

Partitioning of π -Electrons in Rings of Polycyclic Benzenoid Hydrocarbons. 2.¹ Catacondensed Coronoids

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Received July 31, 2003

Various types of coronoids are examined for finding the partitioning of π -electrons in individual benzenoid rings of polycyclic aromatic hydrocarbons. A class of catacondensed coronoids, namely fibonacenes, has four π -electrons in every ring. Most other catacondensed coronoids have more than one type of benzenoid ring, each type with a different partition, but the average per ring is always four π -electrons. For the class of catacondensed coronoids that have an acenic hole, simple quadratic equations in terms of their number R of rings exist for the partitions of π -electrons in the three possible ring types.

1. INTRODUCTION

The enumeration and depiction of Kekulé and Clar structures, correlated with the Valence Bond method, together the development of Pauling's resonance theory, allowed the rationalization of structural and reactivity patterns of polycyclic aromatic hydrocarbons. It has also led to further refinements such as the method of conjugated circuits.²

Benzenoid polycyclic aromatic hydrocarbons are classified into three structural classes according to the way condensed rings are linked among themselves: catafusenes (catacondensed) when no carbon atom is common to more than two rings or when the dualist graph (defined in the next paragraph) is acyclic; perifusenes (peri-condensed or reticulate) when there are carbon atoms common to three rings or the dualist graph contains three-membered rings; and coronafusenes (corona-condensed, or coronoids) when the dualist graph has larger rings. In turn, coronoids may be catacondensed when the dualist graph has no three-membered circuits or peri-condensed when in addition to the larger circuit there is also at least one three-membered ring in the dualist graph. Catacondensed benzenoids may be non-branched (unifilar) or branched (polyfilar).

The best known coronoid is the hydrocarbon kekulene obtained, studied, and reviewed by Staab and co-workers.^{3,4} A book on coronoids was published by Cyvin and co-workers.⁵

By inscribing in the center of each benzenoid ring a vertex and by linking vertices corresponding to rings that share an edge, i.e., rings that are condensed, one obtains the dualist (or inner dual) graph. Unlike normal graphs where bond lengths and angles do not matter, they do matter in dualist graphs.^{6,7}

In the present paper we concentrate on Kekulé structures of coronoids. The total number K of Kekulé structures can be obtained from the adjacency matrix (also called the Hückel matrix) of the benzenoid, by finding its characteristic

polynomial.⁸ The absolute value of the constant term of this polynomial is K^2 for any coronoid having no conjugated circuit with $4k$ π -electrons with integer positive k (such a conjugated circuit with 12 π -electrons is present in system **16** that will be displayed in Figure 6). Another algorithm for finding graphically the value of K ,⁹ refined by Randić,¹⁰ uses the Gordon and Davison procedure¹¹ and will be exemplified in section 5 for compound **16**.

According to a procedure using the algorithm of Gordon and Davison¹¹ one can count Kekulé structures in catacondensed polycyclic benzenoids using a simple algorithm. A similar algorithm allows one also to find easily the partition P of π -electrons to each ring in coronoids. According to the distribution of double bonds in all K Kekulé structures, a ring can have a lower or higher share of π -electrons. We consider that a double bond that is not common to two adjacent rings provides two π -electrons to the ring, whereas a shared double bond provides only one π -electron to each of the two rings sharing this double bond. In a Kekulé structure of a catacondensed coronoids, a benzenoid ring can therefore be assigned according to this convention 2, 3, 4, 5, or 6 π -electrons. In a catacondensed or pericondensed polycyclic aromatic hydrocarbon, it is possible for a benzenoid ring to be assigned also 0 or 1 π -electron. This partition of π -electrons to various rings in benzenoids allows a comparison with the well-known "local aromaticities" and with Schleyer's NICS values that will be discussed in the last section.

The number of benzenoid rings will be denoted by R , the number of carbon atoms (and hence also of π -electrons) by N , and the number of holes by H .

For any benzenoid hydrocarbon (including coronoids) with R rings, each of which has a partition P_j of π -electrons, we have

$$\sum_j P_j = N \quad (1)$$

where the summation involves all rings from $j = 1$ to $j = R$.

For coronoids with H holes, the following general relationship holds (but the number 4 does not have any

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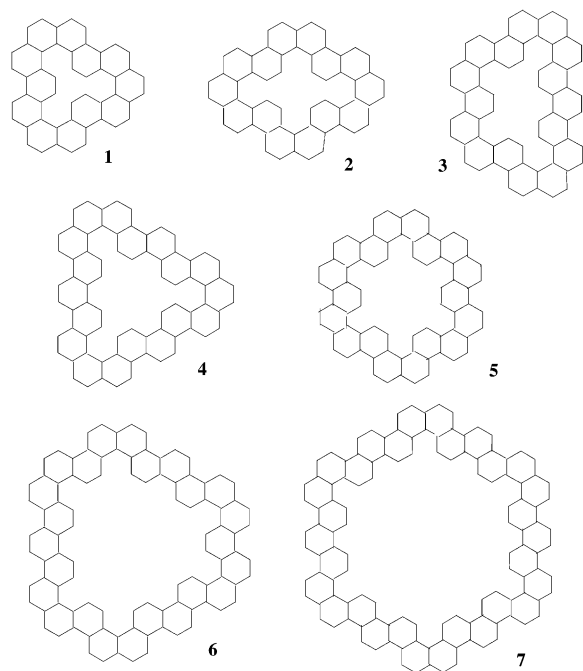


Figure 1. Fibonacenic coronoids 1–7.

connection with Hückel's Rule of aromaticity involving $4n+2$ π -electrons):

$$N = 4R - 2H + 2 \quad (2)$$

In the present paper we will deal only with proper coronoids (cycloarenes), where one or several "polycyclic benzenoid holes" are surrounded by a continuous string of catacondensed benzenoid rings. Therefore, coronene or corannulenes as well as polyphenylenes will not be discussed. The present paper will discuss only coronoids with one hole.

2. FIBONACENIC CORONOIDS

We start by drawing attention that in this paper there will be two kinds of figures, namely 2D for flat or quasi-flat systems and 3D (stereoviews) for systems that deviate substantially from planarity. The former ones will have simple hexagons, whereas the latter whose geometry was optimized with the MM2 program (CambridgeSoft ChemBats3DPro) contain an arbitrary Kekulé structure with delocalized bonds.

In Figure 1 we present several coronoids that share the following property: there are no two collinear edges in their characteristic graphs, or, in other words, there is no linear sequence of three or more benzenoid rings as in anthracene or higher acenes. An interesting property of these systems (that can be named "fibonacenes" as their acyclic counterparts with the same property,¹² for the reason which will become evident in the following) is that each benzenoid ring has an equal share in the Kekulé structure count.

