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CLAR SEXTET THEORY OF REGULAR CORANNULENES

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The number of Clar structures which represent maximal independent sets of vertices of Clar graphs of regular corannulenes are computed and expressed as sum of binomial coefficients. It is concluded that the efficiency of Clar structures in data reduction decreases as the number of linearly annulated hexagons increases.

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1. Introduction, Notations and Definitions:

Theoretical studies of large benzenoid hydrocarbons still remain beyond the reach of non-empirical (Ab-initio) and even some semi-empirical methods. Experience over the past three decades suggests that benzenoid systems are especially vulnerable for methods of graph theory rather than quantum-mechanical MO models[1]. The two most popular approaches are the Structure-Resonance Theory of Herndon[2] and the Conjugated-Circuit Model of Randić[3]. Both approaches are ultimately equivalent[4] and depend on investigation of all Kekülé structures of the benzenoid system under consideration. A third approach which is due to Herndon and Hosoya[5] uses only a selected number of Kekulé structures (which represent what is called Clar's Basis) reproduces resonance energies of Dewar & de-Llano[6] with suitable parametrization. Because of some controversy in the literature of Mathematical Chemistry certain definitions will be clarified which are related to Clar Sextet Theory[7]:

1.1 Clar's Definition:

In 1922 Armit and Robinson[8] advocated novel valence structures for benzenoid systems based on the notion of "aromatic sextets". Based on a vast amount of experimental data, Clar[7] recognized the value of "pi-sextets" and demonstrated how these sextets offer adequate representations of benzenoid polycyclic systems. Further, Clar justified calling valence structures with inscribed circles (denoting pi-aromatic sextets) "Clar Structures". In his review on the topological properties of benzenoid molecules, Gutman[9] stated three rules for the construction of Clar structures as follows:

a) It is not allowed to draw circles in adjacent hexagons.
b) Circles can be drawn in hexagons if the rest of the conjugated system has at least one Kekulé structure.

c) A Clar structure contains the maximal number of circles which can be drawn when rules a) and b) are obeyed.

Examples of Clar structures are shown in Fig. 1.

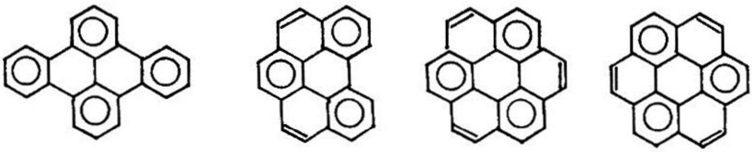


Fig 1

Clar structures of some pericondensed benzenoid hydrocarbons according to the original definition of Clar (rules a-c).

1.2 "Modified" Definition Of Clar Structures:

In 1984 Herndon and Hosoya[5] slightly "loosened" the original Clar's definition by alleviating rule c)above,and keeping only rules a) and b). In Fig 2 we draw some structures which according to Herndon and Hosoya[5] are considered as Clar structures.

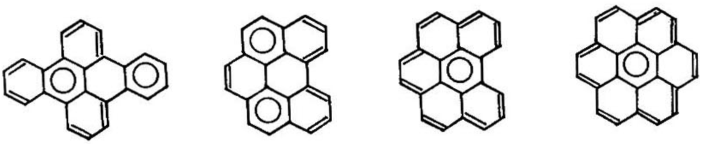


Fig 2

Clar structures according to the definition of Herndon and Hosoya. These structures fulfil conditions a) and b) but not c)

In subsequent papers El-Basil[10] and El-Basil and Randic[11] adopted this later definition of Clar structures.

1.3. Clar Graph[12] (of Gutman) $\emptyset(B) = \emptyset$

Resonance relations among the hexagons of a benzenoid hydrocarbon, B, may be stored in the form of the so called Clar Graph, $\emptyset(B) = \emptyset$, first introduced by Gutman[12]. Denote the set of hexagons of B by $H = \{h_1, h_2, \ldots, h_r\}$. The Clar graph $\emptyset$, is generated when H is replaced by $V = \{v_1, v_2, \ldots, v_r\}$, i.e. by replacing each hexagon $h_i \in H$ by a vertex $v_i \in V$. The second step is to connect any pair $\{v_i\ v_j\} \in V$ if the corresponding hexagons $\{h_i\ h_j\} \in H$ are nonresonant[13]. A systematic procedure to construct $\emptyset(B)$ is to define for the benzenoid system B, the following:

