# Upper and Lower Bounds for the Number of Conjugated Patterns in Carbocyclic and Heterocyclic Compounds*

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It is possible to regard two polygonal skeletons as the same in a special class of carbocyclic and heterocyclic compounds, if the one is reducible to the other by means of the contraction of cyclic subskeletons, and if the numbers of conjugated patterns in them are equal to each other. In such polygonal skeletons, three forms of cyclic subskeletons are defined; the one is called "alternate", and the others, involving the one called "inclusive", have a path $(b, b)$, where $(b)$ is a conjugated vertex connecting with three vertices. Successive eliminations of the cyclic subskeletons enable to estimate the upper and lower bounds for the number of conjugated patterns in a given polygonal skeleton.

## Introduction

The theory of the present paper is based on the same assumption as is [1]: Every polygonal skeleton $P^{(n)}$ in which the degree of each vertex is 2 or 3 belongs to a class of carbocyclic and heterocyclic compounds with no side-chains, and no cycles in $P^{(n)}$ can be separated into fragments in terms of the reduction rules ((1)–(37) in [1], contraction and/or elimination of cycles). Here $P^{(n)}$ stands for a polygonal skeleton with $(n \geq 0)$ unconjugated vertices.

The reduction rules point out that the number $K\{P^{(n)}\}$ of conjugated patterns in $P^{(n)}$ remains unchanged through the reduction if there is at least one unconjugated vertex, $(a')$ or $(b')$, in the cycle eliminated (and if no $K\{P^{(n)}\}$ vanishes). Such an equality reduction terminates when (19) and (34) (and a single polygon $S$) are used; each skeleton resulting from (19) and (34) contains no unconjugated vertex. Hence, $P^{(0)}$ plays an important role in the enumeration of conjugated patterns.

The rules ((1), (2), (8), and (23) in [1]) only, after the reduction of $P^{(0)}$, yield other polygonal skeletons of the same type $(j \geq 0)$.

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

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

**$\mathbf{a^2}$ class:**

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

**$\mathbf{a^0}$ class:**

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

Two adjacent cycles on the left side of (8) and (23) are connected with each other by sharing only the path $(b\, s\, b)$. Equation (38) can further be adopted as an equality relation when the number of vertices in $[b\, r]$ is greater than 2.

$$K\{[b\, a\, a\, r]\} = K\{[b\, r]\}\,. \tag{38}$$

Employing (1), (2), and (38) (contraction of cyclic subskeletons) as an equivalence relation, one can suggest the fact that $P^{(0)}$ is made up of $[b\, b\, r]$ and $[b\, a\, b\, r]$, with

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* *Glossary of Symbols*

| | |
|---|---|
| $(a)$ | conjugated vertex, connecting with two vertices |
| $(a')$ | unconjugated vertex, connecting with two vertices |
| $a^i$ | elimination class of cycles; $i$, the number of vertices $(a)$'s and $(a')$'s |
| $(b)$ | conjugated vertex, connecting with three vertices |
| $(b')$ | unconjugated vertex, connecting with three vertices |
| $K\{P^{(n)}\}$ | number of conjugated patterns in $P^{(n)}$ |
| $K\{[\ldots]\}$ | number of conjugated patterns in a given polygonal skeleton with cycle $[\ldots]$ |
| $[\ldots]$ | cycle (whose number of vertices $\geq 3$) in polygonal skeletons |
| $L_l^{(0)}$ | polygonal skeleton $(n = 0)$ that gives the lower bound for $P^{(0)}$, by the elimination of $l$ cycles |
| $P^{(n)}$ | polygonal skeleton with $n$ $(\geq 0)$ prime marks |
| $r$ | abbreviation for the rest |
| $R(\,)$ | reflection of $(\,)$ |
| $S$ | single polygon |
| $(s)$ | path in cycles |
| $U_l^{(0)}$ | polygonal skeleton $(n = 0)$ that gives the upper bound for $P^{(0)}$, by the elimination of $l$ cycles |

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the exception of $[b\,b\,a\,a]$. In other words, two polygonal skeletons with $n = 0$ are equivalent from the point of view of the calculation of conjugated patterns, if the one is reducible to the other by use of (1), (2) and (38); and (8) becomes equivalent to (23). The present paper is mainly concerned with the elimination of $[b\,b\,r]$ in terms of (23) under the equivalence relation.