It so happens that in fibonacenic coronoids all rings have the same partition of π -electrons, and it is not difficult to find the following relationships for such systems.

Let the Fibonacci series 1, 1, 2, 3, 5, 8, ... be described as F_1, F_2, F_3, F_4 , and so on:

$$F_i = F_{i-1} + F_{i-2} \quad (3)$$

For fibonacenic coronoids the following relationships hold:

$$K = 2 + F_{R-1} + F_{R+1} \quad (4)$$

$$P_j = 4 \quad \text{for any } j \quad (5)$$

Figure 2 presents in detail how one finds all partitions of Kekulé structures for the smallest fibonacenic coronoid (1), which has 12 benzenoid rings. The general rule in this procedure is to write for each topologically distinct type of benzenoid ring all possible modes in which six π -electrons can be grouped in endocyclic or exocyclic double bonds. For every mode one adds then for the ring(s) adjacent to the ring under consideration double bonds in the obligatory positions till the next following ring can have one or the other of the two possible Kekulé structures. From that stage on, one applies the Gordon-Davison algorithm as seen in Figure 2. This consists of inscribing numbers 2, 3, 4, ... in the center of the ring(s) forming a linear portion of the dualist graph. After each kink in the dualist graph, the number preceding the kink is added to each successive number in the center of the next linear portion. It does not matter which direction one takes, because the end number will be the same for both possible directions starting from the ring under consideration. This end number represents the count of all possible Kekulé structures that have the same mode of arrangement of double bonds for the ring under consideration.

Taking into account the symmetry of 1, there are three types of ring in this compound. In Figure 2 the algorithm is presented for one of these ring types. Exactly the same types of stages of the algorithm as for that ring are found for the other two types of ring. We present in Table 1 numerical results for the fibonacenic coronoids 1–7.

One can thus immediately generalize the results for any fibonacenic coronoid, irrespective of its shape, because only the number R of benzenoid rings matters. Indeed, as one may see that for the two different fibonacenic compounds 4 and 5 with $R = 18$, all their numerical values in Table 1 are identical.

There are thus for any ring in a fibonacenic coronoid (e.g. 1) with R benzenoid rings: F_{R-1} Kekulé structures with 6 π -electrons, contributing with $6F_{R-1}$ π -electrons (A, Figure 2); F_{R-1} Kekulé structures with 4 π -electrons, contributing with $4F_{R-1}$ π -electrons (B, Figure 2); F_{R-2} Kekulé structures with 3 π -electrons, contributing with $3F_{R-2}$ π -electrons (C, Figure 2); F_{R-2} Kekulé structures with 3 π -electrons, contributing with $3F_{R-2}$ π -electrons (D, Figure 2); F_{R-3} Kekulé structures with 2 π -electrons, contributing with $2F_{R-3}$ π -electrons (E, Figure 2); 1 Kekulé structure with 6 π -electrons, contributing with 4 π -electrons (F, Figure 2); 1 Kekulé structure with 6 π -electrons, contributing with 4 π -electrons (G, Figure 2).

The last two types of Kekulé structures are quinonoid, and they occur in any catacondensed polycyclic benzenoid aromatic hydrocarbon (including coronoids) when the inner and outer perimeters form two conjugated polyenic circuits. One of the F_{R-1} Kekulé structures with four π -electrons in which every ring has three conjugated double bonds is the so-called Fries structure, which is making the major contribution to the resonance hybrid.

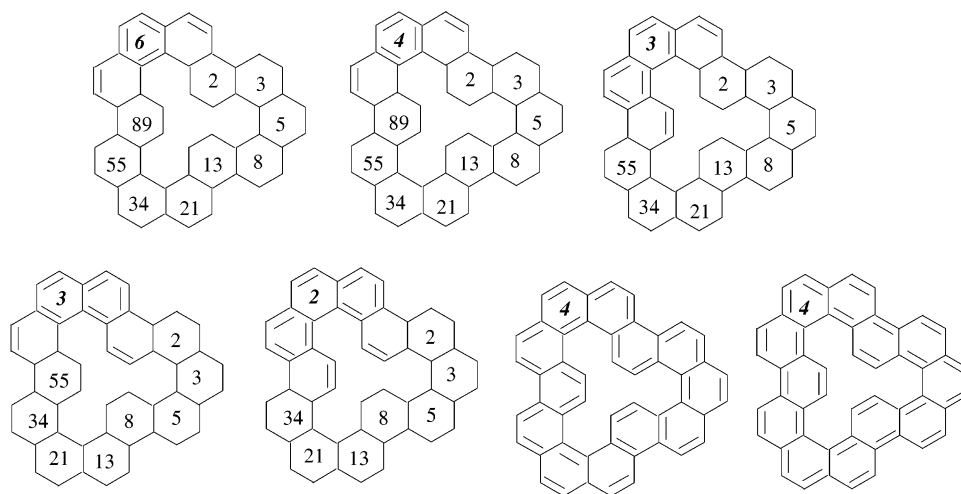


Figure 2. Determination of the partition of π -electrons for the upper left ring (with the number of ascribed π -electrons indicated in italics) for compound **1**.

Table 1. Fibonacenic Coronoids

compound	R	N	K	partition P
1	12	48	324	$4 = 1296/324$
2	14	56	845	$4 = 3380/845$
3	16	64	2209	$4 = 8836/2209$
4	18	72	5780	$4 = 23\ 120/5780$
5	18	72	5780	$4 = 23\ 120/5780$
6	24	96	103 684	$4 = 414\ 736/103\ 684$
7	30	120	1 860 700	$4 = 7\ 442\ 800/1\ 860\ 700$

As a checkup, one can verify by means of repeated operations according to eq 3 that the total number of Kekulé structures for all rings of types **A–G** in **1** is

$$2F_{R-1} + 2F_{R-2} + F_{R-3} + 2 = F_{R-1} + F_{R+1} + 2 = K \quad (6)$$

The partition of π -electrons for any ring in a fibonacenic coronoid with R benzenoid rings is therefore

$$P = (10F_{R-1} + 6F_{R-2} + 2F_{R-3} + 4 + 4)/K \quad (7)$$

By applying repeatedly eq 3 one obtains indeed

$$P = 4(F_{R-1} + F_{R+1} + 2)/K = 4 \quad (8)$$

3. CORONIDS WITH AN ACENIC HOLE

Next we consider coronoids where benzenoid rings surround an “acene hole” starting with compound **8** that has a “naphthalene hole” followed by compound **9** with an “anthracene hole”, etc., till the compound **13** with a heptacene hole (Figure 3). Of course, repulsion between the inner hydrogen atoms would compel such compounds to adopt nonplanar geometries, but we know that helicenes are a special class of stable fibonacenic catafusenes that are nonplanar and present a remarkably strong optical rotation.

