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NUMBER OF KEKULÉ STRUCTURES OF HEXAGON-SHAPED BENZENOIDS

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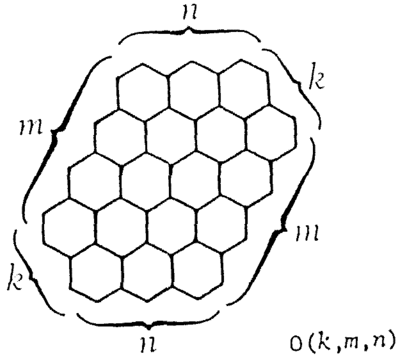
Abstract

An explicit combinatorial formula for the number of Kekulé structures of a hexagon-shaped benzenoid system is deduced. Thus, the validity of the previously proposed, but hitherto unproved formulas of Everett (from 1951), Woodger (from 1951), and Cyvin (from 1986) is confirmed. The proof is based on the application of the John – Sachs theorem.

1. Introduction

The enumeration of Kekulé structures of hexagon-shaped benzenoid hydrocarbons is a problem that was considered even in the earliest papers on the number of Kekulé structures [1,2]. A general hexagon-shaped benzenoid system O(k, m, n) has the following structure:



The parameters k, m and n denote the number of hexagons on the respective side of $O(k, m, n)$. In the above example, $k = 2$, $m = 4$, $n = 3$.

Throughout the present note, "hexagon-shaped" means that in the general case the benzenoid system considered has the form of a hexagon with unequal sides (as is the case in the above example). If all the three sides of $O(k, m, n)$ are equal (i.e. $k = m = n$), then the symmetry group of the molecule is D_{6h}. If $k = m \neq n$, the molecule will have dihedral symmetry D_{2h}. In the case where all the parameters are mutually different, the respective symmetry group is C_{2h}.

The symbol $O(k, m, n)$ is the same as used previously [3] and is part of the systematic notation of classes of benzenoid systems put forward by two of the present authors [4].

Gordon and Davison [1] reported a remarkable combinatorial formula,

$$K\{O(n, n, n)\} = \prod_{i=0}^{n-1} \frac{\binom{2n+i}{n}}{\binom{n+i}{n}}, \tag{1}$$

which reproduced the number of Kekulé structures of the $O(n, n, n)$ series (benzene, coronene, circumcoronene, etc.). According to [1], the discoverer of expression (1) was M.R. Everett. In [1], a generalization of (1) was also given, valid for the dihedral hexagons $O(m, m, n)$:

$$K\{O(m, m, n)\} = \prod_{i=0}^{m-1} \frac{\binom{m+n+i}{n}}{\binom{n+i}{n}}. \tag{2}$$

This formula was attributed [1] to M. Woodger. Neither Everett nor Woodger seem to have revealed the method by which they deduced (1) and (2).

Recently, Cyvin [3] came to the extension of the Everett–Woodger formula to the C_{2h} hexagons, viz.

$$K\{O(k, m, n)\} = \prod_{i=0}^{k-1} \frac{\binom{m+n+i}{n}}{\binom{n+i}{n}}, \tag{3}$$

but again no proof has been given.

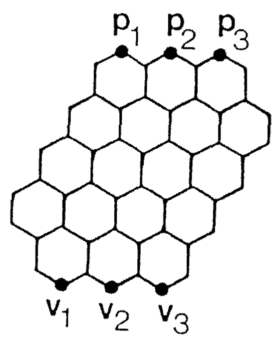
In spite of a number of publications [1–11] in which the formulas (1)–(3) have been mentioned and/or applied, no report on a stringent mathematical derivation of (1)–(3) could be found in either the chemical or mathematical literature.

In the present work, we give for the first time a mathematical proof of (3) and thus also its special cases (1) and (2).

2. The John–Sachs theorem

The proof technique employed in the present work is based on the application of a recent modification [12] of a theorem by John and Sachs [13].

In order to formulate the John–Sachs theorem, we conventionally draw the benzenoid system B so that some of its edges are vertical. Then, a vertex of B is called a peak (respectively, valley) if all its first neighbours lie below (respectively, above) it. A necessary condition for the existence of Kekulé structures in B is that the number of peaks equals the number of valleys. Let this number be n and let the peaks and valleys be labeled by $p_1, p_2, \ldots, p_n$ and $v_1, v_2, \ldots, v_n$. As an example, O(2, 4, 3) may serve:



The intersection graph G_{ij} of the ith peak and the jth valley of B is the subgraph of B spanned by the vertices of B which are accessible from p_i by exclusively going downwards and simultaneously accessible from v_j by exclusively going upwards [12]. The intersection graphs are themselves benzenoid systems or simple derivatives thereof [14]. Exceptionally, G_{ij} may be a path with an even number of vertices or the null graph (the graph without vertices).

