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Kekulé Structure Counts for Some Classes of All-Benzenoid and All-Coronoid Hydrocarbons**

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Summary. A general formula for the Kekulé structure count (K) is deduced for the class of catacondensed all-benzenoids with unbranched backbones. The formula is extended to "thin" pericondensed all-benzenoids, where allowance is made for pyrene units. In this treatment the fragmentation matrices are employed. A generalization of these matrices is furnished. Next some general K formulas for classes of catacondensed and thin pericondensed all-coronoids are deduced. Again the fragmentation matrices are employed, but the problem is also studied in terms of certain polynomials.

Keywords. Kekulé structure; All-benzenoid hydrocarbon; All-coronoid hydrocarbon.

Kekulé-Strukturzählungen für einige Klassen von all-benzenoiden und all-coronoiden Kohlenwasserstoffen

Zusammenfassung. Eine generelle Formel für die Kekulé-Strukturzählung (K) für die Klasse der katakondensierten all-Benzenoiden mit unverzweigter Grundstruktur wird abgeleitet. Die Formel wird auf „dünne" perikondensierte all-Benzenoide ausgeweitet, wobei Pyren-Einheiten mit berücksichtigt werden können. Bei dieser Behandlung werden Fragmentationsmatritzen verwendet und eine Generalisierung dieser Matritzen getroffen. Dann werden einige generelle K-Formeln für Klassen von katakondensierten und dünnen perikondensierten all-coronoiden Verbindungen abgeleitet. Dabei werden wieder Fragmentationsmatritzen angewandt, das Problem wird allerdings auch mit Hilfe bestimmter Polynome untersucht.

Introduction

All-benzenoid (or fully benzenoid [1, 2]) hydrocarbons are important and interesting molecules, which exhibit extraordinary great chemical stability [1 – 3]. Their definition is based on the concept of aromatic sextets, which has long traditions in organic chemistry [1, 2, 4]. Also the corresponding benzenoid systems (all-benzenoid systems or simply all-benzenoids) have been studied with great interest in mathematical chemistry [5 – 11]. A definition of all-benzenoids in the wording of Randić [12] reads: "For these compounds one can write a valence structure in which a ring is either represented as an isolated sextet or is devoid of conjugation."

** Dedicated to the memory of Professor Oskar E. Polansky, who died in January 1989. He was the one who coined the term "all-benzenoid".

A valence structure is here synonymous with what also is called Kekulé structure [13]. Kekulé structure counts (K) for all-benzenoids in general [6] or special classes of all-benzenoids [13 – 19] have been studied to a large extent. Also in the present work the Kekulé structure counts for classes of all-benzenoids are treated, but in a more general sense. Recently developed methods are employed.

A coronoid is, loosely speaking, a benzenoid with a hole. All-coronoids [20 – 22] are defined in the same way as all-benzenoids. In the present work a treatise on the Kekulé structure counts of a broad class of all-coronoids is included, making use of the matrix methods and an expansion into polynomials.

For general references to the relevant theory the reader is referred to some recent monographs [13, 23, 24].

Class of Catacondensed All-Benzenoids

Definitions, Notation and Some Topological Properties

In this section the catacondensed all-benzenoids with unbranched backbones are treated. The backbone of a catacondensed all-benzenoid is defined as the subsystem obtained by deleting all L_1-mode hexagons, which necessarily are full. The full and empty hexagons are identified by symbols F and E, respectively.

The backbone of a member of the defined class is a single chain of hexagons (unbranched catacondensed benzenoid). For $h > 4$ (where h is the number of hexagons of the all-benzenoid system) the backbone can only consist of 2-segments and 3-segments, but not in an arbitrary succession. A necessary and sufficient condition is given in the following.

Propositions. (a) The empty and full hexagons in the backbone alternate ($EFE...E$); (b) both terminal hexagons are empty (E); (c) every 3-segment has the configuration empty-full-empty (EFE).

Corollary. The backbone has an odd number of hexagons.

In the backbone all non-terminal hexagons are angularly annelated (A_2; in the whole all-benzenoid A_3). The non-terminal (apart from L_1) full hexagons (in the backbone) are either in A_2 or L_2. An **LA**-sequence (written in bold) is defined by indicating the modes of the full hexagons in the backbone, only. Correspondingly we shall speak about **A** and **L** hexagons.

Proposition. The system is determined up to isoarithmicity by its **LA**-sequence.

This means that it is immaterial which way the kinks go at every angular annelation, for full and empty hexagons being the same. Different versions of such systems have the same Kekulé structure count. In other words, the K number of the all-benzenoid is determined by its **LA**-sequence.

A useful interpretation of a system of the considered type is a set of compressed triphenylenes. Triphenylene is the $h = 4$ branched benzenoid and the smallest (non-trivial) all-benzenoid (apart from benzene). By compressed it is meant that two neighbouring triphenylenes share one (full) hexagon. This shared hexagon is an **A** (resp. **L**) hexagon for the so-called angular (resp. linear) compression.

The angular and linear compressions are illustrated in Fig. 1. In Fig. 2 a larger all-benzenoid of the class under consideration is depicted. Its **LA**-sequence is **LALLLA**. An **LA**-sequence can always be reversed for the same system.