1.4 Clar Matrix $\underline{C}(B)$:

$\underline{C}(B)$ is an r x r matrix the elements of which C_{ij}'s are given by eqn. 1.

$$C_{ij} = \begin{cases} 1 & \text{if } h_i \text{ is nonresonant with } h_j \\ 0 & \text{otherwise} \end{cases} \qquad ..(1)$$

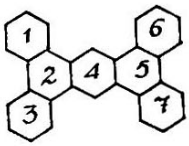
Then eqn.(2) is used to draw $\emptyset(B)$, viz.,

$$\underline{C}(B) = \underline{A}(\emptyset) \qquad ..(2)$$

where $\underline{A}(\emptyset)$ is the adjacency (connection) matrix[14] of $\emptyset(B)$.

<u>Illustration:</u>

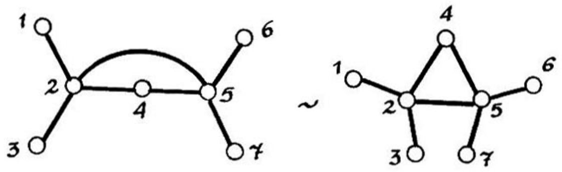
We consider the following benzenoid system B_1



Investigation of resonance relations in the set $H(B_1)$ $= \{h_1, h_2, \ldots, h_7\}$ leads to the following:

$$\underline{C}(B_1) = \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \end{array} \begin{array}{c} \begin{array}{ccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 \end{array} \\ \left(\begin{array}{ccccccc} 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ & 0 & 1 & 1 & 1 & 0 & 0 \\ & & 0 & 0 & 0 & 0 & 0 \\ & & & 0 & 1 & 0 & 0 \\ & & & & 0 & 1 & 1 \\ & & & & & 0 & 0 \\ & & & & & & 0 \end{array} \right) \end{array}$$

where only the upper triangle is written (because naturally $\underline{C}(B_1)$ is symmetric[15]) . Now recalling eqn. 2 one can draw the Clar graph of B_1; $\emptyset(B_1)$ shown below:



$\phi(B_1)$

1.5 <u>Maximal Independent Set of Vertices[16]</u>:

The Clar graph is a device to demonstrate some of the mathematical properties of Clar structures. Namely a bijection[17] can be generated from the set of Clar structures of a benzenoid system to a set of "colored" Clar graphs the vertices of which are colored in the following way: A"black" vertex in $\emptyset(B_i)$ corresponds to a hexagon in B_i which contains a circle while a white vertex corresponds to an "empty " hexagon. (Of course the colors black and white are only arbitrary). The bijective mapping:

$$\text{Set of Clar structures} \longrightarrow \text{Set of "colored" Clar graphs} \quad \ldots.(3)$$

then requires the following two rules:

a') No two black vertices in $\emptyset(B_i)$ are adjacent;

b') Every white vertex is adjacent to at least one black vertex.

Rules a') and b') are to be compared with rules a) and b) described in Section 1.1. Every Clar structure, then, corresponds to a maximal set of independent vertices[16] of the Clar graph[12]. An independent set of vertices V(i) is said to be a maximal[16] set if every vertex of the graph not included in V(i) is adjacent to at least one of the i vertices of V(i). Once all maximal independent sets of vertices of a given Clar graph are obtained, the corresponding Clar structures can easily be retrieved. As an example we consider the following case in Fig. 3.

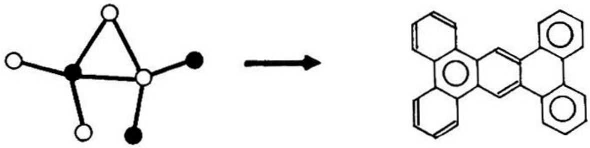


Fig 3

A "colored" Clar graph (to the left) and the corresponding Clar structure. The maximal independent set of vertices V(i) has three black and four white vertices such that every white vertex is adjacent to at least one black vertex.

Since all Kekulé structures can be retrieved from the set of Clar structures of a benzenoid hydrocarbon, Clar structures may be envisaged as "storage devices" which contain enough information on all possible permutations of the double bonds in the parent hydrocarbon. In fact Herndon and Hosoya[5] used Clar structures as quantum-mechanical basis-set and succeeded in computing resonance energies of several types of benzenoid systems of values comparable with those of Dewar and de-Llano[6] using SCF methods. Whence the computation of <u>this</u> <u>type</u> of Clar structures (which do correspond to maximal indepent sets) seems to be a worthy subject, especially knowing the fact that including all Kekulé structures in the Hamiltonian of a benzenoid hydrocarbon of an average size is already beyond the reach of computers. For example the tetrabenzoanthracene B_1 drawn above has 40 Kekulé structures but only <u>three</u> Clar structures, one of which is shown in Fig 3, the other two are drawn below.

