha^6(\alpha+1)^6,\ \kappa_2 = \alpha^6,\ \kappa_3 = 0,\ \kappa_4 = \frac{1}{4}\alpha^6(\alpha+1)^2$$

$$\text{and } \kappa_5 = \frac{1}{16}\alpha^6(\alpha+1)^4,$$

lead to the formula for k_1 in Fig. 2.

One more example will be treated and in some more detail. The third fragment of Fig. 3 has dihedral (D_{2h}) symmetry. Here the edges of the six outer corners were selected as the basis of the symmetry-adapted method of fragmentation. One has the restriction that two nearest neighbours of these edges can never both be single. One comes out with eight patterns of bondings as depicted in Fig. 4. They are in fact the inverted patterns of those of a central hexagon in a dihedral benzenoid [12]. The procedure leads to the eight fragments depicted in Fig. 5. The formulas of their numbers of *Kekulé* structures are denoted $\kappa_1, \ldots, \kappa_8$ and given in Fig. 4. The developments are considerably simplified by the fact that four of these

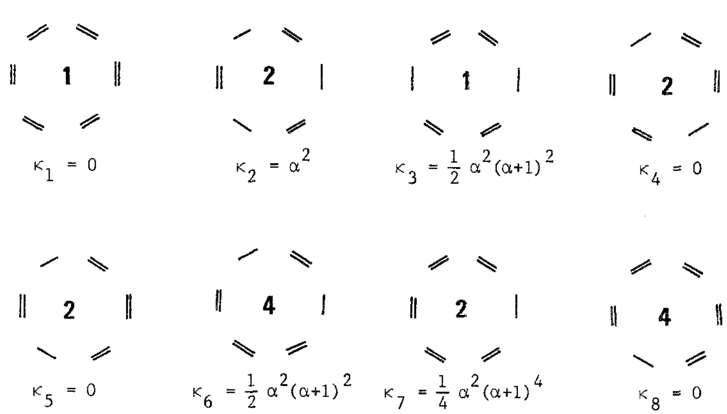


Fig. 4. Patterns of single and double bonds for selected edges with multiplicities inscribed. Formulas for the numbers of *Kekulé* structures of the corresponding fragments (see Fig. 5)

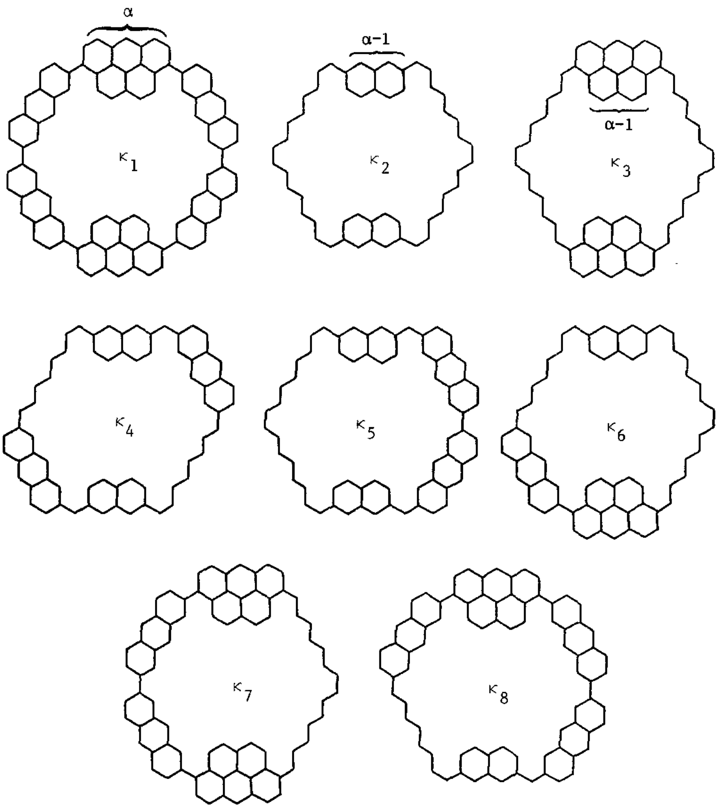


Fig. 5. Eight fragments of the third coronoid of Fig. 3

fragments are non-*Kekuléan* ($\kappa_1 = \kappa_4 = \kappa_5 = \kappa_8 = 0$). The appropriate formula of Fig. 2 is obtained as

$$\begin{aligned} k_3 &= \kappa_1 + 2\kappa_2 + \kappa_3 + 2\kappa_4 + 2\kappa_5 + 4\kappa_6 + 2\kappa_7 + \kappa_8 \\ &= 2\kappa_2 + \kappa_3 + 4\kappa_6 + 2\kappa_7 \end{aligned} \tag{4}$$

Conclusion

The formula for coronoids of the class C_2 (Fig. 1) was derived by an advanced application of the symmetry-adapted method of fragmentation. The formula is a polynomial (2) of 12th degree in the parameter α. True coronoid systems occur for $\alpha > 1$. The K numbers for $\alpha = 2$ and $\alpha = 3$ are given in Fig. 1. It is noted that the formula (2) also reproduces the well-known number $K = 980$ for circumcoronene [15] when $\alpha = 1$.

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