match no. 24 pp. 289-309 1989

DECOMPOSITION THEOREMS FOR CALCULATING THE NUMBER OF KEKULÉ STRUCTURES IN CORONOIDS FUSED VIA PERINAPHTHYL UNITS

Ioan Tomescu

Department of Mathematics, University of Bucharest,

Str. Academiei 14, 70109 Bucharest, Roumania

and

Alexandru T. Balaban

Polytechnic Institute, Organic Chemistry Department,

Splaiul Independenţei 313, 76206 Bucharest, Roumania

(Received: March 1988)

Abstract. The number K of Kekulé structures (perfect matchings) in coronoids with cata-condensed appendages possessing branching points via perinaphthyl units oriented in antiparallel manner is determined as an additive function of the number K_1 of perfect matchings in the string structures into which the coronoid is decomposable. For coronoids with perinaphthyl branching units oriented in parallel manner in the same string structure, the number K of Kekulé structures results as a multiplicative function of the number K_1 of perfect matchings in the string structures. Procedures for decomposing coronoids of this type into string structures are defined recursively.

Introduction

The Gordon-Davison algorithm[1] operates efficiently for determining the number K of Kekulé structures or of perfect matchings for any linearly or angularly cata-condensed polycyclic aromatic hydrocarbon (catafusenic benzenoid structure).The same algorithm can be applied to branched catafusenes,where branchings are as in triphenylene.Such branchings constitute no problem for the Gordon-Davison algorithm or for improved algorithms proposed more recently by Cyvin and Gutman[2,3],by Zivković,Trinajstić, Randić and their coworkers[4-6].Finally,mention should be made of the powerful transfer matrix methods developed by Klein et al.[7] for enumerating Kekulé structures of benzenoids.

A cata-condensed system consisting of an open chain of hexagons such that every two adjacent hexagons have exactly one common edge and its dualist graph[8,9] is a path will be called a string structure (SS) (e.g. as will be seen for graphs G_1,G_2, G_3 of Figure 12).It follows that in a SS every hexagon is adjacent to at most two other hexagons which must be nonadjacent. We shall consider that all structures in this paper (string, parallel,series-parallel,coronoid) are composed from regular, pairwise congruent hexagons lying in the same plane.

For simplifying the discussion and the figures,we shall adopt a unique orientation of benzenoid rings in polyhexes, namely that in which two edges of each hexagon are vertical. In this case one of the edges in each triangle of the dualist graph of perifusenes is horizontal.All figures in the present paper obey this convention.

A decomposition theorem for coronoids with perinaphthyl branching units oriented in antiparallel manner

We shall describe a method for computing the Kekulé number K(G) of a benzenoid graph G based on graph decomposition whenever G can be decomposed into string structures with numbers of perfect matchings which can be calculated via the Gordon-Davison or other algorithms. Such graphs are obtained from string structures and some copies of the perinaphthyl group (Figure 1 a) or b)) and may be defined recur-

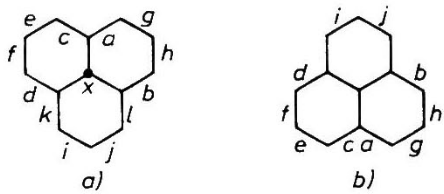


Fig.1

sively as follows:

Every parallel structure (PS) is either:

i) a string structure or

ii) it is composed from two perinaphthyl groups (upper and lower), two parallel structures L_1 and L_2 and two string structures L_3 and L_4 as in Figure 2; L_3 or L_4 or both may be empty. L_1 is annelated to the upper and lower perinaphthyl group through edges e or f, L_2 through g or h, and L_3 and L_4 through i or j, respectively (see Figure 1). The two perinaphthyl groups are oriented in antiparallel manner, i. e. as a) + b).

If L is a PS then the complexity of L, denoted by c(L) is defined as follows: c(L) = 1 if L is a string structure; $c(L) = c(L_1) + c(L_2)$ otherwise, if L verifies condition (ii) in the definition of a PS. For example, c(G) = 3 for G illustrated in Figure 11.

A perfect matching of a graph G is a subset M of the edge set of G such that: every vertex of G is incident to exactly one edge in M; any two distinct edges in M have no common extremity. The chemical analog of a perfect matching is constituted by the double bonds in a Kekulé structure.