It is interesting to observe that all 40 Kekulé structures are "stored" in just three (Clar) structures ! This type of "Data Reduction"[18] seems to be worth investigating.

2. <u>A Special Class Benzenoid Systems</u>:

2.1 <u>Corannulenes</u>[18]

This special class of benzenoid hydrocarbons is the subject of this paper. (They are also called corona-condensed polyhex graphs or simply coronoids).

A coronoid hydrocarbon is defined as a planar system of identical regular hexagons (no overlapping) with at least one hole of a size not less than two hexagons. In Fig 4 a corannulene, B^c, is shown together with its Clar graph, $\emptyset(B^c)$ Also drawn is the dualist[19], $D(B^c)$, which simply "outlines" the annulation of the hexagons of B^c.
The dualist, $D(B^c)$, is composed of two types of vertices : a vertex which makes an angle of 180^o with its two neighbouring vertices is called Linear[20], otherwise a vertex is

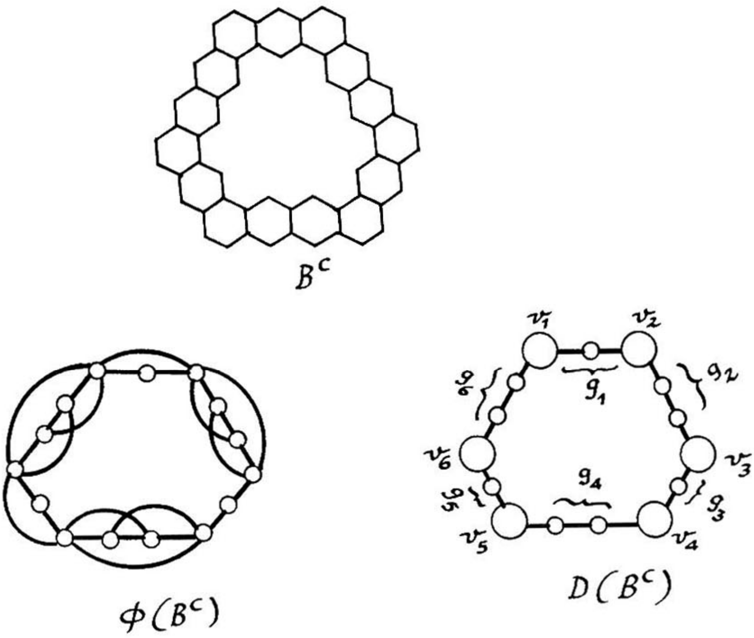


Fig 4

An arbitrary corannulene B^c, its Clar graph $\emptyset(B^c)$ and dualist $D(B^c)$. The latter is subdivided into "linear" subgraphs g_1, g_2,..,g_6. The larger vertices are the angular ones.

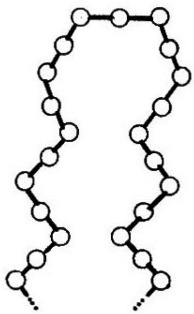
angular[20]. Angular vertices are drawn as larger vertices in $D(B^c)$ of Fig 4. A subgraph of $D(B^c)$ which starts and ends with an angular vertex is called a <u>linear subgraph</u>. The $D(B^c)$ can be expressed as union of all such linear subgraphs, namely

$$D(B) = g_1 \cup g_2 \cup \ldots \cup g_m \qquad \ldots \quad (4)$$

where g_i is an <u>ith</u> linear subgraph and m is the number of g_i's which is the ring size of $D(B^c)$. For example m = 6 for $D(B^c)$ drawn in Fig 4.