The odd-even parity for the number of vertices in $P^{(0)}$ is conserved in the reduction rules (1)–(38); and the number of vertices $(b)$'s in $P^{(0)}$ is even, because $(b)$ has degree three (cf., the assumption mentioned above). Therefore, in $P^{(0)}$ the odd-even parity for the number of $(a)$'s, that for the number of paths $(b\,a\,b)$'s, and that for the total number of vertices, coincide.

An effective way for determining whether or not $K\{P^{(0)}\} > 0$ for a given $P^{(0)}$ is to estimate the upper and lower bounds for $K\{P^{(0)}\}$. If the upper bound for $K\{P^{(0)}\}$ is zero, then there is no conjugated pattern in $P^{(0)}$; if the lower bound for $K\{P^{(0)}\}$ is positive, then it is possible to write at least one conjugated pattern in $P^{(0)}$. The present paper will show that if $P^{(0)}$ has a particular structure (subskeleton) relating to $[\,b\,b\,r]$, then it is possible to estimate the upper and lower bounds for $K\{P^{(0)}\}$.

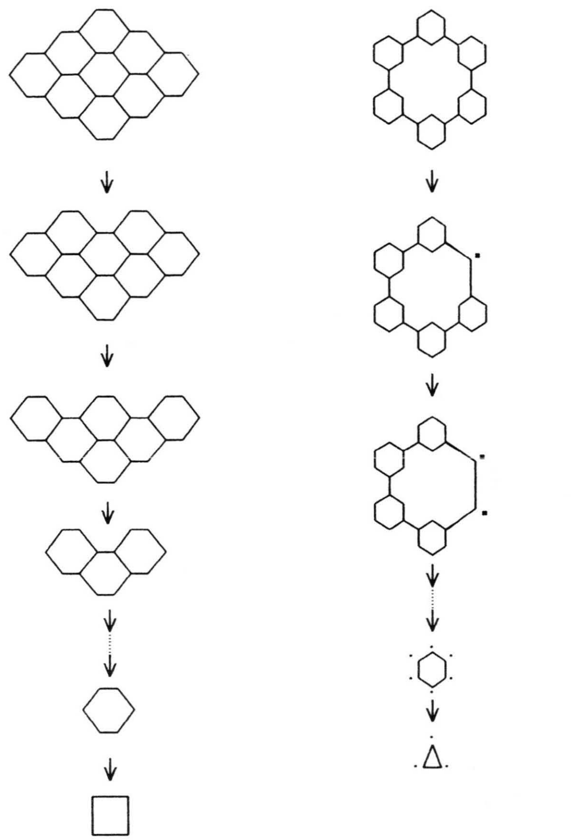

Fig. 1. A series of the lower bounds for $P^{(0)}_{0,2}$ with no Hamiltonian cycles, by use of (23) (left); $P^{(0)}$, reducible by cycle-replacement, but irreducible by use of (23) (right).

## Lower Bounds for Polygonal Skeletons

Let us assume that there is $\{[b\,b\,R(s)]\,[b\,s\,b\,r]\}$ in $P^{(0)}$; and let $L^{(0)}_1$ be a polygonal skeleton to have $[a\,s\,a\,r]$ as part of a whole. Then the elimination rule (23) gives a lower bound for $K\{P^{(0)}\}$; namely, $K\{P^{(0)}\} \geq K\{L^{(0)}_1\}$. Similarly, $L^{(0)}_2$ indicates a lower bound after the application of (23) to $L^{(0)}_1$; i.e., $K\{L^{(0)}_1\} \geq K\{L^{(0)}_2\}$. Such elimination occurs $l$ times; we reach a polygonal skeleton $L^{(0)}_l$ which has no path $(b\,b)$ shared by two cycles.

*Lemma 9:* $$K\{P^{(0)}\} \geq K\{L^{(0)}_1\} \geq K\{L^{(0)}_2\} \geq \dots \geq K\{L^{(0)}_l\}.$$

$L^{(0)}_l$ may or may not be a single polygon $S$. To $P^{(0)}$ in the former, the notation $P^{(0)}_{0,2}$ has been given [1]; namely, $K\{P^{(0)}_{0,2}\} \geq K\{S\}$. When $S$ is tetragon $[a\,a\,a\,a]$, $K\{P^{(0)}_{0,2}\} \geq 2$ (Lemma 3 in [1]). See a series of eliminations for polyhexes (Fig. 1, left); $K\{P^{(0)}_{0,2}\} \geq \dots \geq K\{L^{(0)}_8\} = K\{[a\,a\,a\,a]\} = 2$. $L^{(0)}_l$ in the latter is irreducible by use of (23); see an example for polyhexes (Fig. 1, right); this case will be discussed in the following section.

