

Kekulé structures as graph generators

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Kekulé valence-bond structures of catacondensed conjugated hydrocarbons with no, one, two and three branched cycles (which may be 4-, 6- and/or 8-membered) are used to generate highly regular vertex-transitive graphs through the application of an equivalence relation to the sextet of π -electrons in the *terminal* rings of the hydrocarbon. The partitioning of a given set of Kekulé structures allows the study of certain novel combinatorial aspects of Kekulé counts. The graph- generating character reported here is closely related to the recent work of Randić, Woodworth, Kleiner and Hosoya.

1. Introduction

In a recent development Randić et al. [1] described the generation of highly symmetric vertex-transitive graphs using binary permutation matrices as generators. Successive multiplications of such matrices generate other symmetric matrices (of the same dimension); each new matrix represents a new vertex in the graph to be constructed. In fig. 1 the method of Randić et al. [1] is illustrated on (two forms of) the *cube*. The labeling of the vertices of the cube corresponds to the matrices shown in fig. 2: each vertex v_i corresponds to the permutation matrix A_i while each edge

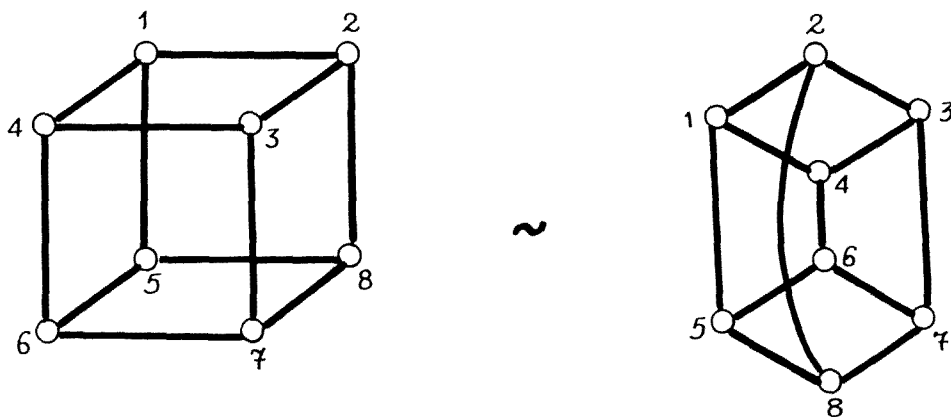
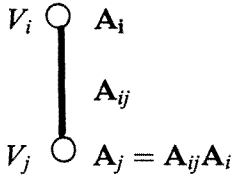


Fig. 1. Two forms of the cube, G_8 . The labels of the vertices are identified in fig. 2 and in fig. 4.

$v_i v_j$ is “weighted”, so to speak, by the matrix A_{ij} . The multiplication is conventionally designed in the following way:



$$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

A_1

A_2

A_3

$$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

A_4

A_5

A_6

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

A_7

A_8

$A_{12} = A_{34} = A_{56} = A_{78}$

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

$A_{23} = A_{14} = A_{58} = A_{67}$

$A_{28} = A_{37} = A_{46} = A_{15}$

Fig. 2. Binary permutation matrices used by Randić et al. [1] to generate the cube. The matrix A_i identifies the vertex v_i of the cube shown in fig. 1 while matrix A_{ij} identifies the edge l_{ij} of the cube.

2. Kekulé structures as graph generators

In the early stages of chemical graph theory Cvetković et al. [2] rigorously proved that Kekulé structures are indeed *permutations* (of double bonds). This classical result suggests the use of Kekulé structures as *graph generators* in place of permutation matrices as demonstrated in ref. [1]. First we state some definitions: In the molecular graph of a polycyclic conjugated hydrocarbon, a ring (which may be 4-, 6- and/or 8-membered) is called *terminal* if it contains only one edge common to two rings. Analogously a conjugated circuit [3] (of Randić) which is *fully contained* in a terminal ring will be called a *terminal conjugated circuit*. Then we define two Kekulé structures as *adjacent* (and hence may be thought of as connected) *if and only if* they give, when superimposed, a Clar formula [4] with *only one* terminal circle.