2.2. <u>Modelling data</u>:

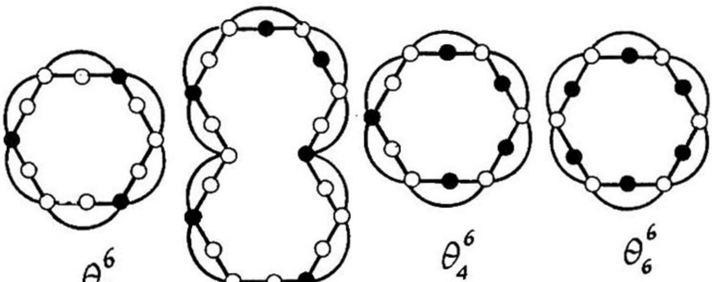
Ideal gas, ideal electrolyte, ideal solution and so on are all "man-made models" designed to focus on the general features of the laws and rules prevailing in a given discipline. Real systems can then be approached in the light of the corresponding "model". This type of modelling is quite important, if not indeed essential to many branches of science. Our model here is a corannulene having the general form whose dualist is drawn below:



Namely each of the linear subgraphs contains only one linear vertex. Working with this type makes the global features of the combinatorics of enumeration transparent. Later, as will be demonstrated more general forms can be handled quite systematically.

2.3. The quantity Θ_j^m :

We define a parameter Θ_j^m to enumerate all possible selections of j linear vertices leading to a maximal independent set of vertices[16] in $\emptyset(B^c)$; the Clar graph of a coronnulene containing m linear subgraphs. Θ_j^m may or may not include contributions from angular vertices: when j=o only angular vertices are involved, when j=m only linear vertices are involved. In the intermediate situations: $0 < j < m$ both linear and angular vertices will be contained in Θ_j^m . Some illustrations are shown below.



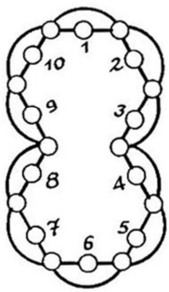
θ_0^6 θ_2^{10} θ_4^6 θ_6^6

All the colorings above represent maximal independent sets of vertices of $\emptyset(B^c)$. For a realistic corannulene $j = 4n + 2$, $n = 1,2,3,..$ All the conclusions and results which follow assumes even values of j.

3. Results:

3.1 Combinatorial Analysis:

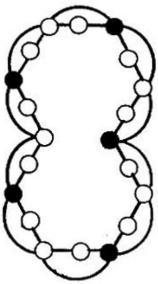
As an illustration we consider a corannulene containing 10 linear subgraphs (j=10), each of which possesses one linear vertex . The Clar graph is drawn below.

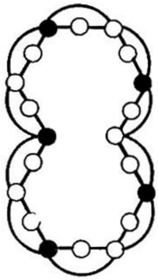


The number of Clar structures which represent maximal independent sets of vertices of the corresponding Clar graph are enumerated as Θ_o^{10}, Θ_2^{10}, Θ_4^{10}, Θ_6^{10}, Θ_8^{10} and Θ_{10}^{10} . Odd subscripts lead to vanishing terms.

Θ_o^{10};

Here only angular vertices are involved. There are only two ways of grouping the vertices such that a maximal independent set is generated regardless of the value of j. These two colorings are shown below

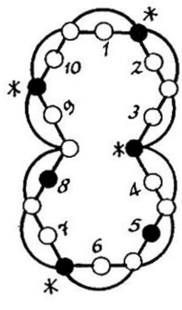




$\underline{\theta_2^{10}}$

(12) , (14) , (16), (18) , (1 10)	5
(23) , (25) , (27), (29) ;	4
(34) , (36) , (38), (3 10);	4
(45) , (47) , (49)	3
(56) , (58) , (5 10);	3
(67) , (69) ;	2
(78) , (7 10);	2
(89) ;	1
(9 10)	1

The numbers in parentheses refer to the labels of the (two) linear vertices involved in the maximal independent set. For example (58) is the following "coloring".



The solid vertices with asterices are <u>angular</u> ones which together the linear vertices at position 5 and 8 lead to one of the maximal independent sets of vertices $\in \theta_2^{10}$. Observe the fullfilments of the two coloring conditions viz., a') and b') of Section 1.5.

θ_2^{10} can be expressed using binomial numbers by classifying the codes according to the first digit to the left: there are 5 codes starting with 1, 4 codes starting with 2 and so on. The θ_2^{10} can be expressed as:

$$\begin{array}{ll} & 5 + 4 + 3 + 2 + 1 \\ + & \quad\; 4 + 3 + 2 + 1 \end{array}$$

