Structural Features for Non-Existence of Conjugated Patterns for Carbocyclic and Heterocyclic Compounds *

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At least one polygonal arc $(a'\,a\,a')$, where (a') and (a) denote unconjugated and conjugated vertices (connected with two vertices), respectively, is involved implicitly and/or explicitly in a skeleton of carbocyclic and heterocyclic compounds with no side-chains, if the number of conjugated vertices is even, and if there is no conjugated structure. This case is discussed in detail.

Introduction

Let P be a polygonal skeleton in a class of carbocyclic and heterocyclic compounds [1]. Two reduction algorithms [1] are applicable to the enumeration of the number $K\{\mathrm{P}\}$ of conjugated patterns of P. By use of the first algorithm *Lemma 1* in [1] stated that: If $K\{\mathrm{P}\}>0$, then $v(\mathrm{P})+n(\mathrm{P})$ is even. Here $v(\mathrm{P})$ is the number of vertices of P, and $n(\mathrm{P})$ is the number of prime marks on P. The odd-even parity for $v(\mathrm{P})+n(\mathrm{P})$ coincides with that for $\{v(\mathrm{P})-n(\mathrm{P})\}$, because

$$v(\mathrm{P})+n(\mathrm{P})=\{v(\mathrm{P})-n(\mathrm{P})\}+2n(\mathrm{P}).$$

$\{v(\mathrm{P})-n(\mathrm{P})\}$ is equal to the number of conjugated vertices because $n(\mathrm{P})$ is just the number of unconjugated vertices.

According to the last paragraph in [1], the second algorithm yields:

Lemma 4: If $K\{\mathrm{P}\}>0$, then there is at least one route from P to S such that four integers, $v(\mathrm{P})+m_{1,3}(\mathrm{P},\mathrm{S})$, $v(\mathrm{S})$, $n(\mathrm{P})+m_{1,3}(\mathrm{P},\mathrm{S})$ and $n(\mathrm{S})$, have the same odd-even parity as one another.

Here $m_{1,3}(\mathrm{P},\mathrm{S})$ stands for the total number of classes a^1 and a^3 along a route from P to a single polygon S.

The inverse of this statement, as well as the inverse of *Lemma 1,* is not valid; in other words, not all P such that the number of conjugated vertices is even, has the value $K\{\mathrm{P}\}>0$. The cause is, as shown in (28), (28′) and (28″) of [1], that there is a type of single polygon S containing the arc $(a'\,a\,a')$ such that $v(\mathrm{S})+n(\mathrm{S})=$ even, and $K\{\mathrm{S}\}=0$. The present note deals mainly with the non-existence conditions of conjugated patterns for P having the arc $(a'\,a\,a')$.

Existence Theorem on Conjugated Patterns

It is impossible to complete the conjugated structure of P if the cycle $[a'\,a\,a'\,r]$ occurs in the route of contraction and elimination of (A). Note that $K\{[a'\,(a)_{2j+1}\,a'\,r]\}=K\{[a'\,a\,a'\,r]\}$. Such a cycle is called "null" hereafter. Three cycles, $[b'\,a\,a'\,r]$, $[a'\,a\,b'\,r]$ and $[b'\,a\,b'\,r]$ (in (27) of [1]), are all null, because (b') is necessarily replaced by (a') after the elimination of cycles. The triangle $[a'\,a'\,a]$, and the tetragons, $[a'\,a\,a'\,a]$ and $[a'\,a'\,a'\,a]$, are all null polygons (cf., (28),

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* *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 class of cycles in the reduction of (A); $v(A)=i$,
- $[\ldots]$ cycle of P,
- (s), (t), (u) path, composed of (a), (a'), (b) and (b'), on a cycle of P
- r abbreviation for the rest,
- w_i definite integer, in calculation,
- i 1, 2,...,
- $R()$ reflection of (),
- $K\{\mathrm{P}\}$ number of conjugated patterns of P,
- $K\{[\ldots]\}$ number of conjugated patterns of a polygonal skeleton having a cycle $[\ldots]$,
- $v()$ number of vertices for (),
- $n(\mathrm{P})$ number of prime marks on the vertices of P,
- S single polygon to which P is reducible,
- $m_{1,3}(\mathrm{P},\mathrm{S})$ number of classes a^1 and a^3 along a route from P to S,
- $\mathrm{P}(n)$ polygonal skeleton with n prime marks.