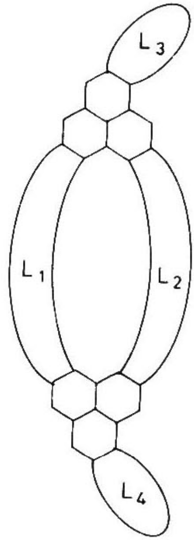


Fig.2

Therefore every edge that belongs to a perfect matching M of a graph G will be called double; the remaining edges of G are simple relatively to M and correspond to single bonds in the Kekulé structure.

The following property is useful for proving the main results of this paper.

Proposition 1. Consider a perfect matching M of a PS represented in Figure 2. If edges a or b of the lower perinaphthyl group (Figure 1a) are double then edges c and d of the same group are both simple relatively to M.

Proof: Suppose that the property does not hold, i.e., a or b are double and c or d are double also. Since a and c have a common extremity it follows that a and c cannot be simultaneously double. If a, b and d are double it follows that vertex x cannot be incident to any double edge which contradicts the assumption that M is a perfect matching. It remains to consider the cases: i) a,d are double and b,c simple ; ii) b,c are double and a,d simple; iii) b,d are double and a,c simple; iv) a is simple and b,c,d are double. Case iv) leads also to a contradiction since x cannot be incident to any double edge and cases i), ii) or iii) lead easily to the property that both k and l are simple.

If L_4 is empty this is not possible since in this case i, j cannot be both double.

Suppose now that L_4 is not empty and k, l are both simple. Since L_4 is annelated to the lower perinaphthyl group through i or j we shall prove by induction on the number of hexagons in L_4 that double edges in each hexagon in L_4 are as in Figure 3. Here arrows indicate the order and position of the annela - tion of each hexagon to the preceding and succeeding ones, by starting from the lower hexagon of the perinaphthyl group in Figure 1a), where k, l are both simple edges.

If the first hexagon of L_4 is annelated through edge i we obtain cases 10-12 and when the annelation is through j cases 16-18 of Figure 3.

Suppose that double edges are as in Figure 3 for any sequence of r hexagons in L_4 and consider the (r+1)-st hexagon H_{r+1} in L_4. If for example H_{r+1} is annelated as in case 13 of Figure

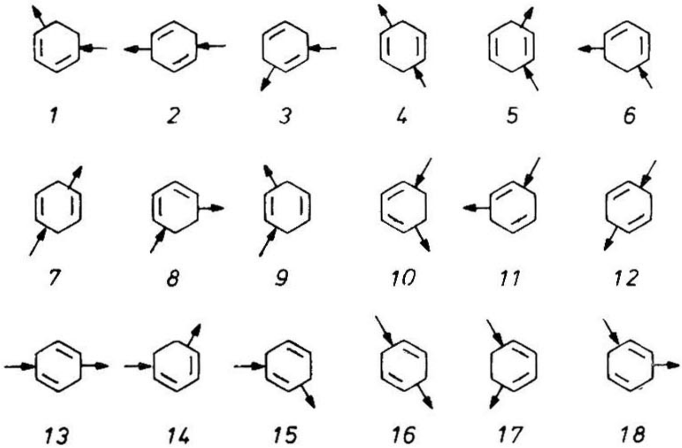


Fig.3

3,the pair H_r,H_{r+1} is as in Figure 4,cases a),b) or c).Double edges in H_r are deduced from cases 18,13 and 8,respectively, by the induction hypothesis.It follows that double edges in H_{r+1} in all cases a),b) and c) are as in case 13 from Figure 3 (we show this in Figure 4).The proof is similar for the remaining 17 cases of Figure 3.

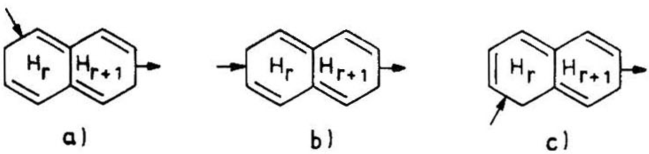


Fig.4

Since in all cases represented in Figure 3 the edge corresponding to the arrow going out of the hexagon contains a vertex which is not the extremity of a double edge,it follows that in the last hexagon of L_4 there exists a vertex which cannot be incident to a double edge,contradicting the definition of a perfect matching.This concludes the proof.