The partitions of π -electrons are found as shown in Figure 4 for compound **9** that has three types of benzenoid rings, denoted by **a**, **b**, and **c**.

For ring **a** there are 25 Kekulé structures with 6 π -electrons, contributing with 6×25 π -electrons (**A**, Figure 4); 25 Kekulé structures with 4 π -electrons, contributing with 4×25 π -electrons (**B**, Figure 4); 7 Kekulé structures with 3 π -electrons, contributing with 3×7 π -electrons (**C**, Figure

4); 7 Kekulé structures with 3 π -electrons, contributing with 3×7 π -electrons (**D**, Figure 4); 2 Kekulé structures with 2 π -electrons, contributing with 2×2 π -electrons (**E**, Figure 4); 1 Kekulé structure with 4 π -electrons, contributing with 4 π -electrons (**F**, Figure 4); 1 Kekulé structure with 4 π -electrons, contributing with 4 π -electrons (**G**, Figure 4).

As a checkup, $25 + 25 + 7 + 7 + 2 + 1 + 1 = 68 = K$ for compound **9**.

The partition of π -electrons for ring **a** in compound **9** is therefore

$$(6 \times 25 + 4 \times 25 + 3 \times 7 + 3 \times 7 + 2 \times 2 + 4 \times 1 + 4 \times 1)/K = 304/68 = 4.47$$

For ring **b** there are 9 Kekulé structures with 6 π -electrons, contributing with 6×9 π -electrons (**A'**, Figure 4); 9 Kekulé structures with 4 π -electrons, contributing with 4×9 π -electrons (**B'**, Figure 4); 23 Kekulé structures with 3 π -electrons, contributing with 3×23 π -electrons (**C'**, Figure 4); 7 Kekulé structures with 3 π -electrons, contributing with 3×7 π -electrons (**D'**, Figure 4); 15 Kekulé structures with 2 π -electrons, contributing with 2×15 π -electrons (**E'**, Figure 4); 1 Kekulé structure with 4 π -electrons, contributing with 4 π -electrons (**F'**, Figure 4); 1 Kekulé structure with 4 π -electrons, contributing with 4 π -electrons (**G'**, Figure 4).

As a checkup, $9 + 9 + 23 + 7 + 15 + 1 + 1 = 68 = K$ for compound **9**.

The partition of π -electrons for ring **b** in compound **9** is therefore

$$(6 \times 9 + 4 \times 9 + 3 \times 23 + 3 \times 7 + 2 \times 15 + 4 \times 1 + 4 \times 1)/K = 224/68 = 3.29$$

For ring **c** there are 16 Kekulé structures with 5 π -electrons, contributing with 5×16 π -electrons (**A''**, Figure 4); 16 Kekulé structures with 4 π -electrons, contributing with 5×16 π -electrons (**B''**, Figure 4); 25 Kekulé structures with 4 π -electrons, contributing with 4×25 π -electrons (**C''**, Figure 4); 9 Kekulé structures with 4 π -electrons, contributing with 4×9 π -electrons (**D''**, Figure 4); 1 Kekulé structure with 4 π -electrons, contributing with 4 π -electrons (**E''**,

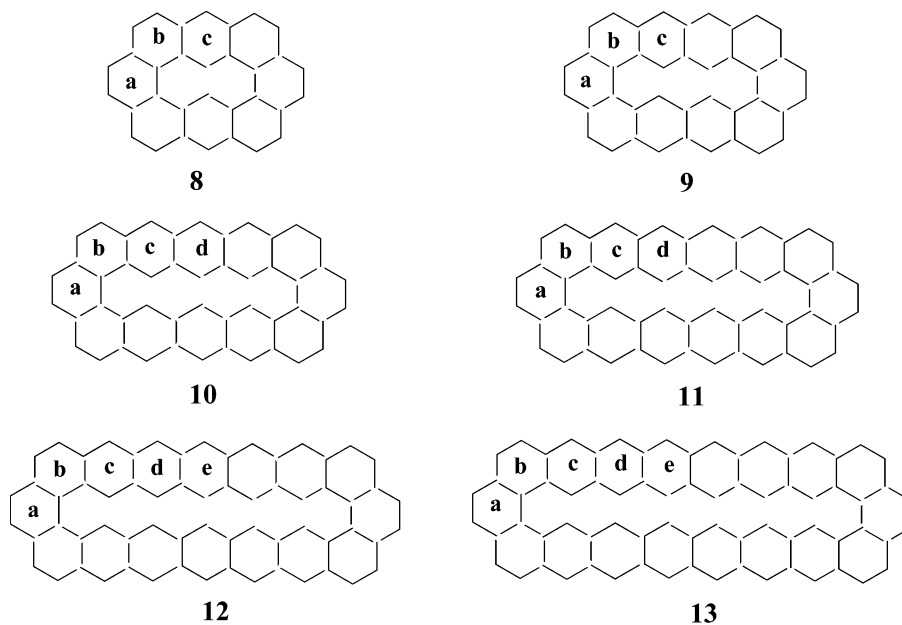


Figure 3. Coronoids 8–13 with an acenic hole.