2.1. UNBRANCHED HYDROCARBONS

A branched hexagon (or cycle of arbitrary size) in a conjugated polycyclic hydrocarbon is defined [5] as being surrounded by three neighboring cycles. If no branched cycles exist in a hydrocarbon, it is called *unbranched*. In fig. 3 we illustrate the generation of a square, which we call here G_4 , starting with a Kekulé structure of an unbranched benzocyclobutadiene system. In an unbranched system there are only two terminal rings and therefore $2^2 = 4$ possible ways of permuting the terminal conjugated circuits. When the individual Kekulé structures are replaced by vertices, then connecting any two vertices corresponding to two adjacent Kekulé structures results in a square. Formally one can define a Kekulé adjacency matrix, \mathbf{K} as a square symmetric binary matrix, the elements of which, k_{ij} , are given by

$$\mathbf{K} = (k_{ij}) = \begin{cases} 1 & \text{if } k_i \cup k_j = \zeta_T, \\ 0 & \text{otherwise,} \end{cases} \quad (1)$$

where $k_i \cup k_j$ is superposition of Kekulé structures k_i and k_j and ζ_T is a Clar formula with *only one* terminal circle. Equation (1) is illustrated in fig. 3.

2.2. BRANCHED CATACONDENSED HYDROCARBONS WITH ONE BRANCHED CENTER

In this case there will be three terminal rings with $2^3 = 8$ possible combinations of terminal conjugated circuits. In fig. 4 we show the nine Kekulé structures of a branched cyclobutadiene hydrocarbon. The first 8 Kekulé structures lead to a *cube*, G_8 , when subjected to eq. (1). The labels given to the individual Kekulé structures correspond to the labels of the vertices of (two forms of) the cube shown in fig. 1. Observe that any two Kekulé structures with labels i and $i + 1$, where $i = [1, 7]$, are adjacent (i.e. connected). In addition, the following pairs are also adjacent as can be tested using eq. (1): $\{3, 7\}$, $\{1, 5\}$, and $\{2, 8\}$.

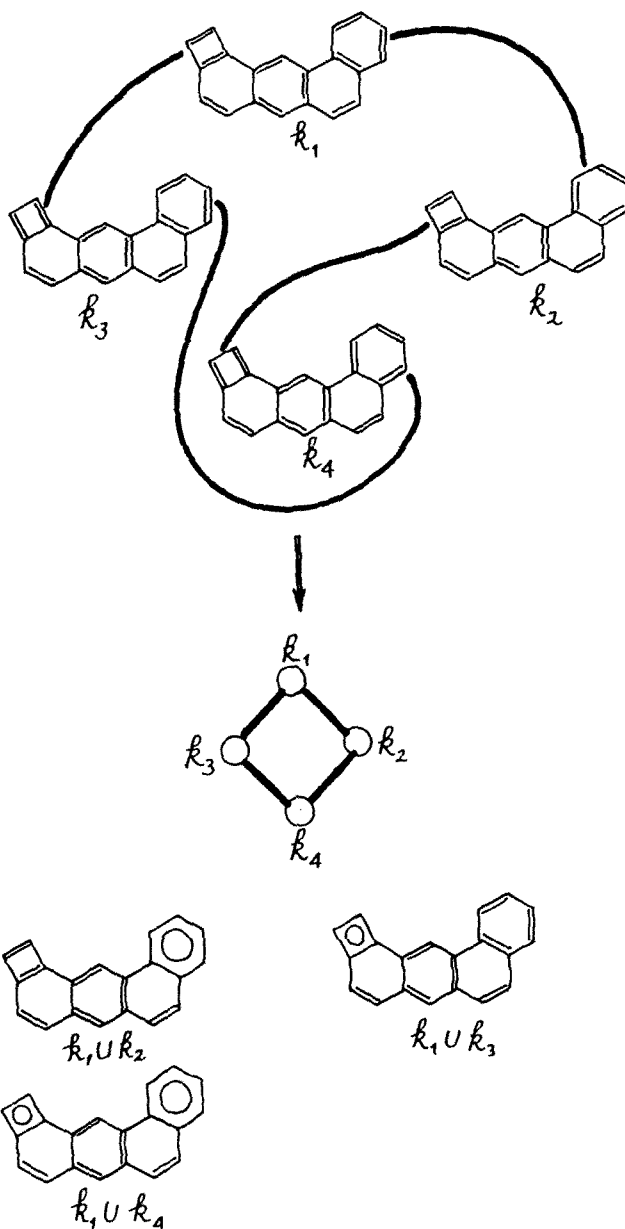


Fig. 3. Generation of the square, G_4 , by application of eq. (1), the definition of adjacency among a set of Kekulé structures. Observe that while k_1 is adjacent to k_2 , it is *not* adjacent to k_4 .