Proposition 2. If edges c and d of the lower perinaphthyl group (Figure 1a) are both simple,then the perfect matching of parallel structure L_1 in Figure 2 is uniquely determined and edges c and d of the upper perinaphthyl group (Figure 1b) are simple also.

Proof: One applies induction on the complexity $c(L_1)$. If $c(L_1) = 1$ then L_1 is a string structure.In this case one deduces by a reasoning similar to that from Proposition 1 that double edges occur in hexagons of L_1 in exactly the same way as indicated in Figure 3 (cases 1-18) since c and d are both simple,for any annelation of the first hexagon in L_1 through edges e or f.It remains to consider three cases when the last hexagon in L_1 is annelated through f and other three for e in the upper perinaphthyl group (Figure 1b). In cases of annelations through f,by taking into account cases 18, 13 and 8 for the last hexagon in L_1 one obtains that d,f,c are simple and e is double (Figure 5).The remaining

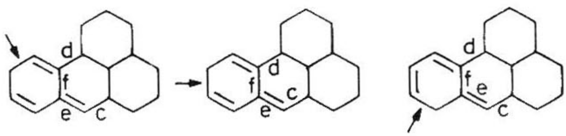


Fig.5

three cases are settled by a similar argument. It follows also that L_1 possesses a unique perfect matching.

Let now $c(L_1) \geq 2$ and suppose that the property is verified for any PS having a complexity of at most $c(L_1)-1$. It follows that L_1 is composed from two perinaphthyl groups A and B, two string structures L_5 and L_8 and two parallel structures L_6 and L_7 such that $c(L_6), c(L_7) < c(L_1)$ (Figure 6).

Because in the lower perinaphthyl group edges c and d are simple it follows that in L_5 double edges satisfy the cases described in Figure 3. Hence if the annelation is through edge j of group A one obtains three cases depicted in Figure 7 and in all these cases edges a,b,c,d of A are simple.

A similar situation occurs whenever the annelation of the last hexagon in L_5 is through edge i of A. Since L_6 and L_7 have a complexity less than $c(L_1)$ it follows by the induction hypothesis that L_6 and L_7 have a unique perfect matching and edges a,b,c,d of group B are simple (Figure 8).

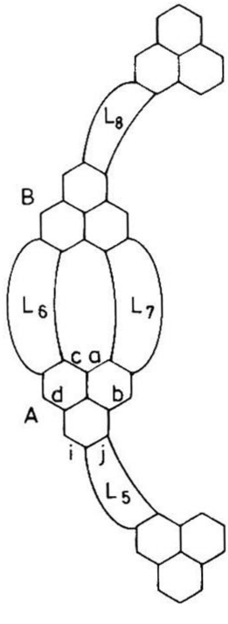


Fig.6

One deduces that edges p,q,r of B are double and that, in the string structure L_8, double edges follow again the patterns in

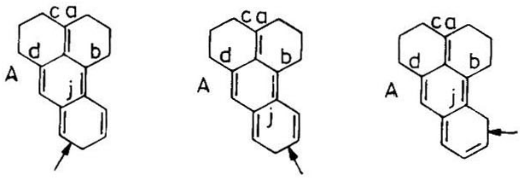


Fig.7

Figure 3. By an argument similar to that in the case $c(L_1) = 1$ one obtains that L_8 has a unique perfect matching and edges c,d in the upper peri-naphthyl group are simple.

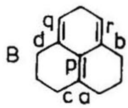


Fig.8

We are now in a position to state the first theorem.

