match no. 19 pp. 229-242 1986

TOPOLOGICAL PROPERTIES OF BENZENOID SYSTEMS. PART XXXVI

ALGORITHM FOR THE NUMBER OF KEKULÉ STRUCTURES IN SOME PERI-CONDENSED BENZENOIDS

S. J. Cyvin

Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

and

I. Gutman

Faculty of Science, University of Kragujevac, YU-34000 Kragujevac, Yugoslavia

(Received: May 1985)

Abstract - A class of peri-condensed benzenoids may be generated from the parallelogram-shaped benzenoids on removing hexagons along two of its edges. An algorithm prescribes the assignment of a numeral to every hexagon. The numerals give information about the number of Kekulé structures. The algorithm is used to deduce formulas for some special cases: explicit formulas for certain classes of V-shaped benzenoids, and a recurrence formula for some triangular benzenoids. Finally the algorithm is extended to cases where all the four edges of the parallelogram may be indented.

INTRODUCTION

An algorithm for the number of Kekulé structures (K) for a single (unbranched) benzenoid chain is well known.[1] Figure 1 shows an example. Here the numerals were entered into the rings (contrary to usual practice[1]) in such a way that the K value is obtainable by adding up the numerals (from left to right). The numeral 1 outside the first hexagon should also be counted. This device has proved to be very useful, and it takes care of the trivial case of $K = 1$ for "no rings". The algorithm has been extended to all cata-condensed (also branched) benzenoids,[1] and algebraic expressions of K have been established.[2] In the present work a similar algorithm was produced for a wide class of peri-condensed benzenoids.

The K number of a reticulate, parallelogram-shaped ($m \times n$) benzenoid is well known.[1,3] The case has recently been extended to the $m \times n + k$ case.[4]

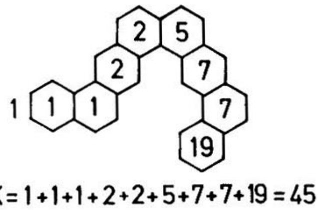


Fig. 1. Example of the algorithm for K of a single benzenoid chain.

The presently considered class is a further generalization. However, the K value is no longer available as an explicit formula in the general case, but in the form of an algorithm. In special cases recurrence formulas are available, and even explicit expressions.

THE CLASS OF BENZENOIDS

Consider a benzenoid with m linear chains of the lengths (number of hexagons) $r_1, r_2, \ldots, r_m$. These are the m rows. Assume the restrictions

$$r_{i+1} \leq r_i \;; \qquad i = 1, 2, \ldots, m-1 \tag{1}$$

Furthermore, the chains should be "aligned", which means that the first rings (conventionally drawn to the left) from all chains also form a stright chain (the first column). Let this reticulate benzenoid be designated $L(r_1; r_2; \ldots; r_m)$. The defined benzenoids will be referred to as belonging to class $\mathcal{C}$. Figure 2 shows the example of L(5; 4; 4; 2), or in a slightly abbreviated form L(5; 2×4; 2).

BASIC RECURRENCE FORMULA

The present algorithm (see below) is based on the following recurrence formula, where $K\{B\}$ denotes the number of Kekulé structures for a benzenoid B.

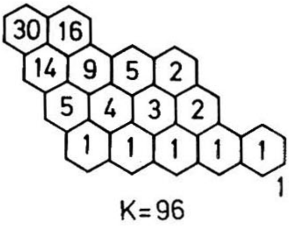


Fig. 2. The benzenoid L(5; 2×4; 2). The number of Kekulé structures (K) is the sum of the given numerals.

$$K\{L(r_1;\ r_2;\ \ldots.;\ r_{m-1};\ r_m)\}$$
$$= K\{L(r_1;\ r_2;\ \ldots.;\ r_{m-1};\ r_m - 1)\}$$
$$+ K\{L(r_1-r_m;\ r_2-r_m;\ \ldots.;\ r_{m-1}-r_m)\} \qquad (2)$$

THE ALGORITHM

Introduction

The algorithm rules (see below) assign one numeral to each benzenoid ring, along with the numeral 1 outside the benzenoid (as in Fig. 1). Fig. 2 anticipates the result for the chosen example. The practical rules for deducing the numerals emerge naturally from the properties specified in the following.