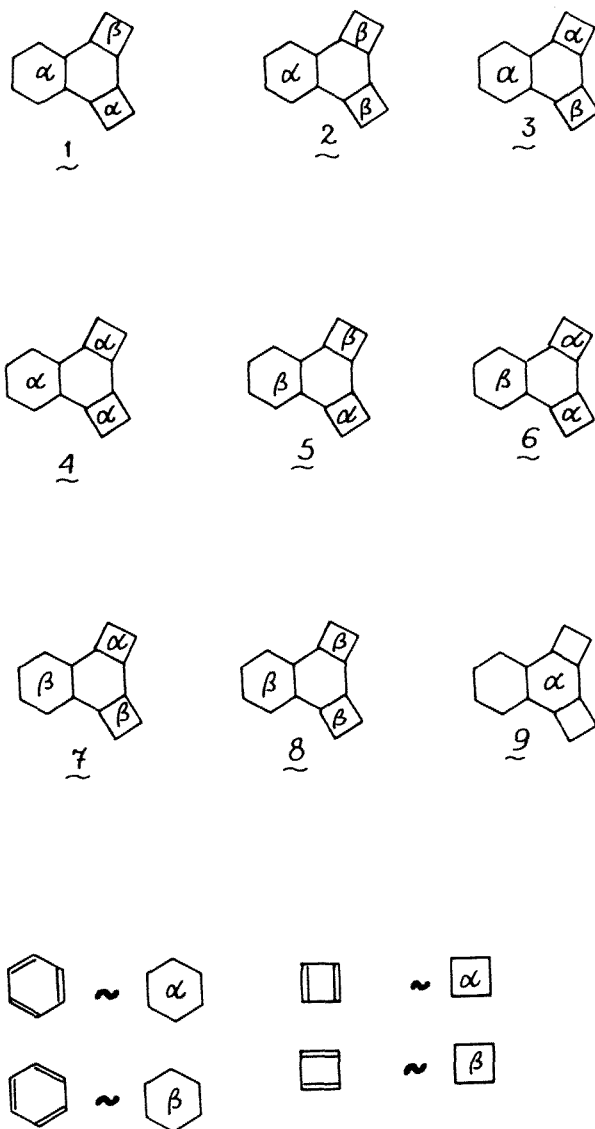


Fig. 4. The nine Kekulé structures of a naphthobicyclobutadiene. The designation α and β are explained for 6- and 4-membered rings. The letter α designates *vertical* double bonds while β designates *horizontal* double bonds. The first 8 Kekulé structures lead to a cube when eq. (1) is applied with labels corresponding to labels of vertices of the cube in fig. 1. The last Kekulé structure, 9, is not adjacent to any of the structures 1-8.