Now we use the well-known combinatorial identity[21]:

$$\binom{n}{o} + \binom{n+1}{1} + \binom{n+2}{2} + .. + \binom{n+r}{r} = \binom{n+r+1}{r} \qquad ..(5)$$

which leads to

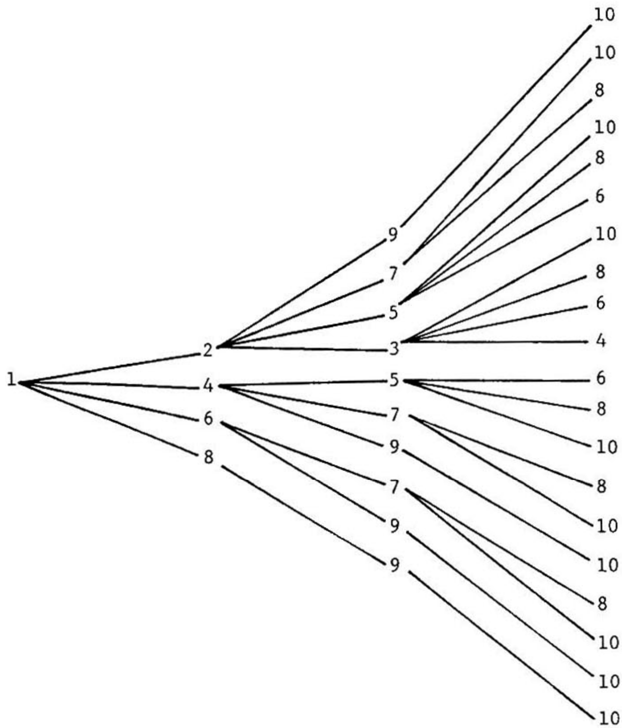
$$1 + 2 + 3 \;..+ r \;=\; \begin{matrix} r+1 \\ r-2 \end{matrix} \qquad ..(6)$$

Then;

$$\begin{aligned} \theta_2^{10} &= (1 + 2 + 3 + 4) + (1 + 2 + 3 + 4 + 5) \\ &= \binom{5}{3} \qquad + \qquad \binom{6}{4} \qquad = \binom{5}{2} + \binom{6}{2} \end{aligned} \qquad ..\ (7)$$

<u>θ_4^{10}</u>

These four-digit codes may start with the labels 1,2,3,4, 5,6 and 7. There are twenty paths starting with label 1. These are graphically generated in Fig 5. There are ten codes



$$\binom{3}{0} + \binom{4}{1} + \binom{5}{2} = \binom{6}{3}$$

<u>Fig 5</u>

Graphical generation of 4-digit codes, θ_4^{10} , starting with the lable 1.

for each of the labels 2 and 3 and four codes for each of the labels 4 and 5. Finally each of the label 6 and 7 generate only one code. All of these codes can be generated as illustrated in Fig 5.

One may analyze higher codes similarly. The results are outlined in Table 1.

Eqn. (8) is a more compact description of ζ, the number of Clar structures of a regular corannulene whose dualist is composed of even number of linear subgraphs, each of which contains one linear vertex

$$\zeta = 3 + \sum_{\substack{j=2,4,\\ \dots,(m-2)}} \binom{\frac{1}{2}(m+j)}{j} + \binom{\frac{1}{2}(m+j)-1}{j} \qquad \dots(8)$$

The factor of 3 accounts for

$$\theta_o^m + \theta_m^m$$

3.2 Description of the codes:

The subclass of codes starting with a given digit, say a, have a general structure dictated by the two properties of vertices of the Clar graph necessary to generate a maximal independent set. We represent such a subset of codes by the following matrix.

$$\begin{matrix} a & a_{12} & a_{13} & \dots & a_{1j} \\ a & a_{22} & a_{23} & \dots & a_{2j} \\ \vdots & & & & \\ a & a_{i2} & a_{i3} & \dots & a_{ij} \end{matrix}$$

<u>Table 1</u> θ_j^m values for $m = 6, 8$ and 10

m \ j	0	2	4	6	8	10
6	$\binom{2}{0} + \binom{3}{0}$	$\binom{3}{2} + \binom{4}{2}$	$\binom{4}{4} + \binom{5}{4}$	$\binom{6}{6}$		
8	$\binom{3}{0} + \binom{4}{0}$	$\binom{4}{2} + \binom{5}{2}$	$\binom{5}{4} + \binom{6}{4}$	$\binom{6}{6} + \binom{7}{6}$	$\binom{8}{8}$	
10	$\binom{4}{0} + \binom{5}{0}$	$\binom{5}{2} + \binom{6}{2}$	$\binom{6}{4} + \binom{7}{4}$	$\binom{7}{6} + \binom{8}{6}$	$\binom{8}{8} + \binom{9}{8}$	$\binom{10}{10}$

The two properties of any such subclass of codes are:

a) The difference between any two successive lables in a row is odd .

b) The difference between any two successive labels in a column is even.