According to [13],

$$K\{B\} = |\det W|, \tag{4}$$

where W is a square matrix of order n whose ij entry was shown [12] to be equal to $K\{G_{ij}\}$, the number of Kekulé structures of the intersection graph G_{ij}. (If G_{ij} is the null graph, then one has to set formally $K\{G_{ij}\} = 0$. If G_{ij} is a path with an even number of vertices then, of course, $K\{G_{ij}\} = 1$.) Note that the number of peaks and valleys, and therefore the order of the matrix W, depend on the way in which we draw a particular benzenoid system. Equation (4), on the other hand, is invariant to the change in the orientation of B. For further details on eq. (4), see [12,14].

In the case of hexagons, we may label the peaks and valleys so that p_{i+1} (respectively, v_{i+1}) lies to the right of p_i (respectively, v_i), $i = 1, \ldots, n-1$. Then, eq. (4) is further simplified [14,15]:

$$K\{B\} = \det W. \tag{5}$$

In order to exemplify the John–Sachs formula (5), we present in fig. 1 the nine intersection graphs of O(2, 4, 3).

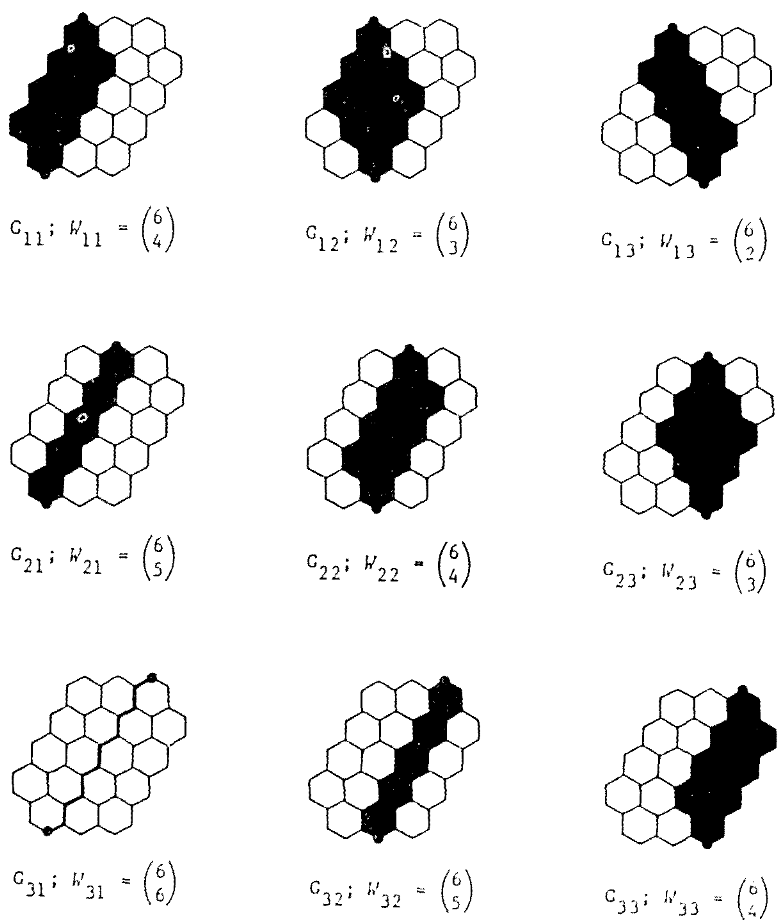
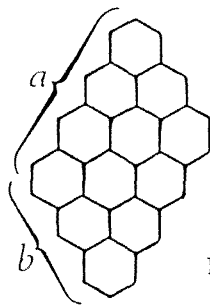


Fig. 1. The nine intersection graphs of O(2, 4, 3) drawn as black silhouettes on the background of the benzenoid system (hexagon).

3. Determinant formula for the number of Kekulé structures of O(k, m, n)

An inspection of fig. 1 suggests that the intersection graphs of O(k, m, n) are either null graphs or paths with an even number of vertices or parallelogram-shaped benzenoid systems. The general form of a parallelogram-shaped benzenoid is



L(a,b)

where a and b indicate the number of hexagons on the respective sides of the parallelogram. (In the above example, $a = 4$, $b = 3$.) It has been known for a long time [1] that

$$K\{L(a, b)\} = \binom{a+b}{a} = \binom{a+b}{b} .$$

We note in passing that also the above formula can be considered as a special case of (2) or (3), when one of the parameters k, m, n is set equal to one. In eqs. (2) and (3), k, m and n are assumed to be greater than unity. More about these details can be found in [4].