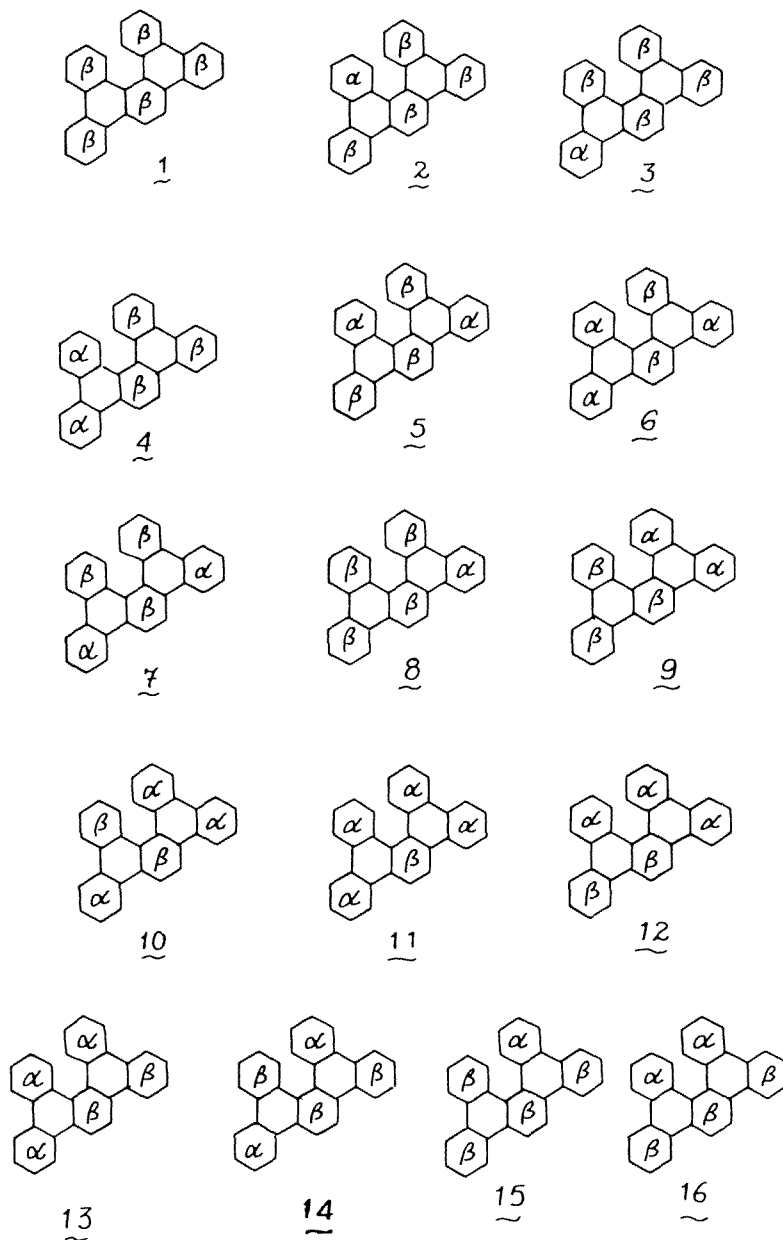


Fig. 5. Sixteen of the Kekulé structures of tetrabenzophenanthrene. The α and β designate the permutation of double bonds in hexagons as envisaged in fig. 4. When the definition of adjacency, eq. (1), is applied to the set a 4-dimensional cube, G_{16} results, see fig. 6. The labels of the vertices of G_{16} correspond to the labels of the Kekulé structures.

2.3. BRANCHED SYSTEMS WITH TWO BRANCHED CENTERS, I.E., FOUR TERMINAL RINGS

Figure 5 shows 16 (of the 41) Kekulé structures of a tetrabenzophenanthrene. In this case eq. (1) leads to a *four-dimensional cube*, G_{16} , shown in fig. 6. The labels of the Kekulé structures in fig. 5 correspond to the labels of the G_{16} graph drawn (in two forms) in fig. 6. It is worth mentioning that the graph G_{16} results in counting certain organometallic six-coordinate complexes [6].

3. Discussion

Two Kekulé structures k_i and k_j (both belonging to a particular hydrocarbon) are adjacent if a *terminal* conjugated circuit in k_i is related to the corresponding terminal circuit in k_j by mirror-reflection or rotation by 60° . Then one can define an operator l which rotates the π -electrons of a terminal ring (which may be 4-, 6-