Theorem 1. If G is the parallel structure depicted in Figure 2 that is decomposed into parallel structures G_1 and G_2 as in Figure 9, then

$$K(G) = K(G_1) + K(G_2)$$

Proof: If edges a or b in the lower perinaphthyl group are double it follows that c and d are both simple by Proposition 1. By Proposition 2 one obtains that L_1 has a unique perfect matching and edges c and d in the upper perinaphthyl group are both simple. Hence in this case the number of perfect matchings of G equals the difference between $K(G_2)$ and the number of perfect matchings of G_2 such that both a and b are simple edges. But every perfect matching of G_2 contains at least one edge among a and b as double edge. To show this suppose that

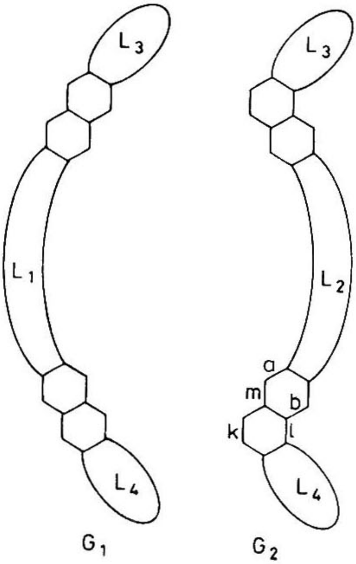


Fig.9

a and b are simple.It follows that m,k,l are double and by exhausting all available hexagons in L_4 one finds the patterns depicted in Figure 10.By the same argument as in the proof of Proposition 1 one obtains that the last hexagon of L_4 contains a vertex which is not incident to any double edge. Hence if a or b are double the number of perfect matchings of G is equal to $K(G_2)$.

Otherwise a and b in the perfect matchings of G are both simple,L_2 has a unique perfect matching and edges a and b in the upper perinaphthyl group are simple,hence in this case the number of perfect matchings of G is equal to $K(G_1)$.The

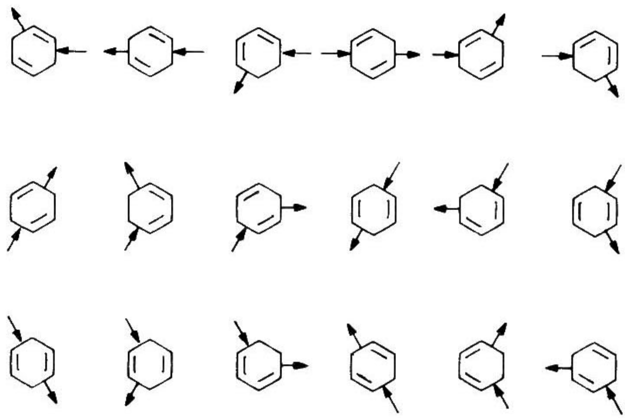


Fig.10

proof is complete.

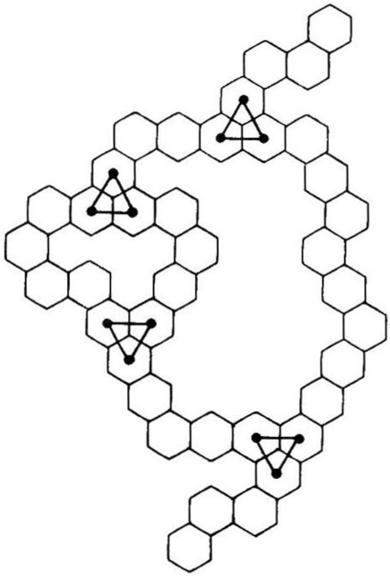
Note that the case when L_1 and L_2 were string structures and L_3 and L_4 were empty was obtained earlier by Randić, Henderson and Stout [10].

Hence by applying several times the theorem every parallel structure G can be decomposed into string structures $G_1, \ldots, G_r$ such that

$$K(G) = \sum_{i=1}^{r} K(G_i)$$

and every $K(G_i)$ may be computed by the Gordon-Davison algorithm or by a modification thereof. For any given orientation of the coronoid, the decomposition according to Theorem 1 is unique. An example is given for graphs G, G_1, G_2, G_3 in Figures 11 and 12.