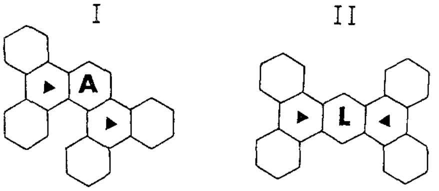


Fig. 1. Two angularly (I) and two linearly (II) compressed triphenylenes. The centres of each triphenylene are marked by black triangles

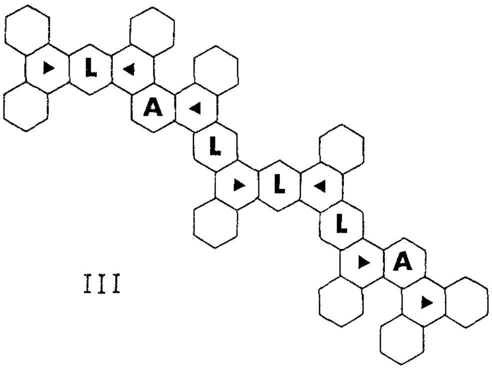


Fig. 2. A catacondensed all-benzenoid with an unbranched backbone

Fragmentation Matrix

Let U be a catacondensed all-benzenoid with unbranched backbone as was described above. The fragmentation matrix associated with U is

$$\mathbf{U} = \begin{bmatrix} U_0 & U_1 \\ U_2 & U_3 \end{bmatrix}, \tag{1}$$

where the elements are the Kekulé structure counts of certain fragments of U; $K\{\mathrm{U}_i\} = U_i$. Let E_1 and E_2 be the two terminal (empty) hexagons of the backbone, while F_1 and F_2 are the two terminal (full) hexagons adjacent to E_1 and E_2, respectively. Then the fragments are obtained by deleting certain hexagons from $\mathrm{U}: \mathrm{U}_0 = \mathrm{U} - F_1 - F_2$, $\mathrm{U}_1 = \mathrm{U}_0 - E_2$, $\mathrm{U}_2 = \mathrm{U}_0 - E_1$, and $\mathrm{U}_3 = \mathrm{U}_1 - E_1 = \mathrm{U}_2 - E_2$.

This definition is analogous to a matrix previously considered for unbranched catacondensed benzenoids [25–28].

Kekulé Structure Counts

The K number of unbranched catacondensed benzenoids have been studied by many investigators; see the monograph on Kekulé structures [13] and references cited therein, in addition to several more recent works [26–37]. In some of these works the fragmentation matrix [26–28, 34] or transfer matrix [33] is employed.

An application of the fragmentation matrix to the catacondensed all-benzenoids with unbranched backbone (U) yields for the K number $U = K\{\mathrm{U}\}$,

$$U = \mathrm{Tr}(\mathbf{U}) + \mathrm{Tr}(\mathbf{j}\mathbf{U}) = U_0 + U_1 + U_2 + U_3 . \tag{2}$$

Here $\mathbf{j}$ is defined by

$$\mathbf{j} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} . \tag{3}$$

Let the fragmentation matrix for the smallest all-benzenoid unit, viz. triphenylene, be denoted by $\boldsymbol{\alpha}$. It is

$$\boldsymbol{\alpha} = \begin{bmatrix} 3 & 2 \\ 2 & 2 \end{bmatrix} . \tag{4}$$

For the two systems I and II (Fig.1) one has

$$\mathbf{U}_{\mathrm{I}} = \boldsymbol{\alpha}^2 = \begin{bmatrix} 13 & 10 \\ 10 & 8 \end{bmatrix} \tag{5}$$

and

$$\mathbf{U}_{\mathrm{II}} = \boldsymbol{\alpha}\mathbf{j}\boldsymbol{\alpha} = \boldsymbol{\alpha}\boldsymbol{\beta} = \begin{bmatrix} 12 & 10 \\ 10 & 8 \end{bmatrix} , \tag{6}$$

respectively. Here

$$\boldsymbol{\beta} = \mathbf{j}\boldsymbol{\alpha} = \begin{bmatrix} 2 & 2 \\ 3 & 2 \end{bmatrix} . \tag{7}$$

Also for the more complex systems like III (Fig. 2) the fragmentation matrix is a product of $\boldsymbol{\alpha}$'s and $\boldsymbol{\beta}$'s. The general rule is very simple: In the **LA**-sequence, replace every **A** by $\boldsymbol{\alpha}$ and every **L** by $\boldsymbol{\beta}$, and pre-multiplicate with $\boldsymbol{\alpha}$. In our example

$$\mathbf{U}_{\mathrm{III}} = \boldsymbol{\alpha}\boldsymbol{\beta}\boldsymbol{\alpha}\boldsymbol{\beta}^3\boldsymbol{\alpha} . \tag{8}$$

According to Eq. (3) the K number in this particular example is

$$U_{\mathrm{III}} = \mathrm{Tr}\,(\boldsymbol{\alpha}\boldsymbol{\beta}\boldsymbol{\alpha}\boldsymbol{\beta}^3\boldsymbol{\alpha}) + \mathrm{Tr}\,(\boldsymbol{\beta}^2\boldsymbol{\alpha}\boldsymbol{\beta}^3\boldsymbol{\alpha}) . \tag{9}$$

Extension to Thin Pericondensed All-Benzenoids

The class of catacondensed all-benzenoids considered above is straightforwardly extended to "thin" pericondensed all-benzenoids by incorporating the unit IV, dibenzo[*fg*,*op*]naphthacence (Fig. 3). Units IV can be either angularly or linearly compressed with triphenylene or with each other. The members of this class are said to be thin (pericondensed) because they only can have isolated pairs of adjacent internal vertices, one pair for each pyrene fragment.

The two P_2-mode (full) hexagons from IV are by definition deleted under the creation of the backbone. We still consider all-benzenoid systems where the backbones are unbranched catacondensed benzenoids only. But now the backbone may have segments of four or more hexagons, where the characteristic configuration is *FEEF*.