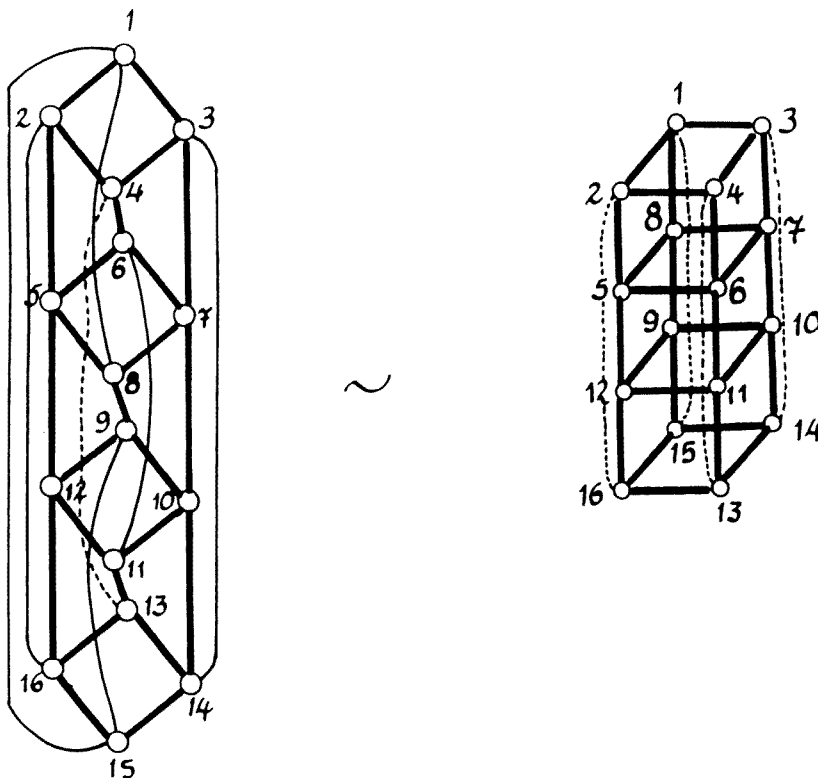


Fig. 6. The four-dimensional cube, G_{16} , generated through the application of eq. (1) on the 16 Kekulé structures shown in fig. 5.

and/or 8-membered) by 60° to generate an adjacent Kekulé structure. Let k_1, k_2, k_3 and k_4 be four Kekulé structures of a given polycyclic conjugated hydrocarbon, so that

$$lk_1 = k_2, \quad (3)$$

$$lk_2 = k_3, \quad (4)$$

$$lk_3 = k_4, \quad (5)$$

then k_2-k_4 form G_4 . The following result applies to the adjacency relation defined by eq. (1).

PROPOSITION

The definition of adjacency given by eq. (1) is an *equivalence relation* [7], i.e., partitions a set of Kekulé structures into a set of connected graphs when each Kekulé structure is replaced by a vertex and then any two vertices which correspond to two adjacent Kekulé structures are connected.

Proof

The *reflexive* part is obvious while the *symmetric* part is clear from eqs. (3)–(5). Finally, the *transitive* property can be envisaged in the following way:

$$lk_r = k_s; \quad lk_s = k_t \rightarrow$$

$$l^2k_r = l(lk_r) = lk_s = k_t. \quad (6)$$

The above equivalence relation, L , is demonstrated in fig. 7, where eq. (1) partitions the (14) Kekulé structures of a pentalene system into a cube, a square and a path on two vertices; G_2 (usually called K_2 graph [8]) depending on the *type* of Kekulé structure one starts the graph-generation with: *type 1* (fig. 7) possesses three terminal conjugated circuits and thus generates G_8 , i.e. a cube, *type 2* with only two terminal circuits can only form a G_4 (square) while *type 3* containing only one terminal circuit can only be linked to other Kekulé structures in pairs and thus form G_2 .

4. On Kekulé counts

Kekulé structures which are formally nothing else but *permutations* [2] of a special type can be made to generate vertex-transitive regular graphs by applying an equivalence relation to the *terminal* conjugated circuits of a given k_i and applying eq. (1). The result here is perhaps a special case of the more general work by Randić

