Graph-Theoretical Enumeration of Conjugated Patterns for Carbocyclic and Heterocyclic Compounds *

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An algorithmic analysis of the existence of conjugated patterns for carbocyclic and heterocyclic compounds is presented. This graph theoretical method is applicable to the enumeration of Kekulé patterns for hydrocarbon benzenoids, as a special case.

Key words: Conjugated pattern, Cyclic compound, Polygonal graph, Enumeration, Kekulé structure.

Introduction

Carbocyclic and heterocyclic compounds without side-chains can be considered to be polygonal skeletons (graphs) in graph theory [1]. The class of polygonal skeletons (both planar and non-planar) under consideration is as follows.

A polygonal skeleton P consists of polygons such as tetragons, pentagons, hexagons, and octagons. Two polygons of P are connected with each other by sharing edges. Let (a) and (b) be vertices of P, for which the numbers of adjacent vertices are two and three, respectively; no P contains spiro-vertices ($>$b$<$). The prime on (a) and (b) indicates unconjugated vertices in a conjugated pattern of P. In chemistry, (a) corresponds to, for example, $-$CH$=$, $-$N$=$, and $-$O$^+=$; (a′) to $-$C*H$-$ (radical site), $-$O$-$, $-$NH$-$, and $-$S$-$; (b) to $>$C$=$, and $>$N$^+=$; (b′) to $>$C*$-$ (radical site), $>$CH$-$, $>$O$^+-$, and $>$N$-$. Dividing the chemical functional groups of cyclic compounds into four classes (a), (a′), (b), and (b′), is a proper procedure for the enumeration of conjugated patterns.

A cycle [2] of P is defined as a closed walk (on P) with more than two vertices, all of which are distinct. It is convenient to represent such a cycle in Graham's notation [3], i.e. in square brackets; e.g., [a a a′ b a a a a b] for the skeleton of thionaphthene (Figure 1). Note that in general [a b ... z] is different from [z ... b a]$=$ [R(a b ... z)]; this is called the reflection of [a b ... z].

Two conjugated patterns, even if one agrees with the other when transferred in the plane, can differ in their structures; e.g., there are two Kekulé patterns [1] for benzene [a a a a a a]. Particular attention should be paid to such cases in the construction of enumeration rules (cf. single polygons in (28)).

We assume that one polygonal skeleton P is reducible to another by means of the elimination of cycles. The present paper will use only the elimination rules by which any cycle of P is not separated into fragments. The reason is that the numbers of conjugated patterns are added together (not multiplied) in such an elimination rule.

Reducing P to a single polygon S constitutes a route of classes of cycles. Reduction rules for polygonal arcs and for cycles can be described in terms of the new cyclic representation. A set of reduction rules is thus established for the enumeration of the conjugated polygonal patterns of P.

* *Glossary of Symbols*
In conjugated patterns of a polygonal skeleton P,

(a)	conjugated vertex, connected with two vertices
(a′)	unconjugated vertex, connected with two vertices
(b)	conjugated vertex, connected with three vertices
(b′)	unconjugated vertex, connected with three vertices
(A)	polygonal arc, composed of (a) and (a′)
$(a)_i$	polygonal arc (a a ... a); i, the number of (a)'s
[...]	cycle of P
(r), (s)	path, composed of (a), (a′), (b), and (b′), on a cycle of P
R( )	reflection of ( )
K{P}	number of conjugated patterns for P
v( )	number of vertices for ( )
a^i	class of cycles in the reduction of (A); v(A)$=i$
n(P)	number of prime marks on the vertices of P
S	single polygon to which P is reducible
$P^{(n)}$	polygonal skeleton with n prime marks
$P_{0,2}$	P that is reducible to S by a^0 and a^2 classes
$m_{1,3}$(P, S)	number of a^1 and a^3 classes along a route from P to S.

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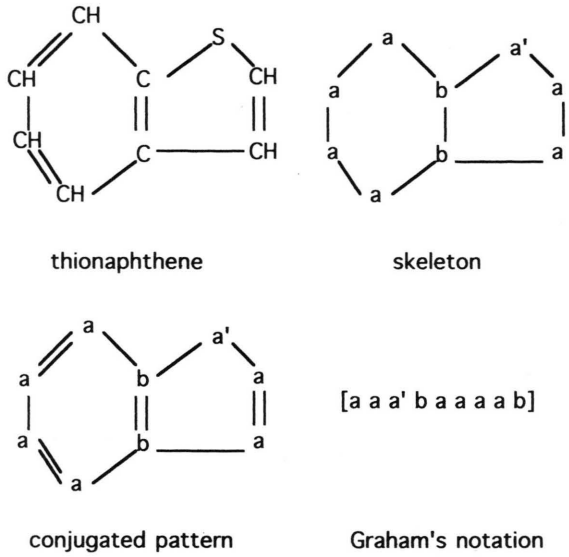

Fig. 1. Representations for thionaphthene.