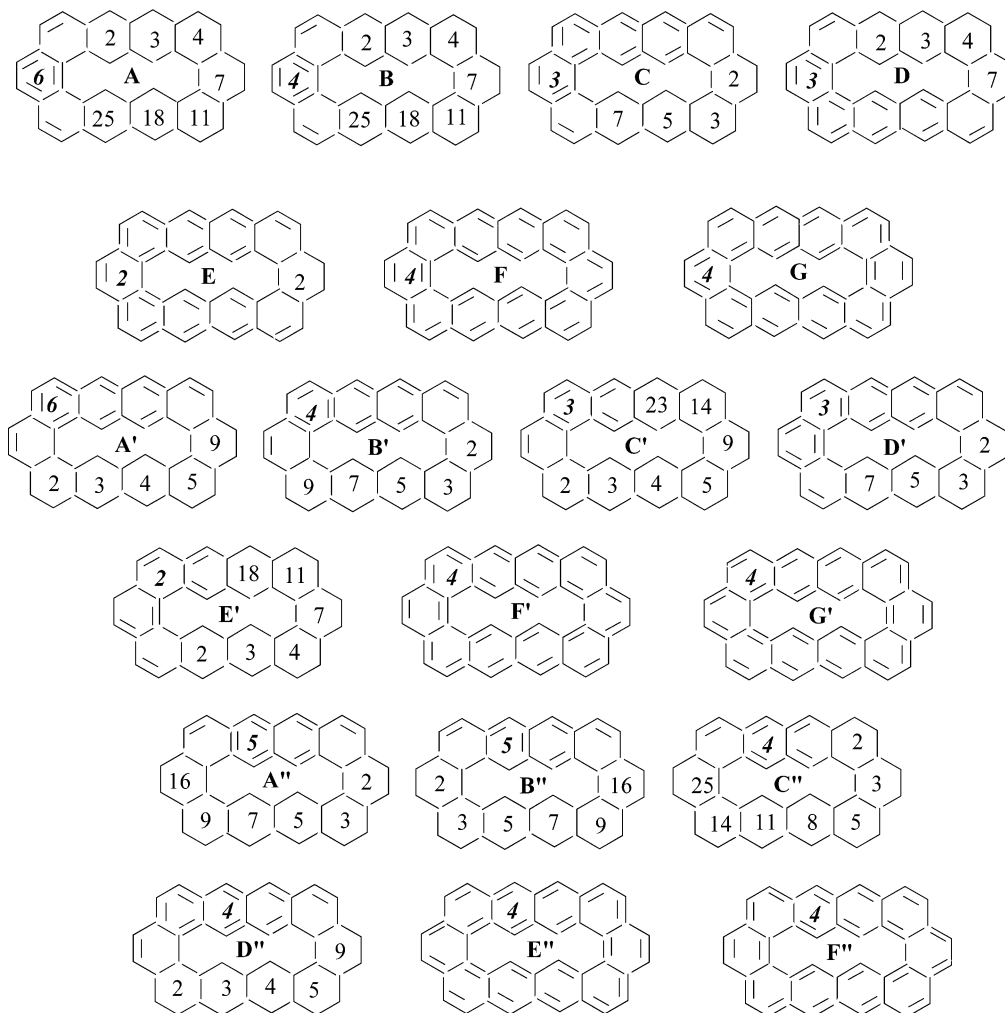


Figure 4. Determination of the partition of π -electrons for the three types of benzenoid rings in compound **9**. The number of π -electrons ascribed to the ring is inscribed in italics.

Figure 4); 1 Kekulé structure with 4 π -electrons, contributing with 4 π -electrons (F'', Figure 4).

As a checkup, $16 + 16 + 25 + 9 + 1 + 1 = 68 = K$ for compound **9**.

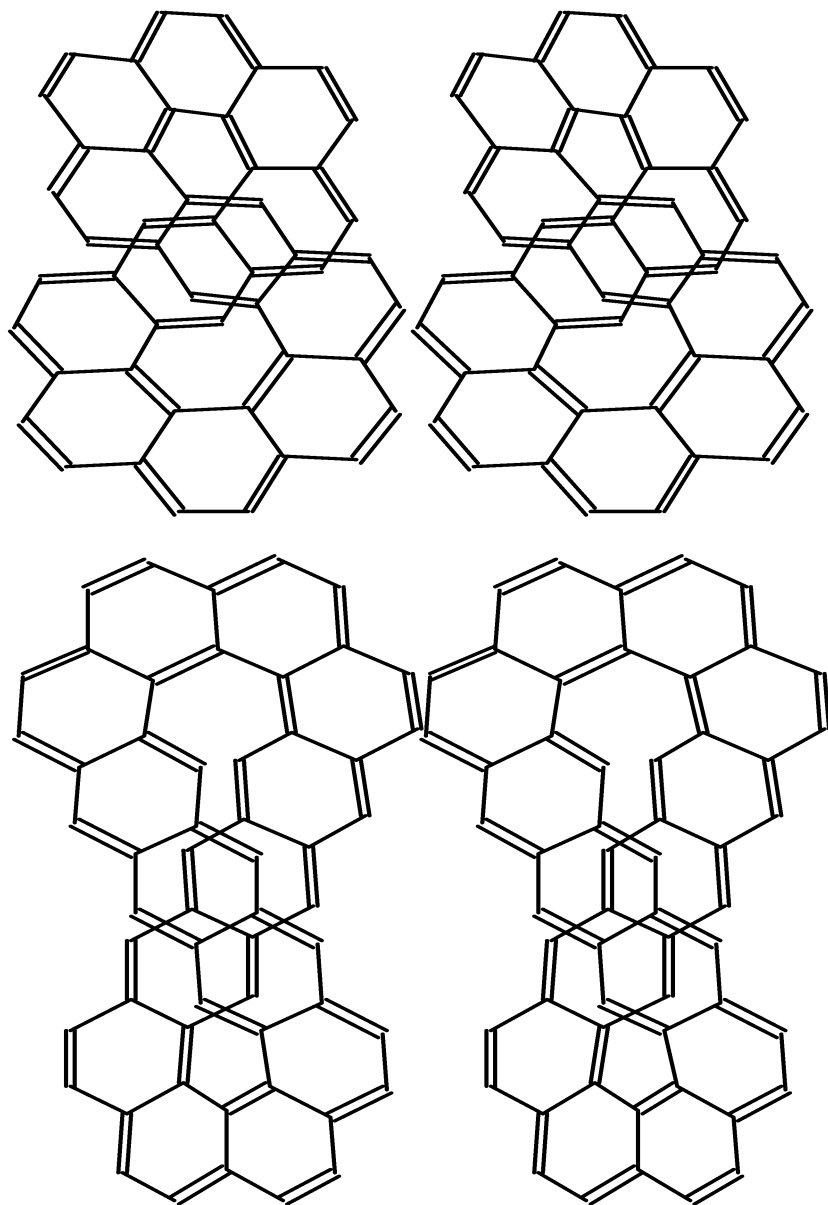


Figure 5. Stereoviews of twisted-ring (or number-8-like) coronoids **14** (top) and **15** (bottom).

Table 2. Coronoids with an Acenic Hole^a

compound	<i>R</i>	<i>N</i>	<i>K</i>	partition P_i (<i>K</i> is the denominator in the partition)
8	8	32	40	4.30, 3.55, 4.60
9	10	40	68	4.47, 3.29, 4.47
10	12	48	104	4.58, 3.13, 4.38, 4.38
11	14	56	148	4.65, 3.03, 4.32, 4.32
12	16	64	200	4.75, 2.95, 4.28, 4.28, 4.28
13	18	72	260	4.74, 2.89, 4.25, 4.25, 4.25

^a The partitions start with a central “phenanthrenic” ring (denoted by **a**) and continue in one direction around the center of the coronoid.

The partition of π -electrons for ring **c** in compound **9** is therefore

$$(5 \times 16 + 5 \times 16 + 4 \times 25 + 4 \times 9 + 4 \times 1 + 4 \times 1)/K = 304/68 = 4.47$$

One may see in Table 2 that the partitions for type-**a** and type-**c** rings is purely coincidental for compound **9**. On the other hand, it will be observed that the partition is the same for all rings which are similar to a central ring in an

anthracenic structure, i.e., for a ring that corresponds to a vertex with an angle of 180° in the dualist graph.