The case where the intersection graph is a path with an even number of vertices can be treated as the parallelogram $L(a, b)$, with $b = 0$. Also, the null graph can be formally described as $L(a, b)$, with $a < 0$ or $b < 0$. Note that null graphs occur among the intersection graphs of O(k, m, n) only if $n - k > 1$.

It is now not difficult to see that for $i = 1, 2, \ldots, n$ and $j = 1, 2, \ldots, n$,

$$G_{ij} = L(m + i - j, k - i + j),$$

and consequently

$$W_{ij} = \binom{m+k}{m+i-j} .$$

Applying the John–Sachs formula (5), we now straightforwardly arrive at the expression

$$K\{O(k, m, n)\} = F(k, m, n), \tag{6}$$

where

$$F(k, m, n) = \begin{vmatrix} \binom{m+k}{m} & \binom{m+k}{m-1} & \binom{m+k}{m-2} & \cdots & \binom{m+k}{m-n+1} \\ \binom{m+k}{m+1} & \binom{m+k}{m} & \binom{m+k}{m-1} & \cdots & \binom{m+k}{m-n+2} \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \binom{m+k}{m+n-1} & \binom{m+k}{m+n-2} & \binom{m+k}{m+n-3} & \cdots & \binom{m+k}{m} \end{vmatrix} \tag{7}$$

4. Proof of formula (3)

In order to prove formula (3), it is necessary to demonstrate that the right-hand side of (3) coincides with $F(k, m, n)$. We will perform the proof in two steps. It will first be established that $F(k, m, n)$ obeys the combinatorial identity (8), given in theorem 1 below. Eventually, we show that $F(k, m, n)$ is invariant to the permutation of the parameters k, m and n. We first need an auxiliary result.

LEMMA 1

The below determinant D_n of order n,

$$D_n = \begin{vmatrix} \binom{k+n-1}{n-1} & \binom{k+n-1}{n-2} & \cdots & \binom{k+n-1}{0} \\ \binom{k+n-2}{n-1} & \binom{k+n-2}{n-2} & \cdots & \binom{k+n-2}{0} \\ \cdot & \cdot & \cdots & \cdot \\ \binom{k}{n-1} & \binom{k}{n-2} & \cdots & \binom{k}{0} \end{vmatrix},$$

is equal to unity for all values of $n \geqslant 1$.

Proof

Consider the determinant D_{n+1}, viz.

$$D_{n+1} = \begin{vmatrix} \binom{k+n}{n} & \binom{k+n}{n-1} & \cdots & \binom{k+n}{0} \\ \binom{k+n-1}{n} & \binom{k+n-1}{n-1} & \cdots & \binom{k+n-1}{0} \\ \cdot & \cdot & \cdots & \cdot \\ \binom{k}{n} & \binom{k}{n-1} & \cdots & \binom{k}{0} \end{vmatrix} .$$

For $i = 1, 2, \ldots, n-1$, the $(i+1)th$ row of D_{n+1} is subtracted from the ith row; this transformation will not change the value of D_{n+1}. Bearing in mind the identity

$$\binom{p}{q} - \binom{p-1}{q} = \binom{p-1}{q-1} ,$$

we conclude that

$$D_{n+1} = \begin{vmatrix} \binom{k+n-1}{n-1} & \binom{k+n-1}{n-2} & \cdots & \binom{k+n-1}{0} & 0 \\ \binom{k+n-2}{n-1} & \binom{k+n-2}{n-2} & \cdots & \binom{k+n-2}{0} & 0 \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \binom{k}{n} & \binom{k}{n-1} & \cdots & \binom{k}{1} & \binom{k}{0} \end{vmatrix} ,$$

from which it is immediately seen that

$$D_{n+1} = D_n .$$

Lemma 1 follows now from the fact that $D_1 = \binom{n}{0} = 1$. ∎

THEOREM 1

$F(k, m, n)$ satisfies the following relation:

$$F(k, m, n) = \prod_{i=0}^{n-1} \frac{\binom{m+k+i}{m}}{\binom{m+i}{m}} . \tag{8}$$