Let π be the fragmentation matrix for IV. It is

$$\pi = \begin{bmatrix} 6 & 5 \\ 5 & 4 \end{bmatrix} \tag{10}$$

IV

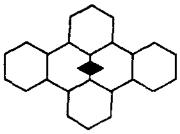


Fig. 3. The dibenzo[*fg*, *op*]naphthacene unit. The centre of it is marked by a black rhomb

and we also put

$$\boldsymbol{\rho} = \mathbf{j}\boldsymbol{\pi} = \begin{bmatrix} 5 & 4 \\ 6 & 5 \end{bmatrix} . \tag{11}$$

The rules for Kekulé structure counts are straightforwardly generalized to the thin pericondensed all-benzenoids under consideration. For the system V of Fig. 4, for instance, the fragmentation matrix is

$$\mathbf{U}_V = \boldsymbol{\pi\alpha}\mathbf{j}\boldsymbol{\pi}^2\mathbf{j}\boldsymbol{\alpha}^2 = \boldsymbol{\pi\alpha\rho\pi\beta\alpha} \tag{12}$$

and the Kekulé structure count

$$U_V = \mathrm{Tr}\,(\boldsymbol{\pi\alpha\rho\pi\beta\alpha}) + \mathrm{Tr}\,(\boldsymbol{\rho\alpha\rho\pi\beta\alpha}) . \tag{13}$$

A class of all-benzenoids sometimes called "pyrenes on a string" has been considered by several investigators [10, 12, 13, 15 – 17]. Its member, P(*n*), may in the present terminology be characterized as *n* linearly compressed units IV. Hence its fragmentation matrix ($\mathbf{U}_p$) is

$$\mathbf{U}_p = \boldsymbol{\pi\rho}^{n-1} \tag{14}$$

and the Kekulé structure count

$$K\{\mathrm{P}(n)\} = \mathrm{Tr}\,(\boldsymbol{\pi\rho}^{n-1}) + \mathrm{Tr}\,(\boldsymbol{\rho}^{n}) . \tag{15}$$

An explicit formula for $K\{\mathrm{P}(n)\}$ has been reported previously [10, 13, 16, 17], but not the form (15). A somewhat more explicit version of (15) reads

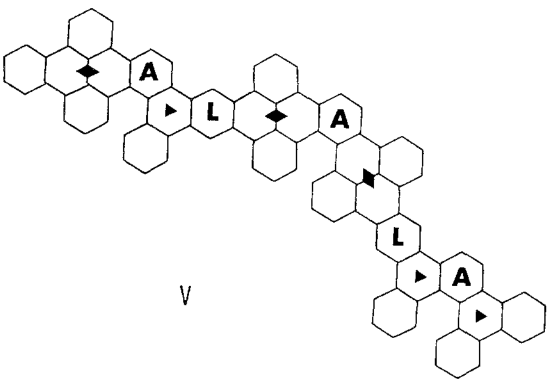
$$K\{\mathrm{P}(n)\} = [1 \quad 1] \begin{bmatrix} 5 & 4 \\ 6 & 5 \end{bmatrix}^n \begin{bmatrix} 1 \\ 1 \end{bmatrix} . \tag{16}$$

Generalized Fragmentation Matrix

General Theory

The determinant of a fragmentation matrix has proved to be of some interest. For an unbranched catacondensed benzenoid, a single chain of *s* segments, it has been found [25 – 27, 34] $(-1)^s$ for the pertinent determinant. Some more general considerations are given in the following.

Let X be an arbitrary molecular graph (not necessarily benzenoid), and e and f its two non-incident free edges. Let A and B be two arbitrary fragments fused



V

Fig. 4. A thin pericondensed all-benzenoid with an unbranched backbone

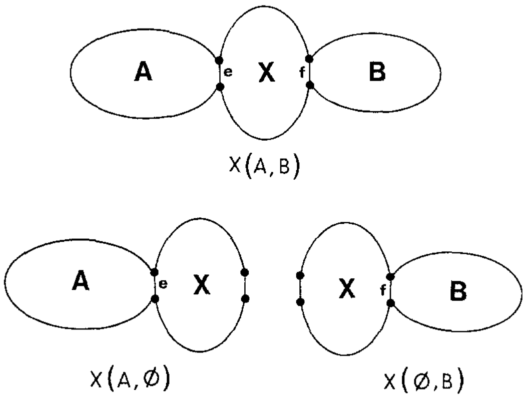


Fig. 5. Definition of X (A, B) and its two fragments, X (A, ∅) and X (∅, B)

with X into X (A, B) as shown in Fig. 5. The graphs X (A, ∅) and X (∅, B) are also produced as shown in Fig. 5, while X (∅, ∅) = X. Consider the determinant

$$D = \begin{vmatrix} K\{X(A,B)\} & K\{X(A,\emptyset)\} \\ K\{X(\emptyset,B)\} & K\{X(\emptyset,\emptyset)\} \end{vmatrix} . \tag{17}$$

Then

$$D = K\{A_e\}\, K\{B_f\} = \begin{vmatrix} K\{X\} & K\{X_f\} \\ K\{X_e\} & K\{X_{ef}\} \end{vmatrix} . \tag{18}$$

Here X_e and X_f denote the subgraphs obtained by deletion of e, f, respectively, from X, while X_{ef} indicates the deletion of both e and f. Similarly A_e is obtained from A by deleting the edge e; B_f is defined analogously.