Properties of numerals

1. *Total K number*. The number of Kekulé structures for the whole benzenoid is obtained as the sum of all numerals.

2. *"Building-up" process*. We may think of the benzenoid as built up successively by adding the rows (upwards) in the sequence 1, 2, ..., m. Each row is built (from the left) in the sequence 1, 2, ..., r_m.

The numerals, when added up in the appropriate sequence, give information on the K number for every benzenoid during the building-up process.

Figure 3 shows two examples on the way, viz. L(5; 2) and L(5; 4; 1). Notice that also each benzenoid during the building-up process belongs to the class C.

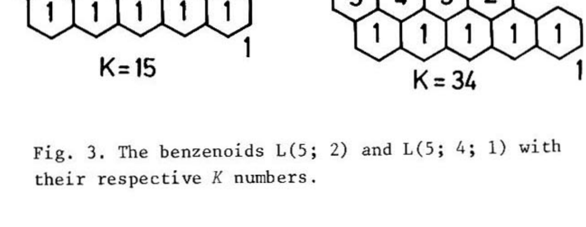


Fig. 3. The benzenoids L(5; 2) and L(5; 4; 1) with their respective K numbers.

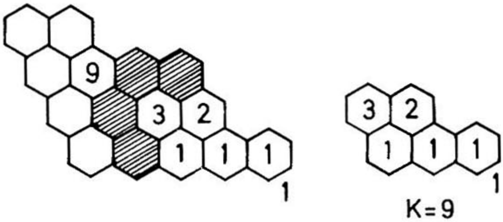


Fig. 4. Example of a sub-benzenoid with reference to Fig. 2.

3. *"Sub-benzenoids"*. Delete the row and column belonging to a given hexagon of the benzenoid. The fragment below and to the right of the deleted chains may suitably be referred to as the sub-benzenoid of that particular hexagon.

The numeral in each hexagon gives the number of Kekulé structures of its sub-benzenoid.

Figure 4 illustrates the sub-benzenoid of the hexagon in the third row and second column of our example (Fig. 2). Notice that also all sub-benzenoids belong to class C.

4. *Summation along a row*. Consider a "backward" summation of numerals in a row, i.e. starting from the last (right-hand side) numeral and proceeding to the left.

The numeral of a hexagon in the i-th row and j-th column is equal to the backward sum in the $(i-1)$-the row up to the numeral of the j-th column.

With reference to Fig. 2 we have, for instance: $30 = 2 + 5 + 9 + 14$, $9 = 2 + 3 + 4$, etc.

5. *Summation along a column*. Consider a summation of numerals in a column from the bottom (first row).

The numeral of a hexagon in the i-th row and j-th column is equal to the sum in the $(j+1)$-th column up to the numeral of the i-th row.

With reference to Fig. 2: $30 = 1 + 4 + 9 + 16$, $9 = 1 + 3 + 5$. It should be noticed that this rule is not applicable to the last hexagon of each row, which may be referred to as the "rim". The rim numerals of our example (Fig. 2) are 1, 2, 2, 16.

6. *Summation of two numerals.* The numeral of a hexagon in the i-th row and j-th column is equal to the sum of (a) the numeral in the $(i-1)$-th row and the same column (j) and (b) the numeral in the $(j+1)$-th column and the same row (i).

In other words, we are here looking for the numerals just below (skew-right) and just to the right of the hexagon in question. For instance (see Fig. 2): 30 = 14 + 16, 9 = 4 + 5. Notice that this rule is not applicable to the hexagons of the first row, and neither to those of the rim, as defined in paragraph 5.

Practical procedure

The following rules seem to give the easiest way to deduce the numerals.

(i) Assign the numeral 1 to all hexagons in the first row and one outside the benzenoid.

(ii) Start backwards on each row in the sequence $i = 2, 3, \ldots, m$. (a) Find the rim numeral according to summation along the preceding row; cf. paragraph 4. As a consequence of this rule rim hexagons, as long as they are aligned ($r_i = r_{i-1}$), appear with equal numerals. (b) Find the rest of the (off-rim) numerals of the row according to the sum of two numerals (paragraph 6).