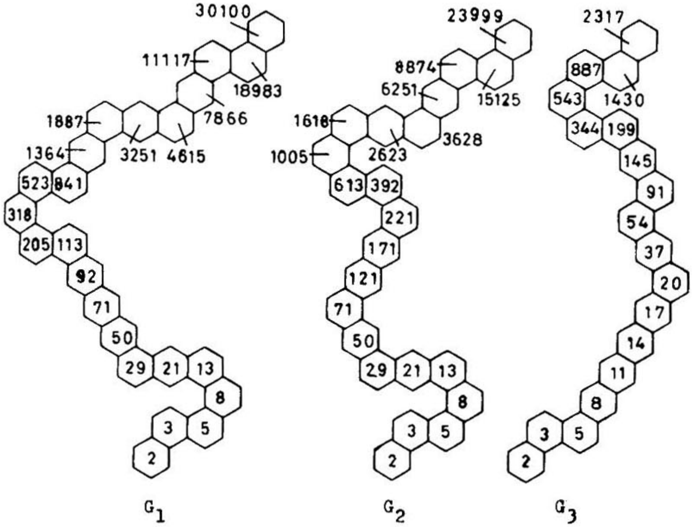
It will be observed, as it is emphasized in Figure 11 by the drawings of dualist subgraphs within each perinaphthyl



G

Fig.11

unit, that a peri-condensed benzenoid has a nonzero number K of Kekulé structures if (i) it has an even number of carbon atoms and if (ii) the numbers of upward and downward pointing triangles in its dualist graph are equal [9,11].
These are necessary but insufficient conditions (other structural requirements have also to be fulfilled, but a complete list of such requirements has not yet been compiled).
Conditions (i) and (ii) are met by all coronoids discussed in the present paper.



$K(G) = K(G_1) + K(G_2) + K(G_3) = 56,416$

Fig.12

For effecting the decomposition of a coronoid as required by Theorem 1,one has to proceed as follows: the coronoid has to be drawn so that two edges of each hexagon are vertical, and the lowest dualist triangular subgraph of a perinaphthyl unit appears pointing downward.Then the decomposition starts from any downwards "dangling" string of polyhexes (L_4 in Figure 2) and goes upward following a starting edge of the perinaphthyl dualist subgraph.Disconnections in the dualist graph occur at each horizontal edge of the triangular perinaphthyl dualist subgraph.At the upwards pointing perinaphthyl dualist subgraph, the same type of disconnection is performed at any horizontal edge of the triangular dualist subgraph. Thus for any pair of triangular dualist subgraphs we obtain a pair of PS. Should a new pair of triangular dualist subgraphs appear on any of the PS, the same procedure has to be applied recursively.

An extension to series-parallel structures

By analogy to series-parallel electrical networks one may define by recursion series-parallel structures (SPS) as follows:

Every SPS is either:

i) a string structure or it is composed from:

ii) two SPS L_1 and L_2 joined in parallel as in Figure 2, or

iii) two SPS L_6 and L_7 joined in series as in Figure 13 through L_5.

L_3, L_4 and L_5 are SS and they may be empty. In Figure 13 the thick lines symbolize a series-parallel polyhex which may contain any number of benzenoid rings; we depict only the upwards-pointing perinaphthyl subgraph of L_6 (there will be at least one downwards pointing perinaphthyl subgraph at a lower level according to our drawing convention), and only the downwards-pointing perinaphthyl subgraph of L_7.
The annelation for Figure 2 holds in the same ways as for PS; for Figure 13, L_5 is annelated to both the upper and the lower perinaphthyl groups through edges i or j (see Figure 1).

If L_1 and L_2 are decomposed into SS: $L_1^1, L_1^2, \ldots, L_1^r$;

$L_2^1, L_2^2, \ldots, L_2^s$ respectively (including two hexagons from each lower and upper perinaphthyl group), then the decomposition of SPS in Figure 2 contains r+s SS obtained by concatenating L_3 to L_4 via $L_1^1, \ldots, L_1^r, L_2^1, \ldots, L_2^s$, respectively.

Similarly, the decomposition of SPS in Figure 13 has rs SS by concatenating every $L_6^1, \ldots, L_6^r$ to every $L_7^1, \ldots, L_7^s$ via L_5 if $L_6^1, \ldots, L_6^r$ and $L_7^1, \ldots, L_7^s$ are, respectively, the decompositions of L_6 and L_7 into SS.