## Upper Bounds by the Elimination of Inclusive Cycles

We are now looking for polygonal skeletons that give the upper bounds for $K\{P^{(0)}\}$. Let $[b\,b\,R(s)]$ be a cycle (in $P^{(0)}$) such that $K\{[a\,s\,a\,r]\} \geq K\{[a'\,s\,a'\,r]\}$ by means of (23). Such a cycle is called "inclusive" hereafter. This inequality requirement means that one subskeleton $[a\,s\,a\,r]$ includes the other subskeleton $[a'\,s\,a'\,r]$ from the point of view of the enumeration of $K$, although the conjugated patterns in the subskeletons are locally different.

It is helpful to illustrate the cause of inclusion by explaining the reduction process in detail.

$$K\{[b\,b\,a\,b\,b\,a]\,[b\,a\,b\,b\,a\,b\,r]\} = K\{[a\,a\,b\,b\,a\,a\,r]\} + K\{[a'\,a\,b\,b\,a\,a'\,r]\},$$

$$K\{[a'\,a\,b\,b\,a\,a'\,r]\} = K\{[-a'-a{=}b-b{=}a-a'-r]\},$$

$K\{[a\,a\,b\,b\,a\,a\,r]\}$

$\quad = K\{[-a{=}a-b{=}b-a{=}a-r]\} + \ldots,$

$K\{[-a'-a{=}b-b{=}a-a'-r]\}$

$\quad = K\{[-a{=}a-b{=}b-a{=}a-r]\}\,.$

Consequently, $K\{[a\,a\,b\,b\,a\,a\,r]\} \geq K\{[a'\,a\,b\,b\,a\,a'\,r]\}$.

The first line represents the elimination of cycle $[b\,b\,a\,b\,b\,a]$ by use of (23), where $(s) = (a\,b\,b\,a) = R(s)$. The second line represents only one conjugated pattern in $[a'\,s\,a'\,r]$; the single bond joins the outside vertex and $(a')$, the single bond joins $(a')$ and $(a)$, the double bond joins $(a)$ and $(b)$, and so on. The third line represents one of the conjugated patterns in $[a\,s\,a\,r]$; the single bond joins the outside vertex and $(a)$, the double bond joins $(a)$ and $(a)$, the single bond joins $(a)$ and $(b)$, and so on. The fourth line represents the equality of the numbers of two conjugated patterns. The last line represents the conclusion. We obtain a list of inclusive cycles (4- to 8-membered).

List of inclusive cycles (Figure 2).

4-membered: $[b\,b\,a\,a]$, $[b\,b\,a\,b]$.
6-membered: $[b\,b\,a\,b\,b\,a]$, $[b\,b\,a\,b\,a\,b]$.
8-membered: $[b\,b\,a\,b\,b\,a\,b\,a]$, $[b\,b\,a\,b\,a\,b\,a\,b]$.

It should be noted that for instance the tetragonal cycles in the list are appropriate for the reduction of polyhex skeletons because of the equivalence relation ((1), (2) and (38)); e.g.,

$$K\{[b\,a\,a\,b\,a\,a]\} = K\{[b\,b\,a\,a\,a\,a]\} = K\{[b\,b\,a\,a]\},$$

$$K\{[b\,a\,a\,b\,a\,b]\} = K\{[b\,b\,a\,a\,a\,b]\} = K\{[b\,b\,a\,b\,a\,a]\} = K\{[b\,b\,a\,b]\};$$

these five hexagonal cycles are all inclusive (remember the cyclic property for cycles as $[b\,b\,a\,b] = [b\,b\,b\,a]$). The hexagonal cycles, $[b\,a\,b\,a\,a\,a]$, $[b\,a\,b\,a\,b\,a]$, $[b\,b\,b\,b\,a\,a]$, $[b\,b\,b\,b\,b\,a]$, and $[b\,b\,b\,b\,b\,b]$, are not inclusive.