Annelation of Single Linear Chains

Important special cases emerge when A and B are single linear chains of a and b hexagons, respectively. Two cases are distinguished: linear and angular annelation. For the sake of simplicity we shall assume that both fragments A and B are either linearly or angularly annelated to X.

(a) *Linear Annelation.* The system is depicted in Fig. 6. It corresponds to

$$K\{A_e\} = a, \qquad K\{B_f\} = b . \tag{19}$$

For $a \neq 0$, $b \neq 0$:

$$K\{X(a,b)\} = (a+1)(b+1)K\{X\} - a(b+1)K\{X_e\} - b(a+1)K\{X_f\} + abK\{X_{ef}\} . \tag{20}$$

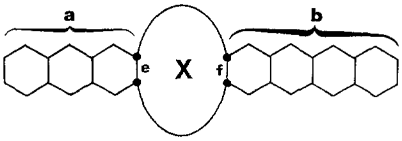


Fig. 6. Linear annelation of two single linear chains to X : X (*a*, *b*)

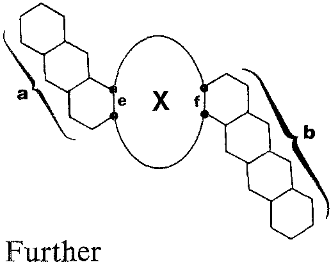


Fig. 7. Angular annelation of two single linear chains X : X′ (a, b)

Further

$$K\{\mathrm{X}(a,0)\} = (a+1)K\{\mathrm{X}\} - aK\{\mathrm{X_e}\} \qquad (a \neq 0), \tag{21}$$

$$K\{\mathrm{X}(0,b)\} = (b+1)K\{\mathrm{X}\} - bK\{\mathrm{X_f}\} \qquad (b \neq 0), \tag{22}$$

$$K\{\mathrm{X}(0,0)\} = K\{\mathrm{X}\}. \tag{23}$$

The determinant in question is

$$D = \begin{vmatrix} K\{\mathrm{X}(a,b)\} & K\{\mathrm{X}(a,0)\} \\ K\{\mathrm{X}(0,b)\} & K\{\mathrm{X}(0,0)\} \end{vmatrix}. \tag{24}$$

On expanding (24) by means of (20)−(23) it is easily verified that

$$D = ab \begin{vmatrix} K\{\mathrm{X}\} & K\{\mathrm{X_f}\} \\ K\{\mathrm{X_e}\} & K\{\mathrm{X_{ef}}\} \end{vmatrix}. \tag{25}$$

in consistency with (18) and (19).

(b) *Angular Annelation.* The system is depicted in Fig. 7. In this case it corresponds to

$$K\{\mathrm{A_e}\} = K\{\mathrm{B_f}\} = 1. \tag{26}$$

Now for $a \neq 0$, $b \neq 0$:

$$K\{\mathrm{X}'(a,b)\} = (a+1)(b+1)K\{\mathrm{X}\} - (a+1)K\{\mathrm{X_f}\} \\ - (b+1)K\{\mathrm{X_e}\} + K\{\mathrm{X_{ef}}\}. \tag{27}$$

Further

$$K\{\mathrm{X}'(a,0)\} = (a+1)K\{\mathrm{X}\} - K\{\mathrm{X_e}\} \qquad (a \neq 0), \tag{28}$$

$$K\{\mathrm{X}'(0,b)\} = (b+1)K\{\mathrm{X}\} - K\{\mathrm{X_f}\} \qquad (b \neq 0), \tag{29}$$

The determinant to be considered is

$$D' = \begin{vmatrix} K\{\mathrm{X}'(a,b)\} & K\{\mathrm{X}'(a,0)\} \\ K\{\mathrm{X}'(0,b)\} & K\{\mathrm{X}'(0,0)\} \end{vmatrix}. \tag{30}$$

By means of (23) and (27)−(29) it is now obtained

$$D' = \begin{vmatrix} K\{\mathrm{X}\} & K\{\mathrm{X_f}\} \\ K\{\mathrm{X_e}\} & K\{\mathrm{X_{ef}}\} \end{vmatrix}, \tag{31}$$

in consistency with (18) and (26). It is most interesting that D' is independent of a and b, and depends only on X and the choice of the edges e and f.

Take the example of X = pyrene, where the edges of annelation are chosen as

VI

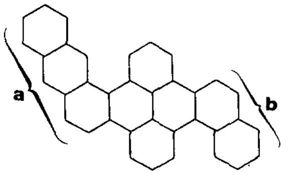


Fig. 8. Angular annelation of two single linear chains to pyrene

in Fig. 8. Then $K\{X\}=6$, $K\{X_e\}=K\{X_f\}=1$, $K\{X_{ef}\}=0$; hence $D'=-1$. In the particular example (VI) of Fig. 8 ($a=3$, $b=2$) one has

$$D'_{\mathrm{VI}}=\begin{vmatrix}65 & 23\\ 17 & 6\end{vmatrix}=-1\,. \qquad (32)$$

Formulas (25) and (31) are more or less straightforward special cases of the identity (18). On the other hand, the identity (18) was recently shown [38] to be a special case of some substantially more general graph-theoretical results.