Since in **9** there are two type-**a** rings, but four type-**b** and type-**c** rings, the weighted contributions will be

$$(2 \times 304 + 4 \times 304 + 4 \times 224)/K = 2720/68 = 40 = N$$

similarly to eq 4.

The weighted average of partitions of π -electrons for one ring in this or any other coronoid is

$$\sum_j P_j/R = 4$$

in agreement with eqs 1 and 2.

The following quadratic relationships hold for coronoids with an acenic hole

$$K = R^2 - 4R + 8$$

$$P_a = (5R^2 - 24R + 44)/K$$

$$P_b = (2.5R^2 - 4R + 14)/K$$

$$P_c = (4R^2 - 12R + 24)/K$$

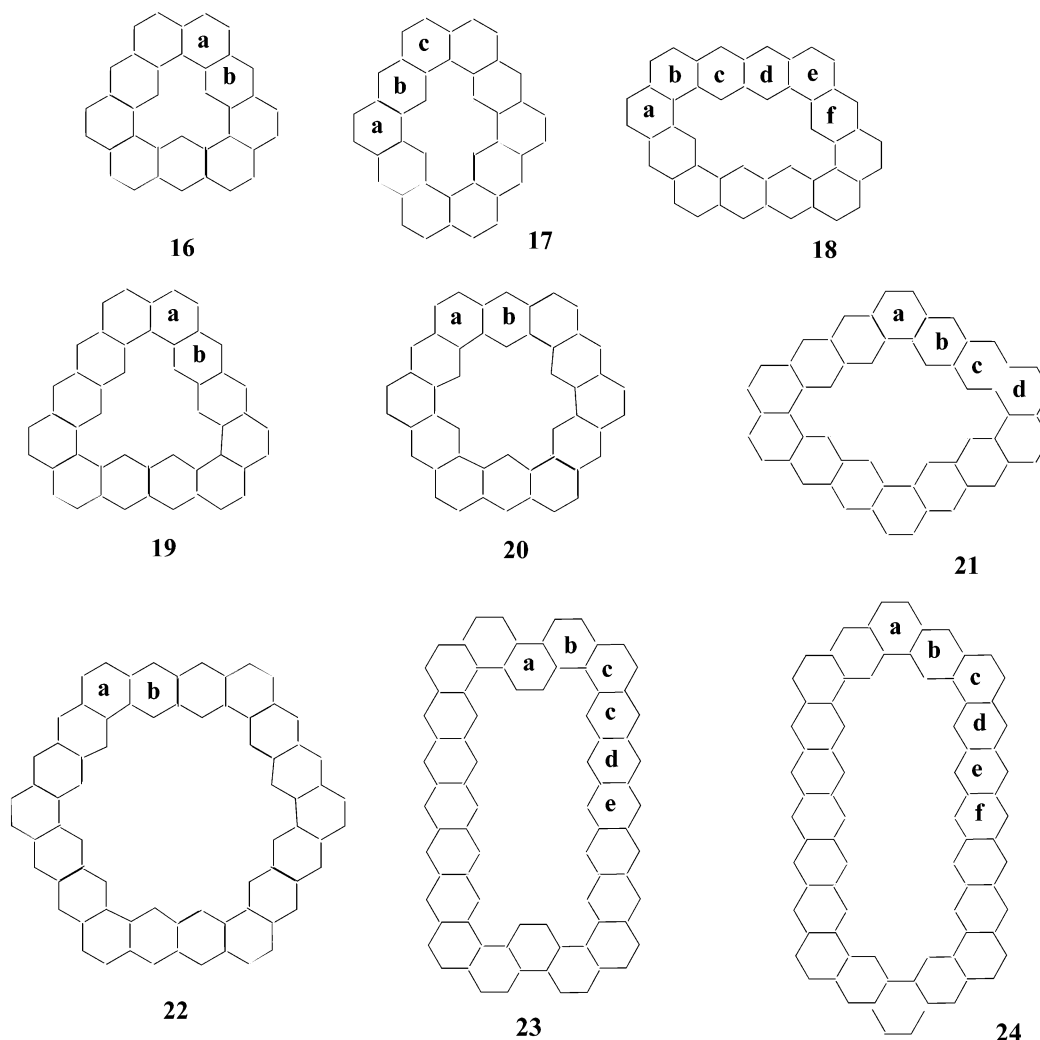


Figure 6. Catacondensed coronoids 16–24.

On examining Table 2, it is immediately apparent that in the series of compounds **8** to **13** the partition of type **a** rings steadily increases, whereas the partition of type **b** and **c** rings steadily decreases. The above relationships indicate that at the limit when R tends toward infinity the partitions of **a**, **b**, and **c** type rings are 5, 2.5, and 4, respectively.

4. TWISTED-RING-LIKE CORONOIDS

We present in Figure 5 stereoviews of two twisted-ring-like coronoids, **14** and **15**, which must be nonplanar because they have overlapping benzenoid rings. The former has two anthracenic moieties, and the latter two pentacenic moieties. For persons who write number 8 in a continuous trait (and not by drawing two tangent circles) it is easy to visualize these coronoids as “number-8-like” structures. Both compounds are chiral but with opposite chiralities. Only one enantiomer for each compound is shown in Figure 5.

Table 3 contains numerical data on these two coronoids. One can observe again that for all rings in **15** which are similar to a central ring in an anthracenic structure, the partition is the same.

One can imagine even stranger structures, e.g. Möbius bands, or cylindrical catacondensed benzenoids. The latter can be either a cyclacene (a cylindrical “polyacenic” belt of

Table 3. Twisted-Ring-like or Number-8-like Coronoids^a

compound	R	N	K	partition P_i (K is the denominator)
14	12	48	260	4.26, 4.18, 3.57, 4.61
15	14	56	256	4.19, 3.25, 4.38, 4.38

^a The partitions start with a central “phenanthrenic” ring (on top of the structure) and continue in one direction.

benzenoid rings with zigzag borders, as the middle belt in C_{70} -fullerene¹³ or fibonacenic with an armchair border (“polyphenanthrenic” as in C_{60} -fullerene); in the latter case, as for any other fibonacenic coronoid, only the number of rings matters, and the relationships indicated in eqs 4 and 5 apply. A cyclacene has only two quinonoid Kekulé structures. Both these beltlike coronoids have all rings with the same partition, equal to four. Coronoid Möbius bands composed of benzenoid rings obey the same numerical relationships as the normal coronoids with the same topology.