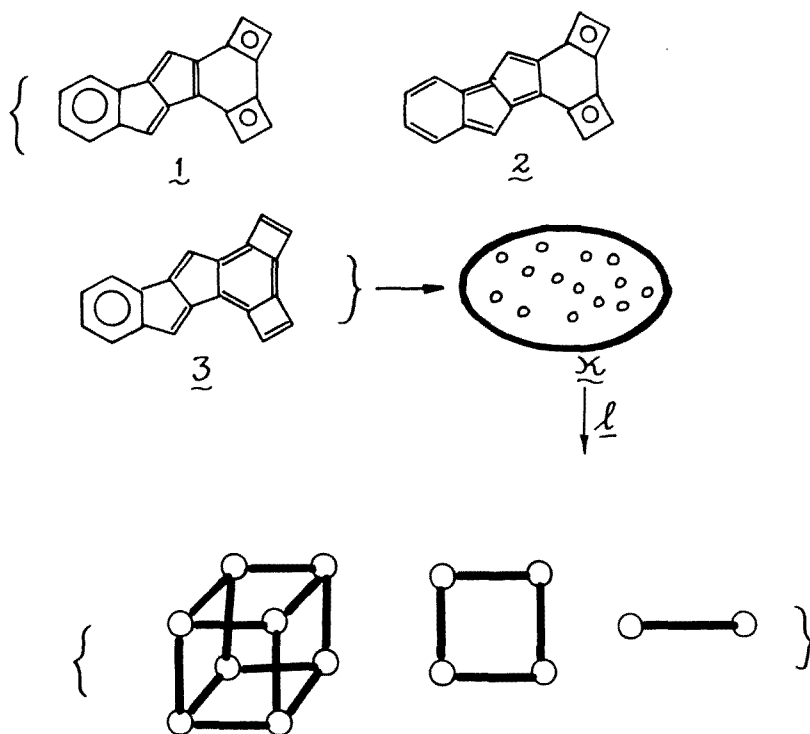


Fig. 7. Pictorial illustration of the equivalence relation l on the Kekulé structures of a benzopentalene derivative. The space \mathcal{K} is a "Kekulé space" containing all 14 Kekulé valence-bond structures of the hydrocarbon. The equivalence relation partitions this set into a cube (from type 1), a square (from type 2) and K_2 graph (from type 3).

et al. [1] using permutation *matrices* as generators. This result is perhaps worth knowing: aside from the graph construction problem which is itself important, the proposition reached here leads to a novel approach to enumeration of K (the Kekulé count); an already "exhausted" topic with an overwhelming number of papers [9] but which still attracts the attention of many workers in mathematical chemistry.

As an illustration we consider a benzenoid hydrocarbon which contains *five* terminal rings. There are 5 types of Kekulé structures for this hydrocarbon, viz.,
Type 1: One sextet of π -electrons in each of the terminal 5 hexagons (fig. 8). This type leads to G_{32} , a *5-dimensional cube* shown in fig. 9.

Type 2: Four terminal conjugated circuits (arrangements $\underline{2}$ and $\underline{3}$ in fig. 8). Each arrangement leads to a G_{16} .

Type 3: Three terminal conjugated circuits: arrangements $\underline{4}$, $\underline{5}$ and $\underline{6}$, each leads to a G_8 .