Simple Fragmentation Matrices

For the simple fragmentation matrices defined in the preceding sections, viz. $\boldsymbol{\alpha}$ for triphenylene and π for dibenzo[*fg*, *op*]naphthacene (IV), one has, in consistency with the theory of the present section,

$$\det\boldsymbol{\alpha}=\begin{vmatrix}3 & 2\\ 2 & 2\end{vmatrix}=2 \qquad (33)$$

and

$$\det\pi=\begin{vmatrix}6 & 5\\ 5 & 4\end{vmatrix}=-1\,. \qquad (34)$$

Classes of Catacondensed and Thin Pericondensed All-Coronoids

Definitions and Some Topological Properties

A primitive coronoid is synonymous with an unbranched catacondensed coronoid. Catacondensed all-coronoids can be constructed so that their backbones are primitive coronoids. The systems are very similar to the catacondensed all-benzenoids with unbranched backbones. Thus: (a) the backbones consist of 2-segments and 3-segments only; (b) the backbone has alternating *E* and *F* hexagons, but now there is no terminal hexagon in the backbone; (c) its 3-segments have the *EFE* configuration; (d) an **LA**-sequence determines the number of normal Kekulé structures, a concept to be defined in the next paragraph. Now any cyclic permutation of the **LA**-sequence can be taken, in addition to its reverse.

The class is again extended straightforwardly to the so-called thin pericondensed all-coronoids by allowing for the dibenzo[*fg*,*op*]naphthacene (IV; see Fig. 3) unit.

A member of the all-coronoid class under consideration is depicted in Fig. 9.

VII

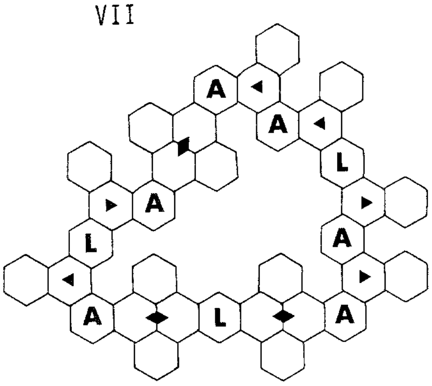


Fig. 9. A thin pericondensed all-coronoid, where the backbone is a primitive coronoid

Number of Normal Kekulé Structures

Polansky and Gutman [6] distinguished between normal and anomalous Kekulé structures of an all-benzenoid. The same viewpoint is presently adapted to all-coronoids. Let the three edges of an empty hexagon (E) which are not shared with full hexagons be referred to as the ε-bonds. In any E of a normal Kekulé structure the ε-bonds are either all double or they are all single. The corresponding hexagons are referred to as starred and unstarred, respectively. Also in all-coronoids we define a normal Kekulé structure as being characterized by possessing only starred and unstarred E hexagons, while no other bonding schemes are present.

The number of normal Kekulé structures of an all-coronoid of the considered class is obtained as the trace of a matrix product, which is created by the following rules:

(i) Start at an arbitrary place and go around the corona hole in an arbitrary direction.
(ii) For every triphenylene centre (marked by black triangle), set $\boldsymbol{\alpha}$.
(iii) For every pyrene centre (marked by black rhomb), set $\boldsymbol{\pi}$.
(iv) For every **L**, set **j**.

In the example of Fig. 9 we have, for instance,

$$K_{\text{norm; VII}} = \mathrm{Tr}\,(\boldsymbol{\pi}\mathbf{j}\boldsymbol{\pi}\boldsymbol{\alpha}^2\mathbf{j}\boldsymbol{\alpha}^2\boldsymbol{\pi}\boldsymbol{\alpha}\mathbf{j}\boldsymbol{\alpha}) = \mathrm{Tr}\,(\mathbf{j}\boldsymbol{\pi}\boldsymbol{\alpha}^2\mathbf{j}\boldsymbol{\alpha}^2\boldsymbol{\pi}\boldsymbol{\alpha}\mathbf{j}\boldsymbol{\alpha}\boldsymbol{\pi}) = 8565184\,. \qquad (35)$$

Number of Anomalous Kekulé Structures

The anomalous Kekulé structures of an all-coronoid have empty hexagons with other bonding schemes than the starred and unstarred types. For an all-coronoid of the type considered here the anomalous Kekulé structures are determined uniquely by the following rules:

(i) Select an arbitrary **A** or **L** hexagon.
(ii) Select in this hexagon two parallel edges, one on the outer and one on the inner perimeter, and assign to them either (a) single/single or (b) double/double bonds.
(iii) Continue to assign single and double bonds as far as they are determined.
(iv) Observe the hexagons in which the bonding is not determined, and let their number be τ.

(v) The number of anomalous Kekulé structures, K_{anom}, is given by

$$K_{\mathrm{anom}} = 2^{\tau} + 2^{T-\tau}, \tag{36}$$

where T is the number of triphenylene centres in the whole system.

The effect of the above prescription is that all bonds in the backbone become determined and also in the P_2-mode (full) hexagons, while the L_{I}-mode (full) hexagons may have either determined or undetermined bonds. The two alternatives (a) and (b) under point (ii) are complementary in the sense that the bonds in an L_{I}-mode hexagon become determined by (b) if they are undetermined by (a) and vice versa. Therefore it is sufficient to go through the process only for one of the alternatives (a) and (b). In order to make the number τ unique we adopt the convention $\tau \leqslant T-\tau$.