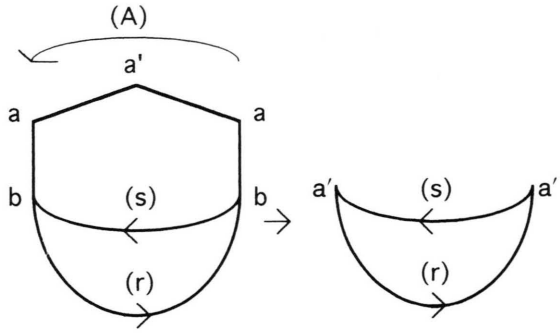

Fig. 2. Reduction of cycle [b a a' a b r] to cycle [a' s a' r].

Recursive Contraction and Elimination of Cycles

We first contract a polygonal arc (A) that is made of only (a) and (a'); (A) is part of cycles of P. Let $K\{P\}$ be the number of conjugated patterns of P. In a conjugated pattern, the arc (a a a) of cycles is a conjugated path of alternating single and double bonds, and every bond which meets with (a') is single. Hence, (a a a) and (a' a') are equivalent to (a) and (a'), respectively, from a calculational point of view of $K\{P\}$. Thus

$$K\{[(a)_{2j+1}\ r]\} = K\{[a\ r]\}\,, \tag{1}$$

$$K\{[(a)_{2j+2}\ r]\} = K\{[a\ a\ r]\}\,, \tag{2}$$

$$K\{[(a')_{j+1}\ r]\} = K\{[a'\ r]\}\,, \tag{3}$$

$$K\{[a'(a)_{2j}\ r]\} = K\{[a'\ r]\}\,, \tag{4}$$

$$K\{[(a)_{2j}a'\ r]\} = K\{[a'\ r]\}\,. \tag{5}$$

Here $(a)_i$ stands for the arc (a a ... a) in which the number of vertices (a) is $i \geq 0$; (r) is an abbreviation for the rest. It is clearly impossible to construct conjugated patterns if the number of (a)'s between (a')'s is odd:

$$K\{[a'(a)_{2j+1}\,a'\ r]\} = K\{[a'\ a\ a'\ r]\} = 0\,. \tag{6}$$

Successive application of (1)–(6) to (A), if it does not vanish, leads to one of the 6 arcs

(a), (a'), (a a), (a' a), (a a'), (a a' a), (A contracted).

The root vertex of (A) is either (b) or (b'). Assume that a cycle [b A b r] is composed of two cycles, [b A b R(s)] and [b s b r]; they are connected by sharing only the path (b s b); see Figure 2. Note that the number v(b A b R(s)) of vertices for cycle [b A b R(s)] is greater than 2. A class of cycles (polygons) eliminated is called a^i when the number v(A) of vertices of (A) equals i. Let us reduce [b A b r], i.e., [b A b R(s)] [b s b r], by the elimination of (A). If (a a' a) is chosen as (A), then

a^3 class:

$$K\{[b\ a\ a'\ a\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a'\ s\ a'\ r]\}\,. \tag{7}$$

The other two-cyclic skeletons are described by [b' A b R(s)] [b' s b r], [b A b' R (s)] [b s b' r], and [b' A b' R (s)] [b' s b' r]. The rules for eliminating the cycles in P are all in the following. Notice that after the reduction, only four cycles, [a s a r], [a' s a r], [a s a' r], and [a' s a' r], occur.

a^2 class:

$$K\{[b\ a\ a\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a\ s\ a\ r]\} + K\{[a'\ s\ a'\ r]\}, \tag{8}$$

$$K\{[b'\ a\ a\ b\ R(s)]\ [b'\ s\ b\ r]\} = K\{[a'\ s\ a\ r]\}, \tag{9}$$

$$K\{[b\ a\ a\ b'\ R(s)]\ [b\ s\ b'\ r]\} = K\{[a\ s\ a'\ r]\}, \tag{10}$$

$$K\{[b'\ a\ a\ b'\ R(s)]\ [b'\ s\ b'\ r]\} = K\{[a'\ s\ a'\ r]\}, \tag{11}$$

$$K\{[b\ a'\ a\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a\ s\ a'\ r]\}, \tag{12}$$