5. OTHER CORONOIDS

Compounds **16**–**24** are presented in Figure 6, and their numerical data are displayed in Table 4.

Kekulene (compound **20**) and compound **19** illustrate in a simple manner the fact that the average of partitions of

Table 4. Other Coronoids^a

compound	<i>R</i>	<i>N</i>	<i>K</i>	partition P_i (<i>K</i> is the denominator)
16	9	36	54	3.80, 4.56
17	10	40	85	3.15, 4.64, 3.79
18	12	48	148	3.90, 3.51, 4.87, 4.46, 2.93, 4.59
19	12	48	112	3.57, 4.43
20	12	48	200	3.30, 4.70
21	14	56	260	2.77, 4.49, 4.46, 3.63
22	18	72	1,300	2.89, 4.55
23	20	80	1300	4.28, 4.28, 4.28, 3.03, 4.42, 3.72
24	20	80	1160	4.29, 4.29, 4.29, 2.77, 4.76, 3.47

^a The partitions start with a central “phenanthrenic” ring (denoted by **a**) and continue in one direction around the center of the coronoid.

π -electrons per ring is 4, because each of these two coronoids with $R = 12$ benzenoid rings has exactly six rings of one type and six rings of another type. Therefore their average of partitions of π -electrons for one ring is

$$(400 + 496)/(2 \times 112) = 4 \text{ for } \mathbf{19}$$

$$(660 + 940)/(2 \times 200) = 4 \text{ for } \mathbf{20}$$

Compound **21** illustrates again the fact that exactly the same partition is obtained rings which are similar to a central ring in an anthracenic structure. On comparing the data from all Tables, one can see that different compounds may have the same K value (148, 200, or 260) but different numbers of rings. The highest K values are observed for fibonacenic coronoids. These are also the only coronoids in which every ring has the same partition of π -electrons.

In addition to the catacondensed coronoids with an acenic hole, we examined related coronoids with two parallel acene strings separated by a wider distance. Two examples (compounds **23** and **24**, each with six types of benzenoid rings, denoted by **a–g**) are presented in Figure 6 and their numerical data in Table 4. One can observe that all rings in the linker catacondensed string portions (both zigzag and V-shaped acenic) have the same partition and that when the linker catacondensed strings consist of V-shaped anthracenic moieties the K values are lower; in such structures the K values (e.g. for **20** and **24**) are given by the quadratic relationship:

$$K = 6.25R^2 - 80R + 260$$

We indicate in Figure 7 the Randić algorithm for finding the number K of Kekulé structures exemplified for compound **16**. One starts from any ring (in this case ring **a**) and writes the possible obligatory Kekulé structures for this ring (four in this case) and the adjacent rings till one meets a ring with two alternative Kekulé structures, then one cuts the single bonds disconnecting the ring from the remaining system, and one counts with the Gordon-Davison algorithm the numbers

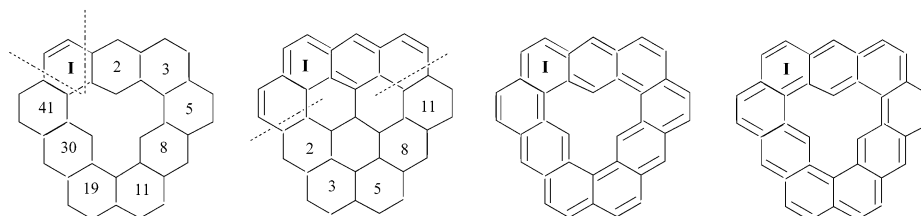


Figure 7. Determination of the number K of Kekulé structures for compound **1**: $K = 41 + 11 + 1 + 1 = 54$.

of Kekulé structures for the remaining systems, adding them at the end to find K .

6. SPECIAL FIBONACENIC CORONOIDS

It is well-known that acenes are less stable than isomeric fibonacenic polycyclic benzenoid hydrocarbons. Therefore in addition to the two acenic twisted-ring-like coronoids that had been displayed in Figure 4, we include in this section two fibonacenic twisted-ring-like coronoids (Figure 8, compounds **25** and **26** with $R = 12$ and 14 rings, respectively). As it was mentioned earlier for the two compounds **14** and **15** from Figure 5, also these two systems **25** and **26** shown in Figure 7 are chiral. Both have one twist resulting in a single “crossing”. Only one enantiomer is shown for each of these compounds.

On examining compound **1** in Figure 1, one can see that this fibonacene has triphenylene as a hole with the three marginal hexagonal holes surrounded by five benzenoid rings. Some fibonacenes in Figure 1, namely **5**, **6**, and **7**, have a marginal hexagonal hole surrounded only with four benzenoid rings, whereas **2**, **3**, and **4** have a marginal hexagonal hole surrounded both with four and with five benzenoid rings. When a hexagonal hole is surrounded by five benzenoid rings as for **1**, interesting structures appear such as **27** and **28** in Figure 9 (with $R = 18$ and 30, respectively), but these compounds can no longer be planar owing to overcrowding of hydrogen atoms, hence their stability will be affected. The last system (**28**) is aesthetically pleasing owing to its snowflake shape. No numerical data are supplied because all these compounds (**25–28**) obey the same relationships (6)–(8) as for all other fibonacenic coronoids.

7. TOPOLOGICAL STEREOISOMERISM WITH CATACONDENSED CORONOIDS

As indicated in previous publications,¹⁴ an interesting topological stereoisomerism emerges when there are two crossings in twisted ring systems (as in a string of three contiguous circles, with a central circle having two tangent circles at the ends of a diameter). If these crossings have the same helicity, a chiral system results (Figure 10, compound **29** with $R = 18$), but when the two helicities are opposite, the result (Figure 10, compound **30** also with $R = 18$) is no longer a chiral compound but a diastereoisomer of **29**. Both **29** and **30** have four anthracenic moieties, and the numerical data for the partition of π -electrons in both these systems are as follows: $R = 18$, $N = 72$, $K = 3604$. Partitions for the five ring types (starting with the top phenanthrenic ring) are as follows: 3.87, 4.20, 3.53, 4.60, and 3.73.