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(28′), (28″) in [1]). We can state, using *Lemmas 1–4*, that:

Lemma 5: If P contains no null cycles, and if the number of conjugated vertices is even, then $K\{\mathrm{P}\} > 0$, and vice versa. (Contraposition) If $K\{\mathrm{P}\} = 0$, then either the number of conjugated vertices is odd, or P involves null cycles, and vice versa.

Radical Sites on Polygonal Skeletons

$\mathrm{P}^{(n)}$ may be called an *n*-radical (conjugated) if $K\{\mathrm{P}^{(n)}\} > 0$ $(n > 0)$ in the case where each vertex with the prime mark can be interpreted as a radical site (cf. Introduction of [1]). We can construct an $(n+k)$-radical $((n-k)$-radical) by adding (deleting) k prime marks to (from) a given skeleton $\mathrm{P}^{(n)}$. Practical construction of $\mathrm{P}^{(n\pm k)}$ is done as follows.

(i) If $K\{\mathrm{P}^{(n)}\} > 0$, then every reduction rule in [1] can be read as an algorithm for forming $\mathrm{P}^{(n\pm k)}$. In the a^2 class ((8) of [1]), for example, $K\{[b\,a\,a\,b\,r]\} = K\{[b\,a\,a\,b\,R(s)]\,[b\,s\,b\,r]\} = K\{[a\,s\,a\,r]\} + K\{[a'\!s\,a'\!r]\} = K\{[b\,a'\,a'\,b\,r]\} + K\{[b'\,a\,a\,b'\,r]\}$; hence, if $K\{[b\,a\,a\,b\,r]\} > 0$, then either $[b\,a'\,a'\,b\,r]$ or $[b'\,a\,a\,b'\,r]$ is an $(n+2)$-radical.

(ii) The classes a^3 and a^1 change the odd-even parity for $n(\mathrm{P})$.
$K\{\text{phenalene}\} = K\{[b\,a\,a\,a\,b\,a\,a\,a\,b\,a\,a\,a]\} = 0$, but $K\{[b\,a'\,a\,a\,b\,a\,a\,a\,b\,a\,a\,a]\} > 0$; i.e., $[b\,a'\,a\,a\,b\,a\,a\,a\,b\,a\,a\,a]$ is a monoradical.

(iii) Assume that $\mathrm{P}^{(n)}$ is reduced to Q; Q is a polygonal skeleton on which null cycles $[a'\,a\,a'\,r]$ appear. Notice that we can prepare Q' such that $K\{Q'\} > 0$, without fail, by adding prime marks to $[a'\,a\,a'\,r]$; the number of prime marks added is equal to $n(Q') - n(Q) = k$. A copy of the k prime marks of Q' is made on $\mathrm{P}^{(n)}$. The resulting $\mathrm{P}^{(n+k)}$ is an $(n+k)$-radical, because $\mathrm{P}^{(n+k)}$ is reducible to Q', and $K\{\mathrm{P}^{(n+k)}\} \geq K\{Q'\} > 0$. Let $\mathrm{P}^{(0)}$ be a polyhex skeleton in the "eight concealed non-Kekuléan benzenoids [4]"; then $\mathrm{P}^{(0)}$ is reducible to the single hexagon $[a'\,a\,a'\,a\,a\,a]$; i.e, $K\{\mathrm{P}^{(0)}\} = 4\,K\{[a'\,a\,a'\,a\,a\,a]\}$ for the 6-hexagonal triangle, and $K\{\mathrm{P}^{(0)}\} = 3\,K\{[a'\,a\,a'\,a\,a\,a]\}$ for the others (cf. Fig. 2, below, and *Lemma 7*). The eight skeletons (benzenoids) are all diradicals, because $K\{[a'\,a\,a'\,a\,a\,a]\} = K\{[a'\,a\,a'\,a]\}$ shows that the number of null arcs is 2.