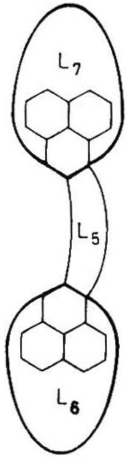


Fig.13

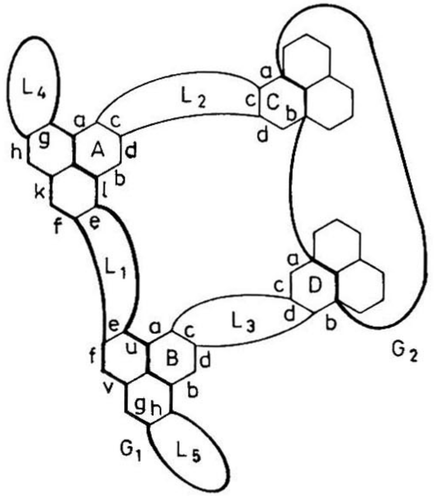
These rules may be applied recursively for every SPS for obtaining a unique decomposition into SS. The following theorem may be proved in the same way as Theorem 1:

Theorem 2. Let G be a SPS which is uniquely decomposed into string structures $G_1, G_2, \ldots, G_r$. The following relation holds:

$$K(G) = \sum_{i=1}^{r} K(G_i)$$

Another decomposition theorem for coronoid structures with perinaphthyl branching units oriented in parallel manner

Consider now the structure G described in Figure 14, where L_1, L_2, L_3, L_4 and L_5 are string structures (all these structures



G

Fig.14

may be empty),and where the thick lines delineate subgraphs G_1 and G_2,respectively. G_1 is a SS obtained by a decomposition in accordance with the procedure described earlier for Theorem 1; G_2 is any polyhex subgraph.Also hexagons A and C or B and D may coincide.

Such an example is given in Figure 16 where string structures G_2 and G_3 are connected by a single lower hexagon.

L_2 is annelated to hexagons A and C through edges c or d; a similar situation occurs for L_3. L_4 and L_5 are annelated to corresponding hexagons in upper and lower perinaphthyl groups through edges g or h; L_1 is annelated to upper and lower hexagons through e or f.

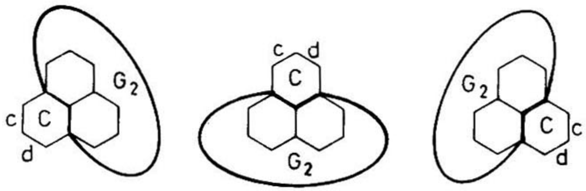


Fig.15

Hexagons C and D belong to perinaphthyl groups whose two other hexagons are in structure G_2.The possible positions of these perinaphthyl groups containing hexagons C or D relative to the topology of G are depicted in Figure 15.

In this case,unlike Figure 2,one cannot apply Theorems 1 or 2 because in G_1 we encounter two perinaphthyl units both pointing downward.

Theorem 3. Let G, G_1, G_2 be the structures depicted in Figure 14.The number of perfect matchings in G verifies

$$K(G) = K(G_1)K(G_2)$$

Proof: As in the proof of Proposition 1 one obtains that if edges a or b of hexagon B are double then both edges u and v in the same perinaphthyl group are simple.By a similar argument one deduces that double edges in the portion of G_1 composed from L_1,two hexagons from the upper perinaphthyl group and L_4 follow the patterns in Figure 3.In this case the last hexagon in the upper portion of G_1 would contain a vertex which is not incident to any double edge,a contradiction.

Hence both edges a and b in hexagon B are simple.
It follows that double edges in string structure L_3 follow the same cases as in Figure 3 and L_3 has a unique perfect matching.As in the proof of Proposition 2 one deduces that both edges a and b in hexagon D are simple edges.
Since a and b in B are both simple it follows that the conclusion of Proposition 1 holds for edges a and b in hexagon A.One may obtain as above that edges a and b in A are both simple,edges a and b in C are also simple and L_2 has a unique perfect matching.
Since edges a and b in all hexagons A,B,C,D are simple for every perfect matching of G and L_2 and L_3 have unique perfect matchings the conclusion of the theorem follows.

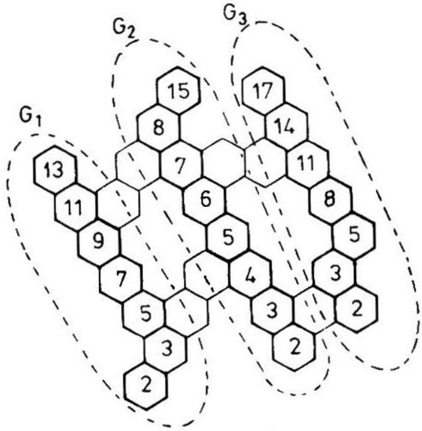
Note that the result stated by Theorem 3 holds also whenever L_2 or L_3 are series-parallel structures provided the centers of three hexagons in any perinaphthyl group of G are vertices of an equilateral triangle and all these triangles have pairwise parallel sides.