The described procedure is illustrated for VII in Fig. 10. In this case $\tau = 3$, $T = 6$, and therefore

$$K_{\mathrm{anom;\,VII}} = 2 \times 2^3 = 16\,. \tag{37}$$

Pyrenes on a Ring

Definition and Notation

The class "pyrenes on a ring" is a subclass of the thin pericondensed all-coronoids considered here. It is similar to the pyrenes on a string (see above) inasmuch as the members consist of the units IV, but now they are angularly compressed rather than linearly. A member of the class with n pyrene units is designated by the symbol

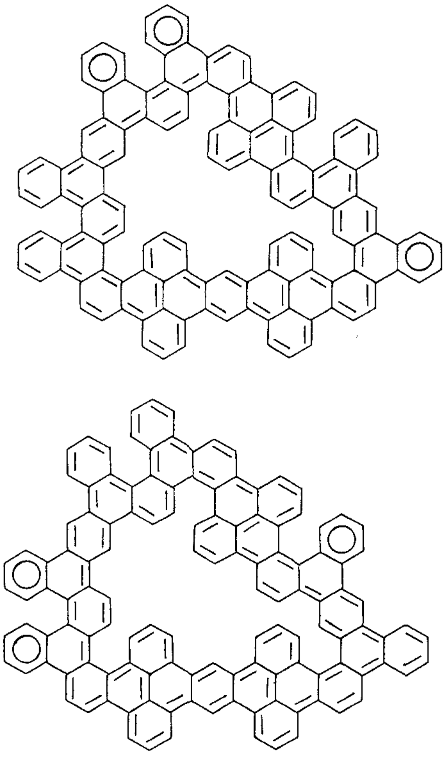


Fig. 10. The anomalous Kekulé structures in the system of Fig. 9 (VII). Inscribed circles into hexagons represent aromatic sextets

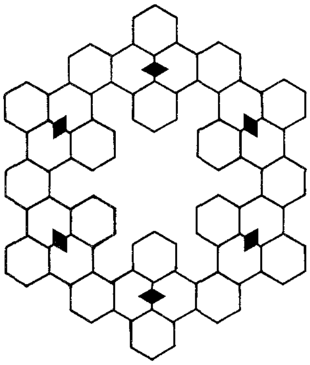


Fig. 11. The smallest member of pyrenes on a ring, P^0 (6)

$P^0(n)$. Fig. 11 shows the example for $n = 6$. For the Kekulé structure count we use the notation

$$K\{P^0(n)\} = P^0_{\text{norm}}(n) + P^0_{\text{anom}}(n). \tag{38}$$

The anomalous Kekulé structures (last term) are found as in the above algorithm, starting with an A hexagon, which links two pyrene units together.

For the number of normal Kekulé structures, $P^0_{\text{norm}}(n)$, the method of fragmentation gives

$$P^0_{\text{norm}}(n) = K\{Q_2(n)\} + K\{Q''(n)\}, \tag{39}$$

wherein the classes on the right-hand side, viz. $Q_2(n)$ and $Q''(n)$ are treated elsewhere in detail [13]. One finds by certain substitutions

$$P^0_{\text{norm}}(n) = \tfrac{1}{2}[K\{Q(n)\} + K\{Q(n-2)\}], \tag{40}$$

where another class, $Q(n)$, is introduced; it was referred to as angularly annelated pyrenes. The following explicit formula for the Kekulé structure count of $Q(n)$ was deduced [13],

$$K\{Q(n)\} = (1/\sqrt{26})[(5+\sqrt{26})^{n+1} - (5-\sqrt{26})^{n+1}]. \tag{41}$$

By means of this expression and Eq. (40) it was attained at the remarkably simple result

$$P^0_{\text{norm}}(n) = (5+\sqrt{26})^n + (5-\sqrt{26})^n. \tag{42}$$

Having the characteristic equation in mind, a recurrence relation for the number of normal Kekulé structures is readily obtained from Eq. (42),

$$P^0_{\text{norm}}(n+2) = 10\,P^0_{\text{norm}}(n+1) + P^0_{\text{norm}}(n). \tag{43}$$

The formula (42) gives positive integer values of $P^0_{\text{norm}}(n)$ for all integer $n \geqslant 0$. For $n \geqslant 1$ all the systems can be realized either as coronoids or "non-coronoids", the latter still consisting of hexagons, but some of them inevitably deformed when drawn in a plane. Such cases have been studied in detail in connection with primitive coronoids [21], and could appropriately be termed "primitive non-coronoids". For the sake of illustration two versions of the P^0 (1) graph are depicted in Fig. 12. Also for the non-coronoids of this kind the Kekulé structures are well defined, and Eq. (42) reproduces their numbers.

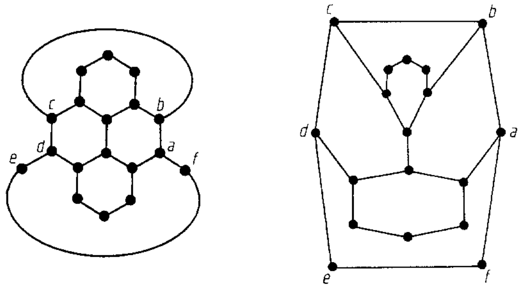


Fig. 12. The P^0 (1) graph

The number of anomalous Kekulé structures is 2 for every $P^0(n)$ which is a coronoid ($n=6$, 10, 12, 14, ...). For the $P^0(n)$ non-coronoids it must be observed that the anomalous Kekulé structures disappear whenever n is odd because of the presence of odd-membered perimeters in those cases. Therefore

$$P^0_{\text{anom}}(n) = 1 + (-1)^n. \tag{44}$$

Table 1 shows the numerical values consistent with Eqs. (42) and (44) for $0 \leqslant n \leqslant 10$.