Null Cycles in Polygonal Skeletons

Let us consider the necessary and sufficient conditions under which a given skeleton P is reduced to another containing $[a'\,a\,a'\,r]$.

1. Let us assume that a given cycle $[b\,t\,b\,r]$ of P is composed of two cycles, $[b\,t\,b]$ and $[b\,b\,r]$; they are connected with each other by sharing the path $(b\,b)$. Here any path (t) may or may not contain (b)'s and (b')'s. Then $[b\,t\,b\,r]$ is separated into 8 factor cycles (Fig. 1 above):

$$K\{[b\,t\,b\,r]\} = K\{[b\,t\,b]\;[b\,b\,r]\}$$
$$= K\{[a'\,a'\,t]\} \times K\{[a\,a\,r]\} + K\{[a\,a'\,t]\} \times K\{[a\,a'\,r]\}$$
$$+ K\{[a'\,a\,t]\} \times K\{[a'\,a\,r]\} + K\{[a\!-\!a\,t]\} \times K\{[a'\,a'\,r]\}.$$

This equation gives two equalities:

$$K\{[b\,t\,b\,r]\}$$
$$= K\{[a'\,a'\,t]\} \times K\{[a\,a\,r]\} + K\{[a\!-\!a\,t]\} \times K\{[a'\,a'\,r]\}$$
$$= K\{[a'\,a'\,t]\} \times K\{[a\,a\,r]\} + (K\{[a\,a\,t]\} - K\{[a'\,a'\,t]\})$$
$$\times K\{[a'\,a'\,\mathrm{r}]\}$$

for either $K\{[a'\,a'\,t]\} > 0$ or $K\{[a\,a\,t]\} > 0$;
and $K\{[b\,t\,b\,r]\} = K\{[a\,a'\,t]\} \times K\{[a\,a'\,r]\} + K\{[a'\,a\,t]\} \times K\{[a'\,a\,r]\}$
for either $K\{[a\,a'\,t]\} > 0$ or $K\{[a'\,a\,t]\} > 0$.

The first equality is rewritten as $K\{[b\,t\,b\,r]\} = K\{[a\!=\!a\,t]\} \times K\{[a\!=\!a\,r]\} + K\{[a\!=\!a\,t]\} \times K\{[a\!-\!a\,r]\} + K\{[a\!-\!a\,t]\} \times K\{[a\!=\!a\,r]\}$;

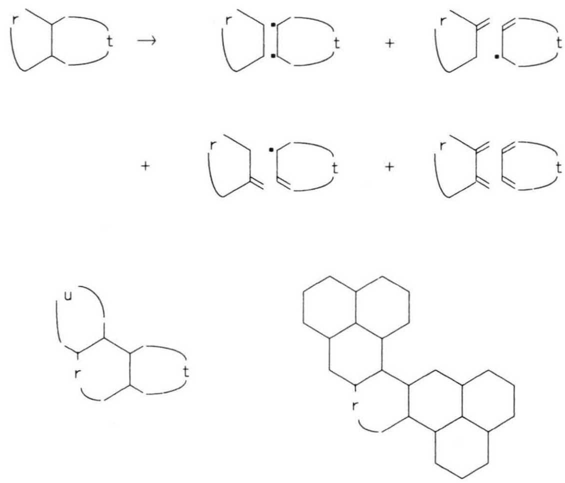

Fig. 1. Decomposition of $[b\,t\,b\,r]$ (above), and $[b\,t\,b\,b\,u\,b\,r]$ (left below); an example for null cycles (right below). Dots on vertices denote prime marks.

this is just Randic's relation [2] in our notation; namely,
$K\{[b\,R(t)\,b\,r]\}=K\{[b\,t\,b\,r]\}$, only if
$K\{[a\,a'\,t]\}=K\{[a'\,a\,t]\}=0$.
We combine the first and the second equality. Then the cycle $[b\,t\,b\,b\,u\,b\,r]$ of P becomes null as follows (Fig. 1, left below).