Theorem 3 may be applied several times by decomposing G into string structures $G_1,\dots,G_r$ and then multiplying the numbers of perfect matchings in each G_i:

$$K(G) = \prod_{i=1}^{r} K(G_i)$$

An example is given in Figure 16.

In order to apply to coronoids Theorem 3,one has to proceed in a similar manner to that discussed earlier for Theorem 1, namely: orientation of the coronoid to yield a "downward-pointing" perinaphthyl subgraph at the lowest level; recognition



$K(G) = K(G_1)K(G_2)K(G_3) = 13\cdot 15\cdot 17 = 3315$

Fig.16

that any decomposition according to deletion of a horizontal edge in the triangular dualist subgraph of the perinaphthyl unit is followed by a similarly oriented triangle (e.g.downward-pointing as in G_1 of Figure 14).

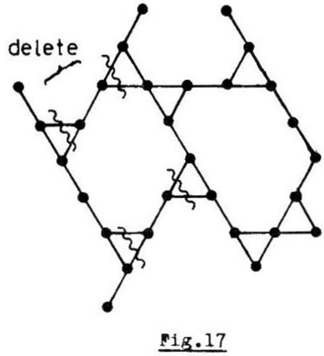


Fig.17

In this case the decomposition proceeds recursively by deleting from the downward pointing triangles of the dualist subgraph the upper right-hand vertex together with any string or edge starting from it,up to,and including,the vertex of the upward-pointing triangle of a dualist subgraph.This procedure is depicted in Figure 17 by the dualist graph of Figure 16 together with the first deletions.Then the same procedure is iterated in the remaining polyhex.

Acknowledgements. Thanks are expressed to Drs.M.Randić and N.Trinajstić for communicating preprints of their papers prior to publication.

Remark. It should be noted that the "perinaphthyl-type branching unit" mentioned in the title and the text is not meant restrictively, but can be extended to "perylene-type branching units". Indeed, the coronoid presented in Figure 16, whose dualist graph is shown in Figure 17, has two such perylene-type units.

REFERENCES

1. M.Gordon and W.H.T.Davison, J.Chem.Phys., 20,428(1952).

2. S.J.Cyvin and I.Gutman, Math.Chem., 19,229(1986).

3. S.J.Cyvin,B.N.Cyvin,J.Brunvoll and I.Gutman, Z.Naturforsch., 42a,722(1987); J.L.Bergan,S.J.Cyvin and B.N.Cyvin, Chem. Phys.Lett., 125,218(1986).

4. T.P.Živković and N.Trinajstić, Chem.Phys.Lett., 136,141(1987).

5. M.Randić, Chem.Phys.Lett. (in press).

6. M.Randić,S.Nikolić and N.Trinajstić, Croat.Chem.Acta (in press).

7. D.J.Klein,G.E.Hite,W.A.Seitz and T.G.Schmalz, Theor.Chim. Acta, 69,409 (1986).

8. A.T.Balaban and F.Harary, Tetrahedron, 24,2505 (1968); A.T.Balaban, ibid., 25,2949 (1969); Pure Appl.Chem., 52, 1409(1980).

9. A.T.Balaban, Pure Appl.Chem., 54,1075 (1982).

10. M.Randić,L.L.Henderson and R.Stout, Croat.Chem.Acta (in press).

11. A.T.Balaban, Rev.Roumaine Chim., 26,407 (1981).

Note added in proof: After completion of the manuscript, we wish to point out that several particular cases of benzenoids pertaining to the topic discussed in the present paper were analyzed recently by S.J. Cyvin, B.N. Cyvin and J. Brunvoll, Chem.Phys.Lett., 140, 124 (1987). Another relevant reference is the recently published book: S.J. Cyvin and I. Gutman, "Kekulé Structures in Benzenoid Hydrocarbons", Lecture Notes in Chemistry No. 46, Springer, Berlin, 1988.