PARALLELOGRAM-SHAPED BENZENOIDS AND THE PASCAL TRIANGLE

The properties from paragraphs 4, 5 and 6 of the preceding section are recognized from the Pascal triangle. Indeed, the numerals inside the familiar $L(m \times n)$ benzenoid form a part of the Pascal triangle, as is illustrated (for $m = 3$, $n = 4$) in Fig. 5. This feature may be compared with an exposition by Gordon and Davison.[1]

TRANSPOSE OF THE BENZENOID

A benzenoid of class C may be considered in two different ways, depending of what is understood as rows and what as columns. The interchanging of rows and columns ("transposing") in the benzenoid of Fig. 2 leads to

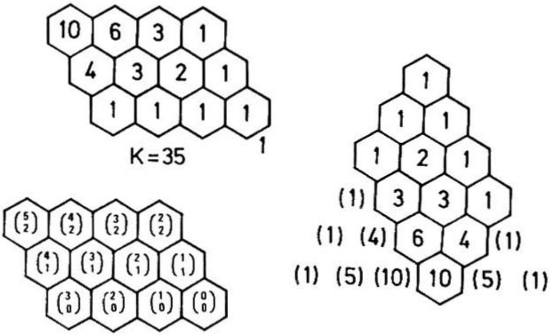


Fig. 5. Analogy between a parallellogram-shaped benzenoid and a part of Pascal's triangle. The triangle is completed by figures in parentheses. The bottom-left part shows the numerals inside the benzenoid in the form of binomial coefficients.

L(2×4; 2×3; 1), which is depicted in Figure 6. The benzenoid and its transpose are in fact identical. The algorithm must consequently give the same K value when applied in the two alternatives, as is exemplified in Figs. 2 and 6.

SPECIAL CASES OF L(r_1; r_2; ....; r_m)

The class of L($m_1 \times n$; $m_2 \times k$); $k \leq n$

In Fig. 7 four examples of this special class of benzenoids are depicted. Let the number of Kekulé structures be denoted by

$$K_{(k)} = K\{\mathrm{L}(m_1 \times n;\ m_2 \times k)\} \tag{3}$$

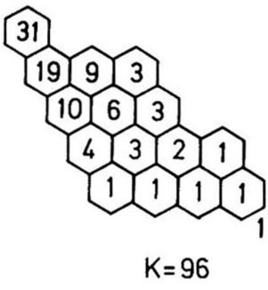


Fig. 6. The benzenoid L(2×4; 2×3; 1), which is the transpose of L(5; 2×4; 2); cf. Fig. 2. The K value is deduced.

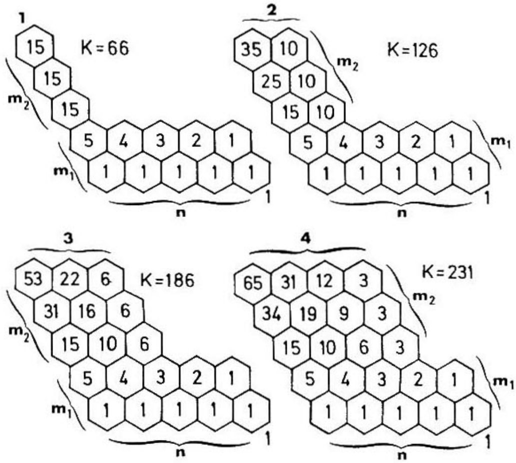


Fig. 7. Examples of $L(m_1{\times}n;\ m_2{\times}k)$ benzenoids with $m_1 = 2$, $m_2 = 3$, $n = 5$ and $k = 1, 2, 3, 4$.

For $k = 0$ the case reduces to the classical parallelogram-shaped benzenoids with[1,3]

$$K_{(0)} = \binom{m_1+n}{m_1} \tag{4}$$

For $k = 1$ it is found

$$K_{(1)} = K_{(0)} + m_2\binom{m_1+n-1}{m_1} = \left[\frac{m_1}{n} + m_2 + 1\right]\binom{m_1+n-1}{m_1}; \qquad n \geq 1 \tag{5}$$

Similarly for $k = 2$:

$$K_{(2)} = K_{(1)} + \binom{m_2+1}{2}\binom{m_1+n-2}{m_1}; \qquad n \geq 2 \tag{6}$$