Lemma 6: Four cycles in P, $[b\,t\,b\,b\,u\,b\,r]$, (its decomposition factors) $[a\,a\,t]$, $[a\,a\,u]$ and $[a\,a\,a\,a\,r]$, are given.

(i) If $K\{[a\,a'\,t]\}=w_1>0$, $K\{[a'\,a\,t]\}=0$, $K\{[a\,a'\,u]\}=w_2>0$, and $K\{[a'\,a\,u]\}=0$, then $K\{[b\,t\,b\,b\,u\,b\,r]\}=w_1\,w_2\,K\{[a\,a'\,a\,a'\,r]\}$, and vice versa.

(ii) If $K\{[a\,a\,t]\}=w_1>0$, $K\{[a'\,a'\,t]\}=0$, $K\{[a\,a'\,u]\}=w_2>0$, and $K\{[a'\,a\,u]\}=0$, then $K\{[b\,t\,b\,b\,u\,b\,r]\}=w_1\,w_2\;K\{[a'\,a'\,a\,a'\,r]\}$, and vice versa.

(iii) If $K\{[a'\,a\,t]\}=w_1>0$, $K\{[a\,a'\,t]\}=0$, $K\{[a'\,a\,u]\}=w_2>0$, and $K\{[a\,a'\,u]\}=0$, then $K\{[b\,t\,b\,b\,u\,b\,r]\}=w_1\,w_2\,K\{[a'\,a\,a'\,a\,r]\}$, and vice versa.

(iv) If $K\{[a'\,a\,t]\}=w_1>0$, $K\{[a\,a'\,t]\}=0$, $K\{[a\,a\,u]\}=w_2>0$, and $K\{[a'\,a'\,u]\}=0$, then $K\{[b\,t\,b\,b\,u\,b\,r]\}=w_1\,w_2\;K\{[a'\,a\,a'\,a'\,r]\}$, and vice versa.

The cycle $[b\,b\,a\,a\,a\,b\,a\,a\,a\,b\,a\,b\,b\,b\,a\,a\,a\,b\,a\,a\,a\,b\,a\,b\,r]$, part of the figure in [3], is an example for (i) of *Lemma 6* (Fig. 1, right below).

2. Assume that the cycle $[b\,t\,b\,r]$ is made up of two cycles, $[b\,t\,b\,R(s)]$ and $[b\,s\,b\,r]$; they are connected with each other by sharing the path $(b\,s\,b)$. First regard (s) as only one (b). Then $[b\,t\,b\,r]$ can be separated into 16 factor cycles (Fig. 2, above). The bonds of $b(-)$ and $b(=)$ are outside the cycle:

$$\begin{aligned}
&K\{[b\,t\,b\,b]\;[b\,b\,b\,r]\}\\
&=K\{[-a-b(-)-a-t]\}\times K\{[a\,a\,a\,r]\}\\
&\quad+K\{[=a-b(-)-a-t]\}\times K\{[a\,a\,a'\,r]\}\\
&\quad+K\{[-a-\mathrm{b}(=)-a-t]\}\times K\{[a\,a'\,a\,r]\}\\
&\quad+K\{[-a-b(-)-a=t]\}\times K\{[a'\,a\,a\,r]\}\\
&\quad+K\{[=a-b(=)-a-t]\}\times K\{[a\,a'\,a'\,r]\}\\
&\quad+K\{[=a-b(-)-a=t]\}\times K\{[a'\,a\,a'\,r]\}\\
&\quad+K\{[-a-b(=)-a=t]\}\times K\{[a'\,a'\,a\,r]\}\\
&\quad+K\{[=a-b(=)-a=t]\}\times K\{[a'\,a'\,a'\,r]\}\\
&=K\{[a'\,b'\,a'\,t]\}\times K\{[a\,a\,a\,r]\}+K\{[a\,b'\,a'\,t]\}\\
&\quad\times K\{[a\,a\,a'\,r]\}+K\{[a'\,b\,a'\,t]\}\times K\{[a\,a'\,a\,r]\}\\
&\quad+K\{[a'\,b'\,a\,t]\}\times K\{[a'\,a\,a\,r]\}+K\{[a-b\,a'\,t]\}\\
&\quad\times K\{[a\,a'\,a'\,r]\}+K\{[a\,b'\,a\,t]\}\times K\{[a'\,a\,a'\,r]\}\\
&\quad+K\{[a'\,b-a\,t]\}\times K\{[a'\,a'\,a\,r]\}+K\{[a-b-a\,t]\}\\
&\quad\times K\{[a'\,a'\,a'\,r]\}.
\end{aligned}$$