$$K\{[b'\ a'\ a\ b\ R(s)]\ [b'\ s\ b\ r]\} = K\{[a'\ s\ a'\ r]\}, \tag{13}$$

$$K\{[b\ a\ a'\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a'\ s\ a\ r]\}, \tag{14}$$

$$K\{[b\ a\ a'\ b'\ R(s)]\ [b\ s\ b'\ r]\} = K\{[a'\ s\ a'\ r]\}. \tag{15}$$

a^1 class:

$$K\{[b\ a\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a'\ s\ a\ r]\} + K\{[a\ s\ a'\ r]\}, \quad (16)$$

$$K\{[b'\ a\ b\ R(s)]\ [b'\ s\ b\ r]\} = K\{[a'\ s\ a'\ r]\}, \quad (17)$$

$$K\{[b\ a\ b'\ R(s)]\ [b\ s\ b'\ r]\} = K\{[a'\ s\ a'\ r]\}, \quad (18)$$

$$K\{[b\ a'\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a\ s\ a\ r]\}, \quad (19)$$

$$K\{[b'\ a'\ b\ R(s)]\ [b'\ s\ b\ r]\} = K\{[a'\ s\ a\ r]\}, \quad (20)$$

$$K\{[b\ a'\ b'\ R(s)]\ [b\ s\ b'\ r]\} = K\{[a\ s\ a'\ r]\}, \quad (21)$$

$$K\{[b'\ a'\ b'\ R(s)]\ [b'\ s\ b'\ r]\} = K\{[a'\ s\ a'\ r]\}. \quad (22)$$

a^0 class:

$$K\{[b\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a\ s\ a\ r]\} + K\{[a'\ s\ a'\ r]\}, \quad (23)$$

$$K\{[b'\ b\ R(s)]\ [b'\ s\ b\ r]\} = K\{[a'\ s\ a\ r]\}, \quad (24)$$

$$K\{[b\ b'\ R(s)]\ [b\ s\ b'\ r]\} = K\{[a\ s\ a'\ r]\}, \quad (25)$$

$$K\{[b'\ b'\ R(s)]\ [b'\ s\ b'\ r]\} = K\{[a'\ s\ a'\ r]\}. \quad (26)$$

The others are all zero:

$$K\{[b'\ a\ a'\ r]\} = K\{[a'\ a\ b'\ r]\} = K\{[b'\ a\ b'\ r]\} = 0. \quad (27)$$

No steps of reduction stated above decompose given cycles into fragments. Repeated use of them must reduce P to a set of single polygons, if no cycles vanish. A list of the numbers of conjugated patterns for single polygons:

$$K\{[a\ a\ a\ a]\} = 2,\ K\{[a'\ a\ a\ ]\} = K\{[a'\ a'\ a']\} = 1,$$
$$K\{[a'\ a\ a\ a]\} = K\{[a'\ a\ a'\ a]\} = K\{[a\ a\ a]\} = K\{[a'\ a'\ a]\} = 0. \quad (28)$$

Existence of Conjugated Patterns

If $K\{P\} > 0$ for given P, then there is at least one route from P to a single polygon S such that $K\{S\} > 0$. Let $n(P)$ denote the number of prime marks on P, and let $v(P)$ denote the number of vertices of P. We can observe that the odd-even parity for $n(P) + v(P)$ is conserved in the contraction of (A) and in the elimination of cycles. Since (28) shows that, if $K\{S\} > 0$, then $n(S) + v(S)$ is even, we can state that

Lemma 1: If $K\{P\} > 0$, then $n(P) + v(P)$ is even. (Contraposition) If $n(P) + v(P)$ is odd, then $K\{P\} = 0$.

Let $P^{(n)}$ be a polygonal skeleton with n prime marks; we obtain $P^{(n+k)}$ and $P^{(n-k)}$ by adding (deleting) k prime marks to (from) $P^{(n)}$. Notice that $P^{(n+k)}$ has the same a^i routes as those for $P^{(n)}$. Hence

Lemma 2: $K\{P^{(n)}\} > 0$ implies $K\{P^{(n+k)}\} = K\{P^{(n-k)}\} = 0$ (k, an odd integer).