This type of recurrence formula holds in the general case:

$$K_{(k)} = K_{(k-1)} + \binom{m_2+k-1}{k}\binom{m_1+n-k}{m_1} \; ; \qquad n \geq k \tag{7}$$

or explicitly in the form of a summation:

$$K_{(k)} = \sum_{j=0}^{k} \binom{m_2+j-1}{j} \binom{m_1+n-j}{m_1} \; ; \qquad n \geq k \tag{8}$$

The class of $L(k \times n;\ (m-k) \times k)$; $\quad m \geq k,\ n \geq k$

This is an interesting class of benzenoids, which emerges as specialization of the preceding case. Put

$$m_1 = k \tag{9}$$

and introduce the notation

$$m_1 + m_2 = m \tag{10}$$

Let the number of Kekulé structures be designated

$$K_{[k]} = K\{L(k \times n;\ (m-k) \times k)\} \tag{11}$$

Figure 7 contains (upper-right part) an example of a benzenoid belonging to this class, where $m_1 = k = 2$.

On combining (9) and (10) with eqn. (7) one obtains

$$K_{[k]} = K\{L(k \times n;\ (m-k) \times (k-1))\} + \binom{m-1}{k}\binom{n}{k} \tag{12}$$

We wish to relate this value of $K_{[k]}$ to $K_{[k-1]}$. Hence we take the transpose of the benzenoid of the right-hand side of eqn. (12) and obtain

$$\begin{aligned} K\{L(k \times n;\ (m-k) \times (k-1))\} &= K\{L((k-1) \times m;\ (n-k+1) \times k)\} \\ &= K\{L((k-1) \times m;\ (n-k+1) \times (k-1))\} + \binom{n}{k}\binom{m-1}{k-1} \end{aligned} \tag{13}$$

Here eqn. (7) has been employed once more. On transposing the benzenoid on the right-hand side of eqn. (13) one realizes that

$$K\{L((k-1) \times m;\ (n-k+1) \times (k-1))\} = K\{L((k-1) \times n;\ (m-k+1) \times (k-1))\} = K_{[k-1]} \tag{14}$$

The net result from eqns. (12)-(14) is

$$K_{[k]} = K_{[k-1]} + \left[\binom{m-1}{k} + \binom{m-1}{k-1}\right]\binom{n}{k}$$

$$= K_{[k-1]} + \binom{m}{k}\binom{n}{k} ; \qquad k \geq 1 \tag{15}$$

The case of $k = 0$ is a trivial one:

$$K_{[0]} = 1 \tag{16}$$

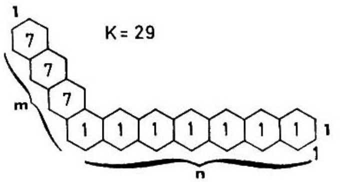
The simplest non-trivial case pertains to $k = 1$. Equations (15) and (16) give the well-known result [5,6]

$$K_{[1]} = K_{[0]} + \binom{m}{1}\binom{n}{1} = mn + 1 ; \qquad m \geq 1,\ n \geq 1 \tag{17}$$

For higher values of k we attain at new formulas, for instance:

$$K_{[2]} = K_{[1]} + \binom{m}{2}\binom{n}{2}$$

$$= \frac{mn}{4}(m-1)(n-1) + mn + 1 ; \qquad m \geq 2,\ n \geq 2 \tag{18}$$



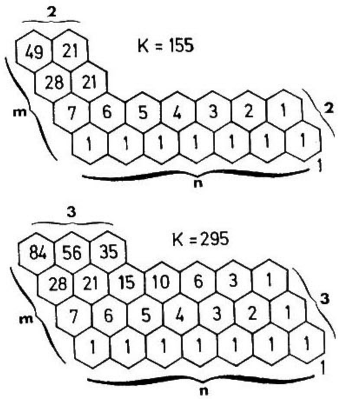


Fig. 8. Examples of $L(k\times n;\ (m-k)\times k)$ benzenoids with $m = 4$, $n = 7$ and $k = 1, 2, 3$: $L(7;\ 3\times1)$, $L(2\times7;\ 2\times2)$ and $L(3\times7;\ 3)$.