It is interesting that the numbers (42) are values of graph polynominal associated with the cycle C_n. More precisely,

$$P^0_{\text{norm}}(n) = \tilde{\alpha}(C_n \,|\, 10), \tag{45}$$

when

$$\alpha(C_n \,|\, n) = i^{-n}\alpha(C_n \,|\, ix) \tag{46}$$

and $\alpha(C_n|x)$ is used to denote the matching polynomial of the cycle [39–42]. One has explicitly

$$\alpha(C_n \,|\, x) = \left(\frac{x + \sqrt{x^2-4}}{2}\right)^n + \left(\frac{x - \sqrt{x^2-4}}{2}\right)^n \tag{47}$$

Table 1. Numerical values for $P^0_{\text{norm}}(n)$ and $P^0_{\text{anom}}(n)$, which include the Kekulé structure counts for pyrenes on a ring when $n=6$ and 10

n	$P^0_{\text{norm}}(n)$	$P^0_{\text{anom}}(n)$
0	2	2
1	10	0
2	102	2
3	1030	0
4	10402	2
5	105050	0
6	1060902	2
7	10714070	0
8	108201602	2
9	1092730090	0
10	11035502502	2

and

$$\bar{\alpha}(\mathrm{C}_n \mid x) = \left(\frac{x+\sqrt{x^2+4}}{2}\right)^n + \left(\frac{x-\sqrt{x^2+4}}{2}\right)^n, \tag{48}$$

where the latter equation (48) immediately gives (42) on inserting $x = 10$.

This brings us naturally to the next section, where the polynomial formulas for Kekulé structure counts of thin pericondensed all-coronoids of the considered type are treated in general.

Polynomial Formulas for Catacondensed and Thin Pericondensed All-Coronoids with Repeated Units

After the first studies of some classes of primitive coronoids with repeated units [21, 22, 43–45] some further systematic investigations resulted in interesting polynomial formulas for their Kekulé structure counts [25–28, 46, 47].

In the present work the same approach is applied to the catacondensed and thin pericondensed all-coronoids.

Let u denote a unit, which is a catacondensed or thin pericondensed benzenoid according to the definitions above. Let n isomorphic or isoarithmic units u be either angularly or linearly compressed into a coronoid and call it $\mathrm{C}^{(n)}$. In the following we shall treat the number of normal Kekulé structures, say $C^{(n)}_{\mathrm{norm}}$, for such a system, which is said to have n repeated units.

Associated Benzenoid

Let an all-coronoid of the considered type be split at an **A** or an **L** hexagon. Hereby an all-benzenoid is created so that the **A** or **L** hexagon is used twice for the purpose of constituting two terminal full hexagons, one at each end of the all-benzenoid system. This is an all-benzenoid associated with the original all-coronoid. Let this be denoted by U^A or U^L, depending on weather the splitting was executed at an **A** or an **L** hexagon, respectively. Let also the corresponding fragmentation matrices be denoted by $\mathbf{U}^A$ and $\mathbf{U}^L$, respectively. Then for the number of normal Kekulé structures of the all-coronoid system one has

$$C_{\mathrm{norm}} = \mathrm{Tr}\,(\mathbf{U}^A) = \mathrm{Tr}\,(\mathbf{j}\mathbf{U}^L)\,. \tag{49}$$

The Case of One Unit

The above analysis reflects a treatment of $\mathrm{C}^{(n)}$ with $n = 1$. In this case it is of course inadequate to speak about one "repeated" unit. If the unit is u^A or u^L it can immediately be identified with U^A or U^L of the preceding paragraph, and we may write

$$C^{(1)}_{\mathrm{norm}} = x\,, \tag{50}$$

where

$$x = \mathrm{Tr}\,(\mathbf{u}^A) = u_0^A + u_3^A \tag{51}$$

in the case of a splitting at an **A** hexagon, or

$$x = \mathrm{Tr}\,(\mathbf{j}\mathbf{u}^L) = u_1^L + u_2^L \tag{52}$$

for the splitting at **L**.

Angular Compression of n Units

For $\mathrm{C}^{(n)}$ with n angularly compressed (repeated) units one has

$$C_{\text{norm}}^{(n)} = \mathrm{Tr}\,[(\mathbf{u}^A)^n]\,. \tag{53}$$

Consider first the case of $n=2$. It is easily obtained that

$$C_{\text{norm}}^{(2)} = (u_0^A)^2 + 2u_1^A u_2^A + (u_3^A)^2\,, \tag{54}$$

and by substituting ${u_1}^A {u_2}^A$ with the aid of the determinant D of $\mathbf{u}^A$,

$$C_{\text{norm}}^{(2)} = (u_2^A)^2 + 2u_0^A u_3^A + (u_3^A)^2 - 2D\,. \tag{55}$$

Consequently,

$$C_{\text{norm}}^{(2)} = x^2 - 2D\,, \tag{56}$$

where x is given by Eq. (51).

Table 2 gives the polynomials for $C_{\text{norm}}^{(n)}$ up to $n=6$. It can be shown that these polynomials for $D=1$ coincide with $\alpha(\mathrm{C}_n\,|\,x)$, the matching polynomial for the cycle C_n; cf. Eq. (47).

The value of D is easily determined with the knowledge of the determinants for $\boldsymbol{\alpha}$ and $\boldsymbol{\pi}$; see Eqs. (33) and (34), respectively. In addition, we observe that

$$\det\mathbf{j} = -1, \qquad \det\boldsymbol{\beta} = -2, \qquad \det\boldsymbol{\rho} = 1\,. \tag{57}$$

Therefore

$$D = (-1)^{j+p}2^t\,. \tag{58}$$

Here, with reference to one unit u^A, j is the number of **L** hexagons, p is the number of pyrenes, and t the number of triphenylene centres.