When the starting polygonal skeleton has no (b'), this situation will remain unchanged in the reduction process, because none of the vertices, (a), (a'), and (b), generate (b'). Let $P^{(0)}_{0,2}$ be a polygonal skeleton having no prime marks, which is reducible to another in terms of classes a^0 and a^2. After the reduction of such a skeleton there is at least one skeleton belonging to the same type as $P^{(0)}_{0,2}$, because $K\{P^{(0)}_{0,2}\} \geq K\{[a\ s\ a\ r]\}$ in the reduction of a^0 and a^2 classes. On repeating these processes one reaches either a tetragon [a a a a] or a triangle [a a a]. Thus

Lemma 3: If $v(P^{(0)}_{0,2})$ is even, then $K\{P^{(0)}_{0,2}\} \geq 2$.

It is easy to confirm by a Schlegel diagram [4] that buckminsterfullerene C_{60} belongs to the class $P^{(0)}_{0,2}$; kekulene is also reducible by means of a^0 and a^2. An example for $P^{(0)}_0$: Planar $P^{(0)}$ having no holes and no internal vertices (b).

Another Set of Reduction Rules

It is possible to construct a finer algorithm than (1)–(28). The odd-even parity for either $n(P)$ or $v(P)$ is not conserved in both (3) and classes a^1 and a^3. By use of

$$K\{[(a')_{2j+1}\ r]\} = K\{[a'\ r]\}, \quad (3')$$

$$K\{[(a')_{2j+2}\ r]\} = K\{[a'\ a'\ r]\} \quad (3'')$$

instead of (3), (A) is reduced to

(a), (a'), (a a), (a' a), (a a'), (a' a'), (a a' a), (a' a' a), (a a' a'), (a a' a' a),

(A contracted, finer).

There is no difficulty in adding the following rules to (7)–(27):

a^4 class:

$$K\{[b\ a\ a'\ a'\ a\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a'\ s\ a'\ r]\}. \quad (29)$$

a^3 class:

$$K\{[b\ a'\ a'\ a\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a\ s\ a'\ r]\}, \quad (30)$$

$$K\{[b'\ a'\ a'\ a\ b\ R(s)]\ [b'\ s\ b\ r]\} = K\{[a'\ s\ a'\ r]\}, \quad (31)$$

$$K\{[b\ a\ a'\ a'\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a'\ s\ a\ r]\}, \quad (32)$$

$$K\{[b\ a\ a'\ a'\ b'\ R(s)]\ [b\ s\ b'\ r]\} = K\{[a'\ s\ a'\ r]\}. \quad (33)$$

a^2 class:

$$K\{[b\ a'\ a'\ b\ R(s)]\ [b\ s\ b\ r]\} = K\{[a\ s\ a\ r]\}\ , \quad (34)$$

$$K\{[b'\ a'\ a'\ b\ R(s)]\ [b'\ s\ b\ r]\} = K\{[a'\ s\ a\ r]\}\ , \quad (35)$$

$$K\{[b\ a'\ a'\ b'\ R(s)]\ [b\ s\ b'\ r]\} = K\{[a\ s\ a'\ r]\}\ , \quad (36)$$

$$K\{[b'\ a'\ a'\ b'\ R(s)]\ [b'\ s\ b'\ r]\} = K\{[a'\ s\ a'\ r]\}\ . \quad (37)$$

Equation (28) is replaced by the following list for two single polygons:

Tetragon: $K\{[a\ a\ a\ a]\} = 2$, $K\{[a'\ a'\ a\ a]\}$
$= K\{[a'\ a'\ a'\ a']\} = 1$, $K\{[a'\ a\ a\ a]\}$
$= K\{[a'\ a\ a'\ a]\} = K\{[a'\ a'\ a'\ a]\} = 0$. (28′)

Triangle: $K\{[a'\ a\ a]\} = K\{[a'\ a'\ a']\} = 1$, $K\{[a\ a\ a]\}$
$= K\{[a'\ a'\ a]\} = 0$. (28″)

The odd-even parity for $n(P)$ either is unchanged in the contraction of (A) and in the elimination of class a^{2j}, or is changed in the elimination of class a^{2j+1}; i.e., the odd-even parity for $n(P)+m_{1,3}(P, S)$ coincides with that for $n(S)$, where $m_{1,3}(P, S)$ is the total number of classes a^1 and a^3 along a route from P to S. The same discussion on $v(P)$ as that on $n(P)$ leads to: Two integers, $v(P)+m_{1,3}(P, S)$ and $v(S)$, have the same odd-even parity as each other. Thus the first theorem in the finer reduction rules takes the following form:

If $K\{P\} > 0$, then four integers, $n(P)+m_{1,3}(P, S)$; $n(S)$; $v(P)+m_{1,3}(P, S)$; and $v(S)$, along any route from P to S, have the same odd-even parity as one another.

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