Let $[b\,b\,R(s)]$ be an inclusive cycle in $P^{(0)}$, and let $U_1^{(0)}$ denote a polygonal skeleton with $[a\,s\,a\,r]$ that is obtainable in terms of (23). Easily we get the inequality relation $K\{P^{(0)}\} \leq 2K\{U_1^{(0)}\}$. Repeating this inclusive elimination $l$ times necessarily comes to an end; the polygonal skeleton $U_l^{(0)}$ at the end has no inclusive cycles.

*Lemma 10:* $K\{P^{(0)}\} \leq 2K\{U_1^{(0)}\} \leq 2^2 K\{U_2^{(0)}\} \leq \ldots \leq 2^l K\{U_l^{(0)}\}\,.$

It is easy to calculate $K\{U_l^{(0)}\}$ when $U_l^{(0)}$ is a single polygon $S$; then, $K\{P^{(0)}\} \leq 2^{l+1}$ if the number of vertices in $S$ is even, and $K\{P^{(0)}\} = 0$ if the number of vertices in $S$ is odd. Figure 3 represents two examples for polyhexes, in which $U_l^{(0)}$ is not a single polygon.

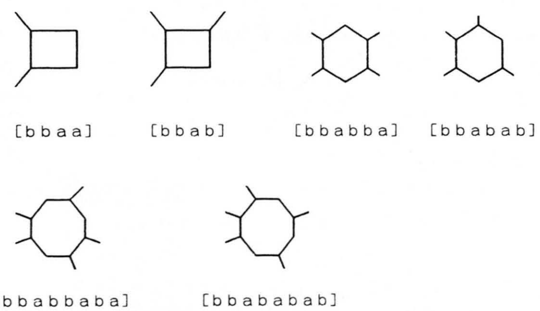


Fig. 2. List of inclusive cycles (4- to 8-membered).

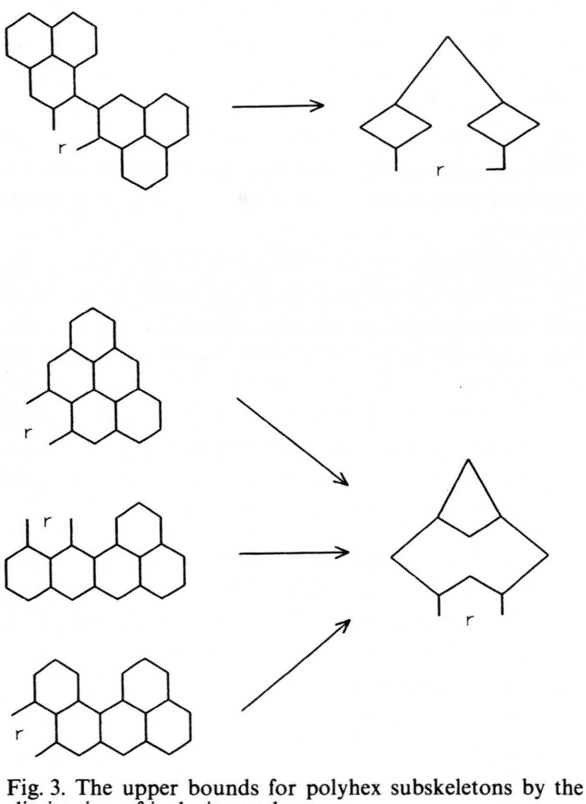


Fig. 3. The upper bounds for polyhex subskeletons by the elimination of inclusive cycles.

(i) The polyhex skeleton at the top of Fig. 3 is taken from [2]; then,

$$K\{[b\,b\,a\,a\,a\,b\,a\,a\,a\,b\,a\,b\,b\,b\,a\,a\,a\,b\,a\,a\,a\,b\,a\,b\,r]\} \le 2^4 K\{U_4^{(0)}\}\,.$$

(ii) It has been reported [3] that the "eight concealed non-Kekuléan benzenoids" [4] are composed of five parts (three polyhexes at the bottom of Fig. 3, and two reflections of the last two); every part (polyhex) is reducible to a symmetrical skeleton $U_3^{(0)}$; e.g., for the last polyhex in Figure 3,

$$K\{[b\,a\,b\,a\,b\,a\,a\,a\,b\,a\,a\,a\,b\,b\,b\,a\,a\,a\,b\,r]\} \le 2^3 K\{U_3^{(0)}\}\,.$$

One observes two cycles, $[b\,a\,b\,a]$ and $[b\,a\,b\,a\,b\,a\,b\,a]$, in $U_4^{(0)}$ and $U_3^{(0)}$. The estimation of such cycles is discussed in the next section.