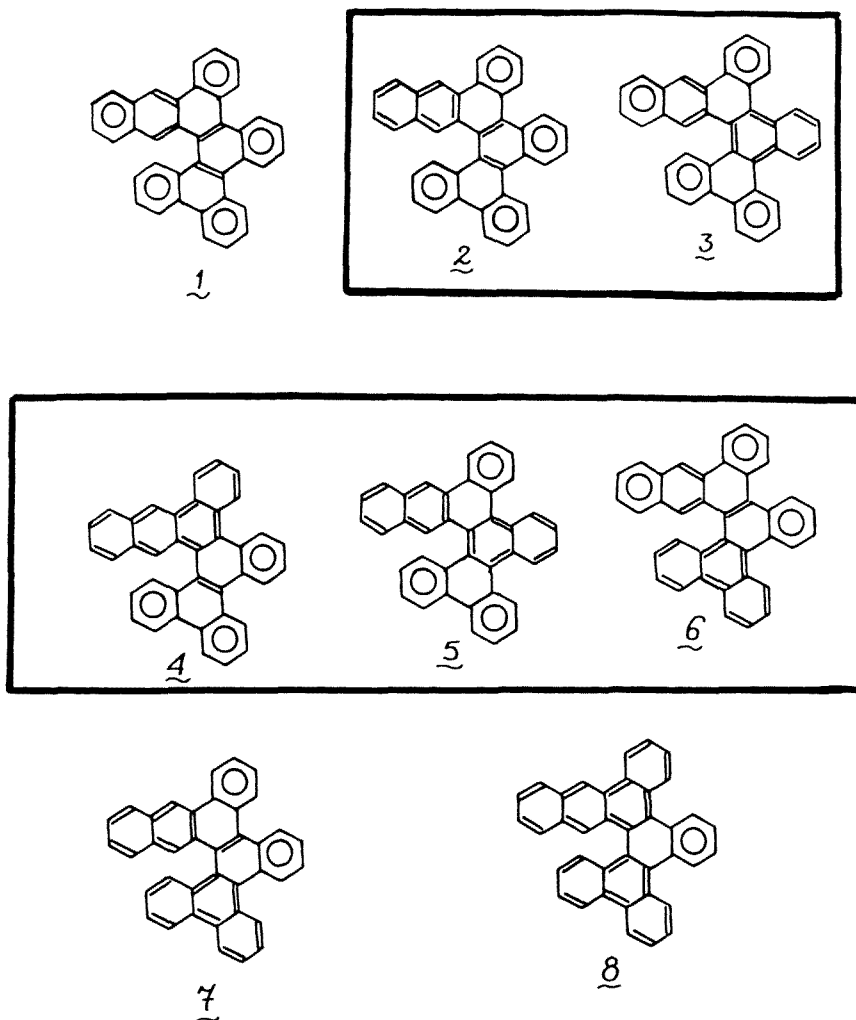


Fig. 8. The five *types* of Kekulé structures of a benzenoid hydrocarbon which contains 5 terminal hexagons. Type 1 generates G_{32} (five-dimensional cube shown in fig. 9), type 2 generates G_{16} , type 3 leads to a cube, type 4 produces a square, and finally type 5 generates G_2 . This partitioning allows the computation of K as described by eq. (7).

Type 4: Two terminal conjugated circuits: arrangement 7 leading to a G_4 .

Type 5: Only one terminal circuit which generates G_2 , cf. arrangement 8, fig. 8.

Then

$$\begin{aligned}
 K &= 32 + (2)(16) + (3)(8) + 4 + 2 \\
 &= 94, \quad \text{in agreement with the reported value [10]}.
 \end{aligned}
 \tag{7}$$

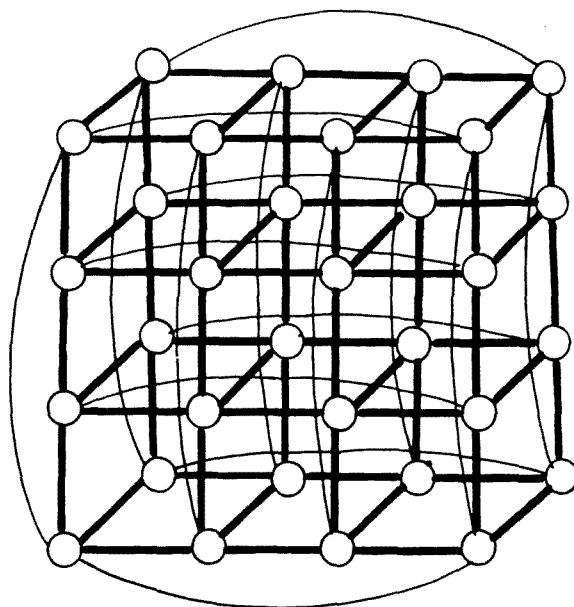


Fig. 9. The five-dimensional cube, G_{32} , produced when the equivalence relation is applied to the subset of Kekulé structures which contains 5 *terminal* conjugated circuits of type R_1 .

5. On fractal benzenoids [11a,b]

Recently Klein et al. [11a] studied several classes of *deterministically* fractal benzenoid systems. We choose in this paper the trigonal triphenylenoid family and focus on the member which represents the third stage in this family, cf. fig. 10. We use our approach here to find its K value. There are *four* types of double bond permutations, namely:

1. $R_1 R_1 R_1$. Three conjugated circuits containing 6 π -electrons each: one circuit in each of the three terminal rings. This configuration generates 2^6 cubes and hence contributes 8×2^6 to the value of K . The factor of 2^6 is the Kekulé count of 6 isolated benzene rings (heavily outlined in fig. 10).
2. $R_1 R_1$. Two terminal R_1 circuits, the third cycle being blocked to the equivalence relation. This particular arrangement leads to 3×2^4 squares: The factor of 3 accounts for symmetry and $2^4 = K$ value of the 4 isolated benzene rings (boldly outlined in fig. 10).
3. R_1 . Only one R_1 terminal circuit leading to $3 \times 2^2 K_2 (\equiv G_2)$ graphs.
4. No terminal R_1 s. There are two arrangements, each contributing a 1 to the total value of K .