Proof

We transform the determinant (7) so that the $(i + 1)th$ row is added to the ith row, for $i = 1, 2, 3, \ldots, n - 1$. Because of the identity

$$\binom{p}{q} + \binom{p}{q+1} = \binom{p+1}{q+1} ,$$

we obtain

$$F(k, m, n) = \begin{vmatrix} \binom{m+k+1}{m+1} & \binom{m+k+1}{m} & \ldots & \binom{m+k+1}{m-n+2} \\ \binom{m+k+1}{m+2} & \binom{m+k+1}{m+1} & \ldots & \binom{m+k+1}{m-n+3} \\ \cdot & \cdot & \ldots & \cdot \\ \binom{m+k+1}{m+n-1} & \binom{m+k+1}{m+n-2} & \ldots & \binom{m+k+1}{m} \\ \binom{m+k}{m+n-1} & \binom{m+k}{m+n-2} & \ldots & \binom{m+k}{m} \end{vmatrix} .$$

Now, for $i = 1, 2, \ldots, n - 2$, the $(i + 1)th$ row is added to the ith row, yielding

$$F(k,m,n) = \begin{vmatrix} \binom{m+k+2}{m+2} & \binom{m+k+2}{m+1} & \cdots & \binom{m+k+2}{m-n+3} \\ \binom{m+k+2}{m+3} & \binom{m+k+2}{m+2} & \cdots & \binom{m+k+2}{m-n+4} \\ \cdot & \cdot & \cdots & \cdot \\ \binom{m+k+2}{m+n-1} & \binom{m+k+2}{m+n-2} & \cdots & \binom{m+k+2}{m} \\ \binom{m+k+1}{m+n-1} & \binom{m+k+1}{m+n-2} & \cdots & \binom{m+k+1}{m} \\ \binom{m+k}{m+n-1} & \binom{m+k}{m+n-2} & \cdots & \binom{m+k+1}{m} \end{vmatrix} .$$

Then, for $i = 1, 2, \ldots, n-3$, the $(i+1)th$ row is added to the ith row, etc. Continuing this procedure, we finally obtain

$$F(k,m,n) = \begin{vmatrix} \binom{m+k+n-1}{m+n-1} & \binom{m+k+n-1}{m+n-2} & \cdots & \binom{m+k+n-1}{m} \\ \binom{m+k+n-2}{m+n-1} & \binom{m+k+n-2}{m+n-2} & \cdots & \binom{m+k+n-2}{m} \\ \cdot & \cdot & \cdots & \cdot \\ \binom{m+k}{m+n-1} & \binom{m+k}{m+n-2} & \cdots & \binom{m+k}{m} \end{vmatrix} . \qquad (9)$$

Bearing in mind that

$$\binom{p}{q} = \frac{p!}{q!(p-q)!} , \qquad (10)$$

we can now easily transform the right-hand side of (9) into

$$\frac{(m+k+n-1)!\,(m+k+n-2)!\ldots(m+k)!}{(m+n-1)!\,(m+n-2)!\ldots m!}\begin{vmatrix}\frac{1}{k!} & \frac{1}{(k+1)!} & \cdots & \frac{1}{(k+n-1)!}\\ \frac{1}{(k-1)!} & \frac{1}{k!} & \cdots & \frac{1}{(k+n-2)!}\\ \cdot & \cdot & \cdots & \cdot\\ \frac{1}{(k-n+1)!} & \frac{1}{(k-n+2)!} & \cdots & \frac{1}{k!}\end{vmatrix}$$

$$=\frac{\frac{(m+k+n-1)!}{(k+n-1)!}\ \frac{(m+k+n-2)!}{(k+n-2)!}\ \cdots\ \frac{(m+k)!}{k!}}{\frac{(m+n-1)!}{(n-1)!}\ \frac{(m+n-2)!}{(n-2)!}\ \cdots\ \frac{m!}{0!}}\begin{vmatrix}\frac{(k+n-1)!}{k!\,(n-1)!} & \frac{(k+n-1)!}{(k+1)!\,(n-2)!} & \cdots & \frac{(k+n-1)!}{(k+n-1)!\,0!}\\ \frac{(k+n-2)!}{(k-1)!\,(n-1)!} & \frac{(k+n-2)!}{k!\,(n-2)!} & \cdots & \frac{(k+n-2)!}{(k+n-2)!\,0!}\\ \cdot & \cdot & \cdots & \cdot\\ \frac{k!}{(k-n+1)!\,(n-1)!} & \frac{k!}{(k-n+2)!\,(n-2)!} & \cdots & \frac{k!}{k!\,0!}\end{vmatrix}.$$