In the general case the following summation formula holds.

$$K_{[k]} = \sum_{i=0}^{k} \binom{m}{i}\binom{n}{i} \tag{19}$$

Provided that $n \geq m$, the maximal possible value of k is m, and

$$K_{[m]} = \binom{m+n}{m} \tag{20}$$

whereas

$$K_{[m-1]} = \binom{m+n}{m} - \binom{n}{m} \tag{21}$$

Eqn. (20) is again the case of $L(m \times n)$.[1,3] Also eqn. (21) is consistent with previous results.[4] Figure 8 shows examples for $k = 1$, 2 and 3 of the class of benzenoids considered here. In particular, the case with $k = 3$ exemplifies $k = m-1$, which is relevant to eqn. (21).

The basic theory of the present treatment imposes the restrictions on the numbers m and n as given in eqns. (17) and (18). Curiously enough these equations appear to have a wider applicability. Both of them reproduce the trivial result of $K_{[1]} = K_{[2]} = 1$ for m and/or n equal to zero. For $m = 1$ eqn. (18), as well as (17), gives $K = n + 1$, which applies to $L(n)$; for $n = 1$ they give $K = m + 1$, which applies to $L(m)$. This feature is quite general, since $\binom{m}{i} = 0$ for $m < i$, and $\binom{n}{i} = 0$ for $n < i$. Hence the restrictions on m and n are unnecessary in eqn. (19).

"Triangular" benzenoids

As a last example consider the triangular benzenoids;

$$T_n = L(n;\ n-1;\ n-2;\ \ldots.;\ 1)\ , \qquad K\{T_n\} = K_n \tag{22}$$

For the number of Kekulé structures (K_n) we have arrived at the following recurrence property.

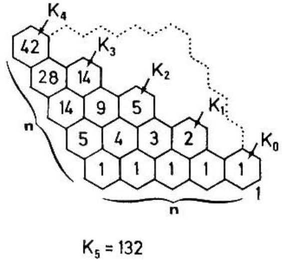


Fig. 9. The triangular benzenoid $T_5 = L(5; 4; 3; 2; 1)$.

$$K_0 = \binom{0}{0} = 1 \tag{23}$$

$$K_1 = \binom{2}{1} = 2 \tag{24}$$

$$K_n = \binom{2n}{n} - \sum_{i=0}^{n-2} K_i \binom{2n-2-2i}{n-i}; \qquad n \geq 2 \tag{25}$$

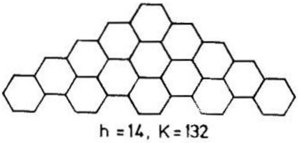
The first term, $\binom{2n}{n}$, designates the number of Kekulé structures for the "rhombic" $L(n \times n)$ benzenoid, while the subsequent terms (for $n \geq 2$) represent a deduction when the "triangle" is formed. Figure 9 shows the example of T_5. In this case

$$K_5 = \binom{10}{5} - K_0\binom{8}{5} - K_1\binom{6}{4} - K_2\binom{4}{3} - K_3\binom{2}{2}$$

$$= 252 - 56K_0 - 15K_1 - 4K_2 - K_3 \tag{26}$$

When the appropriate numerals are filled in (cf. Fig. 9) the K_i values for $i < n$ (K_0, ..., K_4 in the figure) are found in the rim hexagons. This follows from the rule about sub-benzenoid.

The present class of benzenoids should not be confused with the well-known non-Kekuléan triangular benzenoids.[7] The difference is emphasized in Figure 10.



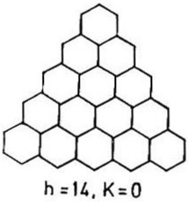


Fig. 10. Kekuléan and non-Kekuléan triangular benzenoids with equal number of rings (h).

GENERALIZATION OF THE ALGORITHM

Extended class of benzenoids

The algorthm is applicable (with slight additions) to a wider class of benzenoids. Assume a benzenoid of class C and a smaller one of the same class and common origin deleted from it. Such restrictions are imposed on the lengths of rows and columns that the smaller benzenoid does not trespass the boarders of the larger one. Figure 11 shows an example, where L(3; 2) is deleted from the benzenoid of Fig. 2. It may conveniently be designated L(5; 2×4; 2)∖L(3; 2) or L(5-3; 4-2; 4; 2).