Table 2. Polynomials for numbers of normal Kekulé structures of $\mathrm{C}^{(n)}$

n	Angular compression	Linear compression
	$C_{\text{norm}}^{(n)}$; $x = u_0^A + u_3^A$	$C_{\text{norm}}^{(n)}$; $x = u_1^L + u_2^L$
1	x	x
2	x^2-2D	x^2+2D
3	x^3-3Dx	x^3+3Dx
4	$x^4-4Dx^2+2D^2$	$x^4+4Dx^2+2D^2$
5	$x^5-5Dx^3+5D^2x$	$x^5+5Dx^3+5D^2x$
6	$x^6-6Dx^4+9D^2x^2-2D^3$	$x^6+6Dx^4+9D^2x^2+2D^3$

Linear Compression of n Units

Assume now that $C^{(n)}$ has n linearly compressed (repeated) units. Then

$$C^{(n)}_{\mathrm{norm}} = \mathrm{Tr}\,[(\mathbf{j}\mathbf{u}^L)^n]\,. \tag{59}$$

Consider again the case of $n=2$. In this case one obtains

$$C^{(2)}_{\mathrm{norm}} = (u^L_1)^2 + 2u^L_0 u^L_3 + (u^L_2)^2 \tag{60}$$

and with the aid of the determinant D of $\mathbf{u}^L$,

$$C^{(2)}_{\mathrm{norm}} = (u^L_1)^2 + 2u^L_1 u^L_2 + (u^L_2)^2 + 2D\,. \tag{61}$$

Consequently,

$$C^{(2)}_{\mathrm{norm}} = x^2 + 2D\,, \tag{62}$$

where x now is given by Eq. (52).

Table 2 includes the polynomials also of this kind up to $n=6$. For $D=1$ they coincide with $\bar{\alpha}\,(C_n\,|\,x)$, the class of polynomials related to the matching polynomials for the cycle C_n; cf. Eq. (48).

The value of D may also in this case be determined by Eq. (58), where p and t are the numbers of pyrenes and triphenylene centres, respectively, in the unit u^L. This unit, in the all-coronoid, spans from one **L** hexagon to another **L**. In the number j of Eq. (58) either both of these **L** hexagons should be counted or both should be omitted.

Some Examples

Example 1. Interpret the system of Fig. 11 as six angularly compressed units, for which $\mathbf{u}^A=\boldsymbol{\pi}$. Hence $x=\mathrm{Tr}\,(\boldsymbol{\pi})=10$; cf. Eq. (10). Furthermore, $D=-1$ in consistency with both Eq. (34) and Eq. (58), where $j=0$, $p=1$, and $t=0$ is to be inserted. Now the last polynomial in the first column of Table 2 reproduces P^0_{norm} (6) of Table 1.

Example 2. Consider the system of Fig. 13, which consists of three angularly compressed units, where

$$\mathbf{u} = \boldsymbol{\alpha}\mathbf{j}\boldsymbol{\pi} = \boldsymbol{\alpha}\mathbf{p} = \begin{bmatrix} 27 & 22 \\ 22 & 18 \end{bmatrix}. \tag{63}$$

Hence $x=45$ and $D=2$, which should be inserted into the third polynomial in the first column of Table 2. It yields $C_{\mathrm{norm}}=90\,855$. Together with $C_{\mathrm{anom}}=1+2^3=9$ one arrives at the total number of 90 864 Kekulé structures.

Example 3. In the system of Fig. 14 one has six linearly compressed units, for which the fragmentation matrix is the same as in the above example; see Eq. (63). But now $x=44$, while $D=2$ as above. This determinant value is consistent with Eq. (58), where $j=1$ or 3, $p=1$, and $t=1$. The values of x and D are now inserted into the last polynomial of the second column of Table 2 and yield $C_{\mathrm{norm}}=7\,301\,360\,720$, which together with $C_{\mathrm{anom}}=2\times 2^3=16$ gives a total of 7 301 360 736 Kekulé structures.

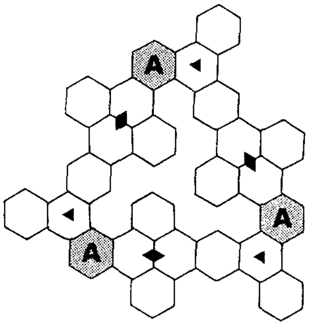


Fig. 13. A thin pericondensed all-coronoid with three repeated units. The shaded **A** hexagons are shared by neighbouring units

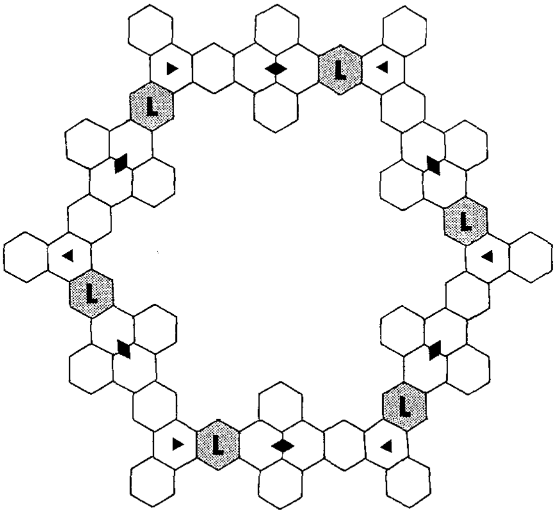


Fig. 14. A thin pericondensed all-coronoid with six repeated units. The shaded **L** hexagons are shared by neighbouring units

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