## Alternate Cycles and Alternate Paths

A cycle (cyclic subskeleton) in $P^{(n)}$ is referred to "alternate" hereafter, if two vertices, $(b)$ and $(a)$, appear one after the other in the cycle; e.g., $[b\,a\,b\,a\,b\,a]$. Notice that the hexagonal cycle $[b\,a\,b\,a\,a\,a]$ in Fig. 1 (right) is alternate, because $K\{[b\,a\,b\,a\,a\,a]\} = K\{[b\,a\,b\,a]\}$. A conjugated pattern in alternate cycles has the property that if $K > 0$, then every bond that meets at the outside vertices of the cycle is necessarily single, and then the single and double bonds arrange by turns in the cycle; the conjugated patterns in alternate cycles are similar to the aromatic sextet [5] in benzenoid skeletons.

A path $(b\,(a\,b)_j\,a\,b)$ $(j \ge 0)$ is called "alternate" hereafter. A path beginning at $(b)$ and ending at $(b)$ in alternate cycles is an example of this. If every bond that joins the terminal $(b)$ and the nearest $(a)$ in an alternate path is single, then there is no conjugated pattern in the alternate path; i.e., $K\{[b-(a\,b)_j\,a-b\,r]\} = 0$. It is possible to put the terminal vertex $(b)$ in an alternate path upon the vertex $(b)$ in alternate cycles as the root vertex. We can thus state that:

*Lemma 11:* If $P^{(n)}$ $(n \ge 0)$ has two alternate cycles such that either they are connected by an alternate path or they share an alternate path, then $K\{P^{(n)}\} = 0$.

We now have a lemma to estimate two examples, $U_4^{(0)}$ and $U_3^{(0)}$, described in the previous section (Figure 3). (i) In $U_4^{(0)}$, the alternate path $(b\,a\,b)$ links one $[b\,a\,b\,a]$ with the other $[b\,a\,b\,a]$. (ii) In $U_3^{(0)}$, the alternate cycle $[b\,a\,b\,a]$ shares the alternate path $(b\,a\,b)$ with the alternate cycle $[b\,a\,b\,a\,b\,a\,b\,a]$. Lemma 11 tells us that $K\{U_4^{(0)}\} = K\{U_3^{(0)}\} = 0$; i.e., each polyhex subskeleton in Fig. 3 is non-Kekuléan.

## Reduction of Polygonal Skeletons by Cycle-Replacement

There is yet another $P^{(0)}$ for an inquiry, to which (23) is not applicable; e.g., the right top of Figure 1. Let $[[b\,a\,b\,a]\,r]$ be a cycle into which $[b\,a\,b\,a]$ is put. The alternate cycle $[b\,a\,b\,a]$ looks like an $(a')$, because each bond that joins the cycle and the outside vertex of the cycle is single. Noting that there are only two conjugated patterns in an alternate cycle (if $K > 0$), we have:

*Lemma 12:* $K\{[[b\,a\,b\,a]\,r]\} = 2K\{[a'\,r]\}\,.$

This lemma successively leads to $K$ {skeleton at the right top of Fig. 1} $= 2^6 K\{[a'a'a'a'a'a']\} = 2^6 K\{[a'a'a']\} = 2^6$. Arguments for the alternate cycle $[b\,a\,b\,a\,b\,a]$, which can be replaced by $(b')$, are similar to those mentioned above.

*Lemma 13:* $K\{[[b\,a\,b\,a\,b\,a]\,r]\} = 2K\{[b'\,r]\}\,.$

*Lemma 14:* $K\{[[(b\,a)_{j+3}]\,r]\} = 2K\{[(b')_{j+1}\,r]\}\,.$

When the reduction of $P^{(0)}$ by means of the cycle-replacement yields more general $P^{(n)}$ $(n > 0)$, we should return to the discussion in the Introduction. If two cycles, $[b\,a'\,b\,R(s)]$ and $[b\,s\,b\,r]$, are connected with each other by sharing the path $(b\,s\,b)$, then it is possible to bring $P^{(n)}$ $(n > 0)$ back to other polygonal skeletons of the type $P^{(0)}$ by use of Lemma 12 and (19) in [1].

*Lemma 15:* $$K\{[b\,[b\,a\,b\,a]\,b\,R(s)]\,[b\,s\,b\,r]\} = 2K\{[a\,s\,a\,r]\}\,.$$


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