A similar situation occurs with fibonacenic coronoids **31** (chiral) and **32** (achiral) with $R = 22$ (Figure 11) which need

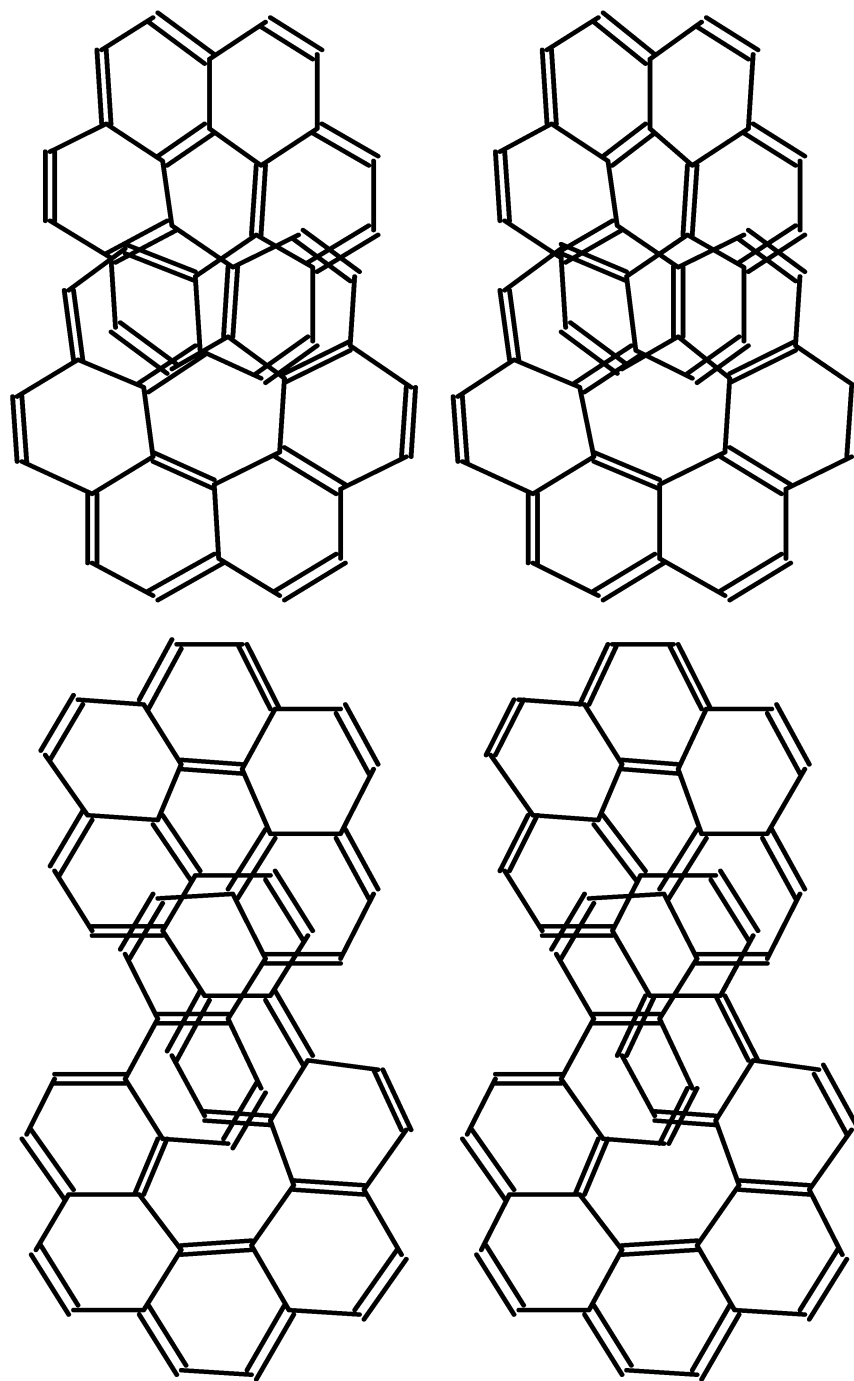


Figure 8. Stereoviews of fibonacenic coronoids **25** (top) and **26** (bottom).

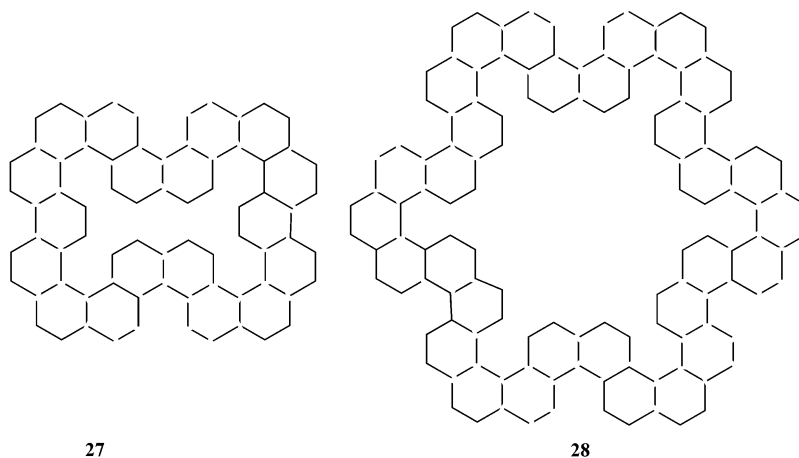


Figure 9. Two fibonacenic coronoids, **27** and **28**, with marginal hexagonal holes surrounded by five benzenoid rings.