Using (10) once again, we arrive at

$$F(k, m, n) = D_n \prod_{i=0}^{n-1} \frac{\binom{m+k+i}{m}}{\binom{m+i}{m}},$$

where D_n is defined in lemma 1. According to lemma 1, $D_n = 1$, and thus the identity (8) is proved. ■

THEOREM 2

$$F(k, m, n) = F(k, n, m) = F(m, k, n) = F(m, n, k) = F(n, k, m) = F(n, m, k).$$

Proof

It is intuitively clear that the statement of theorem 2 must hold because there were no restrictions on the ordering of the sides k, m, n of the hexagon-shaped benzenoid system considered. However, the formal demonstration of the validity of theorem 2 is somewhat more complicated. As already explained in the introductory part of this section, theorem 2 provides a necessary step in the proof of eq. (3). It is sufficient to demonstrate that two of the above relations hold, viz.,

$$F(k, m, n) = F(n, m, k) \tag{11}$$

and

$$F(k, m, n) = F(m, k, n). \tag{12}$$

Proof of (11)

Because of eq. (8), the condition (11) is equivalent to

$$\prod_{i=0}^{k-1} \binom{m+i}{m} \prod_{i=0}^{n-1} \binom{m+k+i}{m} = \prod_{i=0}^{n-1} \binom{m+i}{m} \prod_{i=0}^{k-1} \binom{m+n+i}{m},$$

which is obviously satisfied. ■

Proof of (12)

Transforming the right-hand side of eq. (8), one obtains

$$F(k,m,n) = \binom{m+k}{m}^n \frac{\left(\frac{m+k+1}{k+1}\right)^{n-1} \left(\frac{m+k+2}{k+2}\right)^{n-2} \cdots \frac{m+k+n-1}{k+n-1}}{(m+1)^{n-1} \left(\frac{m+2}{2}\right)^{n-2} \cdots \frac{m+n-1}{n-1}}$$

$$= \binom{m+k}{m}^n \frac{[(m+k+1)^{n-1}(m+k+2)^{n-2} \ldots (m+k+n-1)]\,[2^{n-2} \cdot 3^{n-3} \ldots (n}{[(m+1)(k+1)]^{n-1}\,[(m+2)(k+2)]^{n-2} \ldots [(m+n-1)(k+n-1}$$

Because of $\binom{m+k}{m} = \binom{m+k}{k}$, the latter expression will not change its value if the parameters k and m are interchanged. Thus, $F(k, m, n)$ obeys the condition (12). ■

Therefore, also theorem 2 is proved. ■

Formula (3) is now obtained from (6) and (8) by a consecutive application of (11) and (12). Formulas (2) and (1) are obvious, special cases of (3).

This completes the proof of the Everett–Woodger–Cyvin combinatorial formula for the number of Kekulé structures of a hexagon-shaped benzenoid hydrocarbon.

References

[1] M. Gordon and W.H.T. Davison, J. Chem Phys. 20(1952)428.
[2] T.F. Yen, Theor. Chim. Acta 20(1971)399.
[3] S.J. Cyvin, Monatsh. Chem. 117(1986)33.
[4] S.J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons,* Lecture Notes in Chemistry 46 (Springer-Verlag, Berlin, 1988).
[5] I. Gutman, Z. Naturforsch. 36a(1981)128.
[6] I. Gutman, Bull. Soc. Chim. Beograd 47(1982)453.
[7] N. Ohkami and H. Hosoya, Theor. Chim. Acta 64(1983)153.
[8] N. Trinajstić, *Chemical Graph Theory,* Vol. II (CRC Press, Boca Raton, FL, 1983).
[9] S.J. Cyvin, B.N. Cyvin and I. Gutman, Z. Naturforsch. 40a(1985)1253.
[10] S.J. Cyvin, B.N. Cyvin and I. Gutman, Coll. Sci. Papers Fac. Sci. Kragujevac 7(1986)5.
[11] H. Hosoya, Comp. & Maths. with Appls. 12B(1986)271.
[12] I. Gutman and S.J. Cyvin, Chem. Phys. Lett. 136(1987)137.
[13] P. John and H. Sachs, in: *Graphen in Forschung und Unterricht,* ed. R. Bodendiek, H. Schumacher and G. Walter (Verlag Barbara Franzbecker, Bad Salzdetfurth, FRG, 1985) pp. 85–101.
[14] I. Gutman, L.X. Su and S.J. Cyvin, J. Serb. Chem. Soc. 52(1987)263.
[15] S.J. Cyvin and I. Gutman, J. Mol. Struct. (Theochem) 164(1988)183.