Summing the above contributions leads to the value of K :

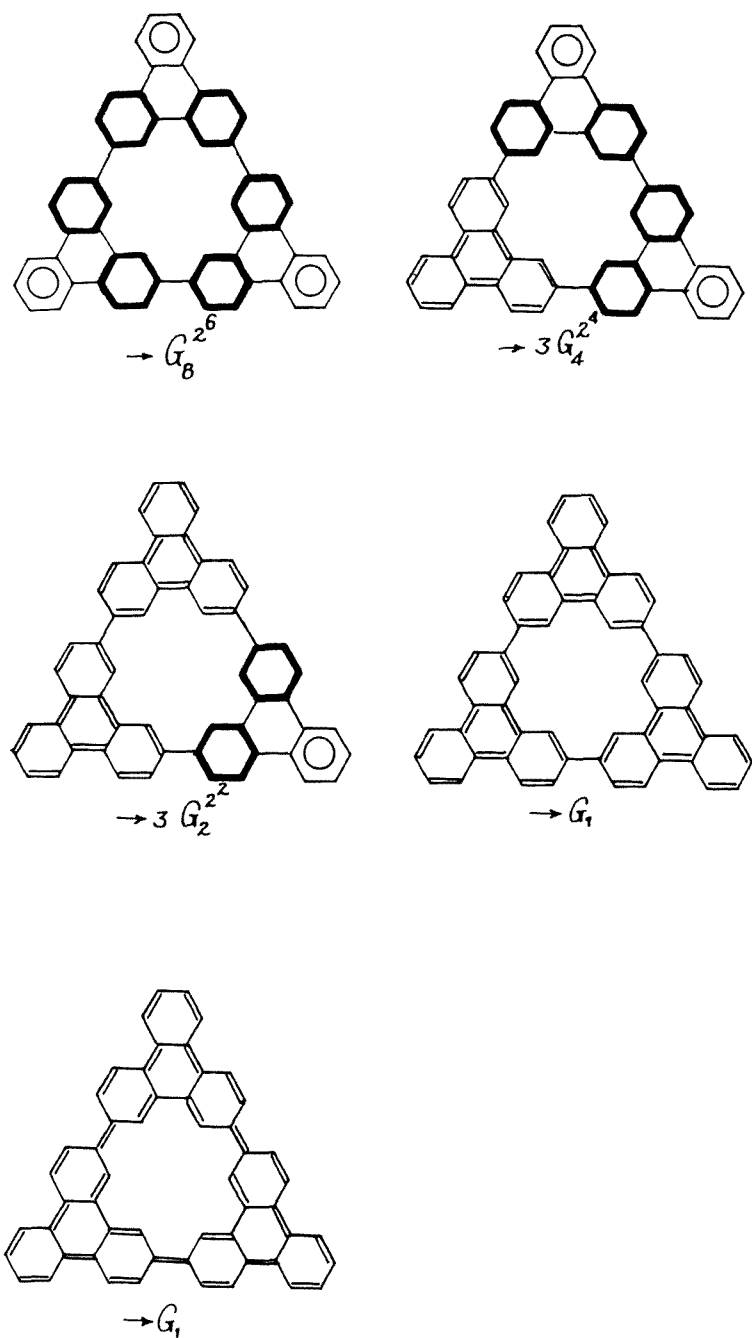


Fig. 10. The computation of the number of Kekulé structures of a hydrocarbon which has trigonal fractivity [11a], eq. (8). The four types of valence-bond structures are drawn.

$$K = 8 \times 2^6 + 3 \times 4 \times 2^4 + 3 \times 2 \times 2^2 + 1 + 1 = 730 \quad (8)$$

as computed by Klein et al. [11a] considering the trigonal fractility of this triphenylenoid hydrocarbon.

6. Conclusion

The topic of graph generation is still a virgin and worthy one in mathematical applications. In this work regular vertex-transitive graphs which may be of interest in chemistry are generated by the application of an equivalence relation on the terminal conjugated circuits in Kekulé structures. Some of the regular graphs synthesized here have chemical existence, namely:

- i) G_2 : represents compounds such as ethylene.
- ii) G_4 : represents “hypothetical” cyclobutadiene.
- iii) G_8 : represents cubane which was already prepared sometime ago [12]. Also some transition metal clusters [13] such as $\text{Ni}_8(\text{PPh})_6(\text{CO})_8$.
- iv) G_{16} : is a 4-dimensional cube used in counting organometallic six-coordinate complexes [6].

It is important to mention the pioneering work of Balaban [14], who seems to have *initiated* this subject.

Acknowledgements

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