Properties a) and b) result from the conditions a')and b') of "coloring" leading to a maximal independent set(= Clar structure) described in section 1.

3.3. Vector Generation of the Codes[22]:

A systematic method for the generation of the set of codes $\in \theta_j^m$:

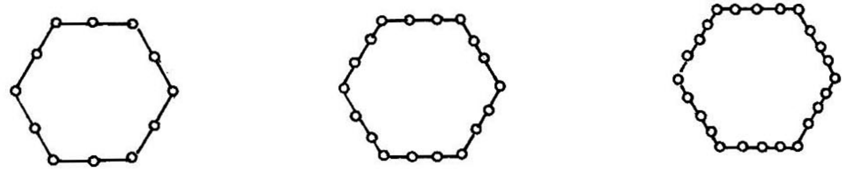
Step 1 An m-dimensional (row) vector is constructed : $(a_1 a_2 \ldots a_m)$
The elements of the vector are defined by eqn.(12), viz.,

$$a_i = \begin{cases} 1 & \text{if } v_i \text{ is a selected vertex} \\ o & \text{otherwise} \end{cases} \qquad \ldots(12)$$

Step 2 The leading vector is constructed by placing a number of 1's equal to j in the natural order of numbers.

Step 3 Other vectors are generated by moving all 1's which are followed by two zeros: each movement is defined by $a_i \longrightarrow a_{i+2}$. The process terminates when no new vectors are generated.

The process is illustrated by the generation of all vectors θ_2^6



K	200	1300	5780
$\mathcal{C}$	18	198	1298
$\%(\mathcal{C}/K)$	9.00	15.23	22.46

Fig 6 Three regular corannulenes (in their dualists), number of Kekulé structures, K and number of Clar structures $\mathcal{C}$. The ratio $\mathcal{C}/K$ increases with the number of linear vertices in the relevant dualist.

$$
\begin{array}{ccc}
\begin{array}{c}
1\;2\;3\;4\;5\;6 \\
(1\;\vec{1}\;0\;0\;0\;0) \\
\downarrow \\
(\vec{1}\;0\;0\;\vec{1}\;0\;0) \\
\downarrow \\
(\vec{1}\;0\;0\;0\;0\;1) \\
\\ \\ \\ \\ \\ \\
\end{array}
&
\begin{array}{c}
1\;2\;3\;4\;5\;6 \\
\\ \\
(0\;0\;1\;\vec{1}\;0\;0) \\
\downarrow \\
(0\;0\;\vec{1}\;0\;0\;\vec{1}) \rightarrow \\
\downarrow \\
(0\;0\;0\;0\;1\;\vec{1}) \\
\downarrow \\
(0\;\vec{1}\;0\;0\;1\;0) \\
\downarrow \\
(0\;0\;0\;1\;1\;0)
\end{array}
&
\begin{array}{c}
1\;2\;3\;4\;5\;6 \\
\\ \\ \\ \\
(0\;1\;1\;0\;0\;0) \\
\\ \\ \\ \\ \\ \\
\end{array}
\end{array}
$$

3.4 Generalization to other Corannulenes:

For a corannulene whose dualist is composed of j linear subgraphs: $g_1, g_2, \ldots, g_j$ where g_i contains ℓ_i linear vertices each code is multiplied by the product.

$$\prod_i \ell_i$$

where i runs over all linear vertices selected. As an illustration we consider three coronoid systems of hexagonal symmetries in Fig 6. Both K and $\mathcal{C}$ values are given. It seems clear that as the number of linear vertices increases the efficiency of "data reduction" using Clar structures decreases.

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12. I. Gutman, Z. Naturforsch 37a, 69 (1982); I. Gutman and S. El-Basil, Z.Naturforsch 39a, 276 (1984).
13. Two hexagons in a benzenoid system are called nonresonant if a sextet of pi-electrons cannot be drawn simultaneously in both of them.
14. The adjacency matrix is defined in F.Harary, " Graph Theory" (Addison-Wesley, Reading 1969).p. 150.
15. I.e., $\underline{C}(B_1) = \underline{C}^T(B_1) \equiv$ the transpose of Clar matrix.
16. N. Christofides, "Graph Theory; An Algorithmic Approach" (Academic Press, New York 1975) Chapt. 3.
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