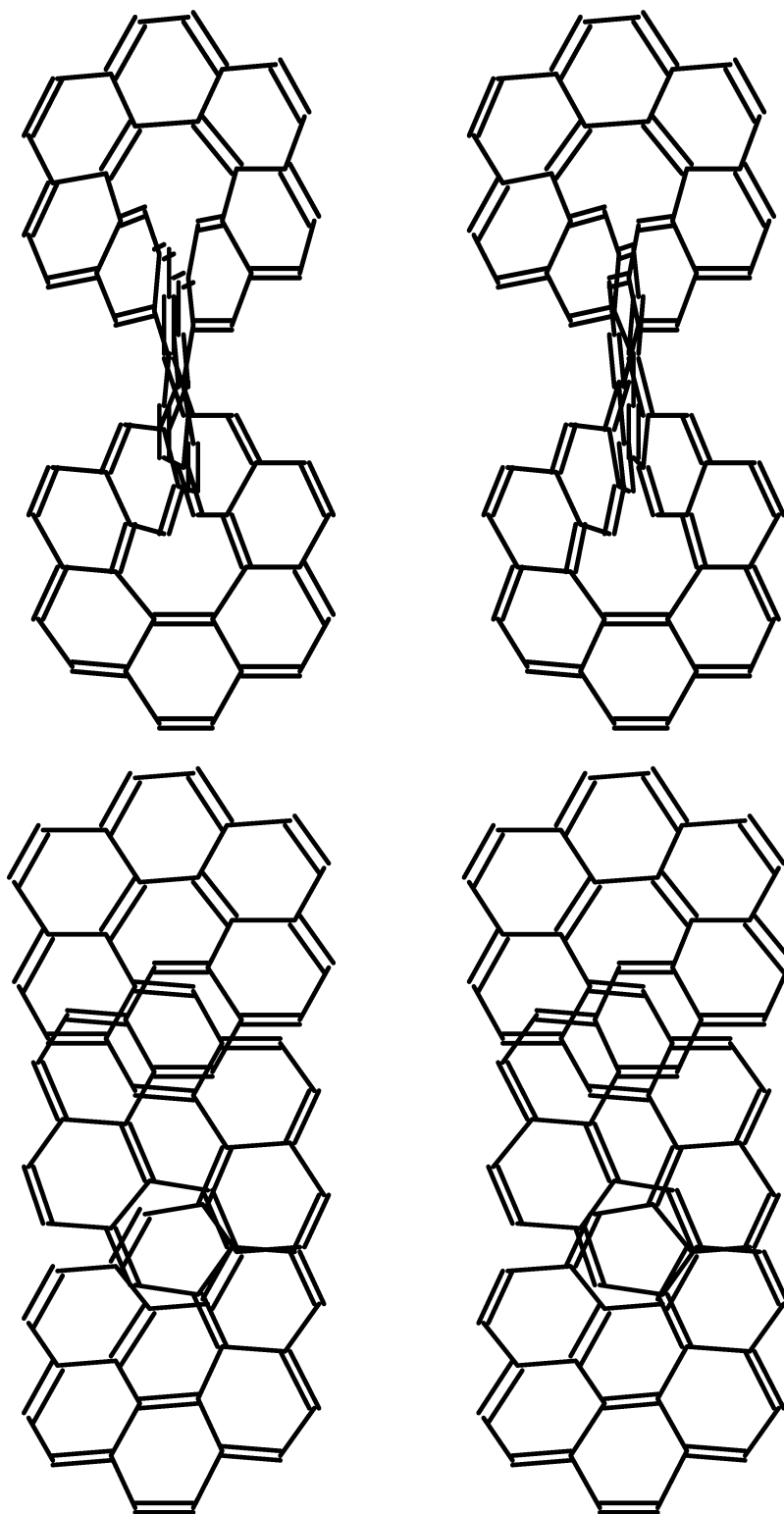


Figure 10. Stereoview of diastomeric catacondensed coronoids **29** (top) and **30** (bottom).

no numerical data because they obey relationships (4) and (5), and all their rings have four π -electrons.

DISCUSSION OF THE RESULTS

On looking at partition values through all of the tables, one can see that in the coronoids **8–13** with acenic holes, a “central phenanthrenic” ring has the highest partition value, and the ring next to this the lowest value. However, the situation becomes reversed for coronoids **14–22** in which

rings within linear (anthracenic) portions of the dualist graph have higher partition values than central phenanthrenic rings, which have the lowest values.

In catacondensed coronoids with one hole, the middle ring in an anthracenic moiety flanked by fibonacenic moieties as in **17**, **20**, **24**, **31**, and **32** has the largest partition (≥ 4.6). The smallest partition (≤ 2.9) is found in a middle ring of a phenanthrenic moiety flanked by acenic strings as for **a**-type rings in **12**, **13**, **21**, and **22** or **c**-type rings in **24**. These trends

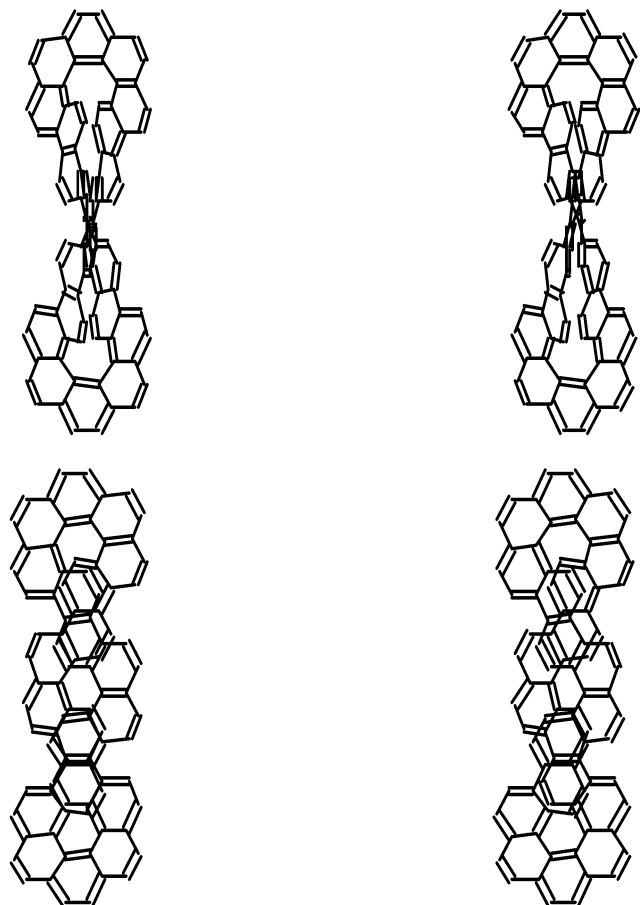


Figure 11. Stereoviews of diastereomeric fibonacenic coronoids **31** (top) and **32** (bottom).

can be explained that for Clar structures one places a circle in rings of polyacene moieties once removed from the marginal rings such as ring **b** in **24** or in kekulene **20**. Such a Clar circle may move along the acenic moiety. On the other hand, a Clar circle is never placed on a central phenanthrenic ring.

Because at present the only data for local aromaticity in coronoids refer to kekulene, this compound will be the sole point of comparison with literature values. It was shown by Jiao and Schleyer, by means of nucleus independent chemical shift (NICS) values,¹⁵ that kekulene is not superaromatic and that a Clar structure with circles in the central rings of the anthracenic portions represents best the electronic distribution,¹⁶ in agreement with the present findings.

CONCLUSION

On assigning to rings in polycyclic aromatic hydrocarbons a certain partition of their π -electrons in accordance with shared or unshared double bonds, it was possible to find certain regularities that may be correlated with higher partition values for the rings that have circles in Clar structures. Schleyer's NICS values for kekulene also agree with the present findings. One should recall that as outlined in Part 1 of the present series, the partitions of π -electrons can also be found from Pauling bond orders.¹

Whenever there are no anthracenic subgraphs in the coronafusene, all rings in the resulting fibonacenic coronafusene have the same partition, which is equal to four π -electrons. Another such case with all partitions equal to 4 is in cyclacenes (anthracenic belts composed of benzenoid rings), which have only two Kekulé structures. All other coronafusenes that were investigated have two or more types of aromatic rings, but always the weighted average partition per ring in a coronoid amounts to four π -electrons.

Note Added after ASAP Posting. This article was released ASAP on 9/27/2003. The correct version was posted on 10/15/2003 with minor rearrangement of the artwork.

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CI034164L