Generalized algorithm

In Fig. 11 the numerals are filled in. They obey the same properties as specified for the algorithm under the above paragraphs:

The number of Kekulé structures for the whole benzenoid, as well as those during the building-up process, are obtained by adding the numerals. A special feature is encountered here, inasmuch as the benzenoids may be disconnected. Figure 12 explains this feature. The numbers of K are consis-

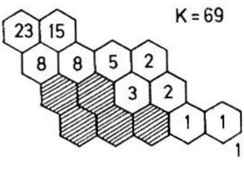
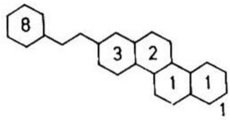
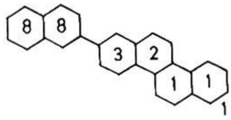


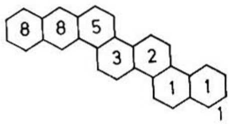
Fig. 11. The benzenoid of Fig. 2 with L(3; 2) deleted from it. Here also the number of Kekulé structures (K) is the sum of the given numerals.

I 

K = 16

II 

K = 24

III 

K = 29

Fig. 12. Three steps during the building-up process of the benzenoid of Fig. 11.
I: L(5-3; 4-2; 1)
II: L(5-3; 4-2; 2)
III: L(5-3; 4-2; 3)

tent with the classical results[1] for disconnected parts; I: $2 \cdot 8 = 16$ and II: $3 \cdot 8 = 24$. The result for III (Fig. 12) may be checked by means of the well-known algorithm[1] for cata-condensed benzenoids.

The concept of sub-benzenoids applies also in the generalized case. The two hexagons with numeral 8 in Fig. 11, for instance, possess the same sub-benzenoid: L(3-1; 2) with $K = 8$.

In the present case we have two types of rim hexagons: (a) the "row-rim" (right-hand boarder) as before; on Fig. 11 with the numerals 1, 2, 2, 15, and (b) the "column-rim" (bottom boarder); on Fig. 11 with the numerals 1, 1, 3, 8, 8. (In the previous case, e.g. Fig. 2, the first row is a trivial column-rim.) The rule about backward summation along a row applies for all hexagons except those of the column-rim. The summation along a column (from the bottom) works (as before) for all hexagons not on the row-rim. There may occur hexagons belonging to both the row-rim and the column-rim. Fig. 11 does not display such an example (except a trivial one), because the small benzenoid (to be deleted) is not large enough. Two examples are depicted in Fig. 13. The summation of two numerals is applicable for all hexagons on neither of the rims.

The practical procedure to deduce the numerals in the general case runs as follows. (a) Use the summation of two numerals whenever applicable. (b) Use the summation along a row or a column when the hexagon in question lies on one of the rims. (c) For hexagons belonging to both rims the numeral is found by means of the rule for sub-benzenoids.

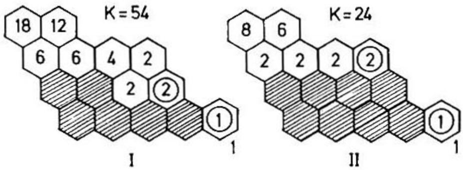


Fig. 13. The benzenoids (I) L(5; 2×4; 2)⟍L(4; 2) and (II) L(5; 2×4; 2)⟍L(2×4). The encircled numerals belong to hexagons on both the row-rim and the column-rim.

Transposed benzenoid

The transpose of the benzenoid of Fig. 11 is shown in Fig. 14. It may be designated L(2×4; 2×3; 1)⟍L(2×2; 1) or L(2×(4-2); 3-1; 3; 1). The numerals are filled in and give, as expected, the same K value as in Fig. 11, since the two benzenoids actually are identical.

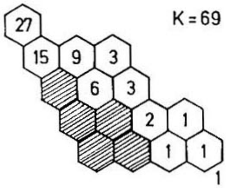


Fig. 14. The transpose of the benzenoid in Fig. 11. The K value is deduced.

REFERENCES

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

2 A.T. Balaban and I. Tomescu, *Communications in mathematical chemistry (match)* 14, 155 (1983).

3 T.F. Yen, *Theoret. Chim. Acta* 20, 399 (1971).

4 I. Gutman and S.J. Cyvin, *to be published.*

5 D. Biermann and W. Schmidt, *J. Electron Spectr. Rel. Phenom.* 20, 312 (1980).

6 Y. Jiang, *Sci. Sinica* 23, 847 (1980).

7 I. Gutman, *Croat. Chem. Acta* 46, 209 (1974).