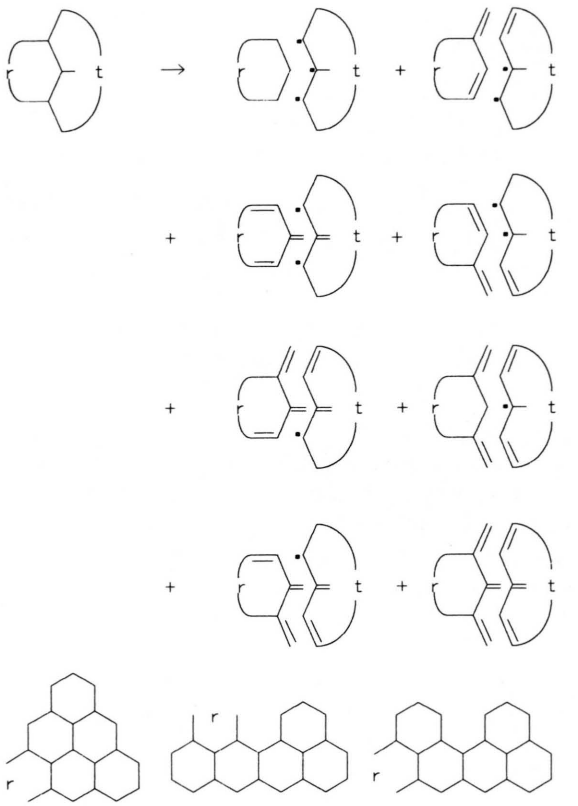

Fig. 2. Decomposition of $[b\,t\,b\,r]$ (above); three examples for null cycles (below). Dots on vertices denote prime marks.

Notice that if $K\{[a\,b'\,a\,t]\}>0$ (the coefficient of $K\{[a'\,a\,a'\,r]\}$), then $K\{[a\,b'\,a'\,t]\}=K\{[a'\,b\,a'\,t]\}=K\{[a'\,b'\,a\,t]\}=K\{[a\,b\,a\,t]\}=0$ (*Lemma 2* of [1]), and that $K\{[a\,b\,a\,t]\}=K\{[a-b-a\,t]\}+K\{[a\,b'\,a'\,t]\}+K\{[a'\,b'\,a\,t]\}$, $K\{[a\,b\,a'\,t]\}=K\{[a-b\,a'\,t]\}+K\{[a'\,b'\,a'\,t]\}$, and $K\{[a'\,b\,a\,t]\}=K\{[a'\,b-a\,t]\}+K\{[a'\,b'\,a'\,t]\}$. Thus we obtain

Lemma 7: A cycle $[b\,t\,b\,r]$ in P, composed of $[b\,t\,b\,b]$ and $[b\,b\,b\,r]$, is given; they are connected with each other by sharing the path $(b\,b\,b)$. If $K\{[a\,b'\,a\,t]\}=w>0$ and $K\{[a\,b\,a'\,t]\}=K\{[a'\,b\,a\,t]\}=0$, then $K\{[b\,t\,b\,r]\}=w\;K\{[a'\,a\,a'\,r]\}$, that is, $[b\,t\,b\,r]$ is null, and vice versa.

If $[b\,t\,b\,r]$ is null, then $[b\,R(t)\,b\,r]$ is also null, because $0<K\{[a\,b'\,a\,t]\}=K\{R([a\,b'\,a\,t])\}=K\{[R(t)\,a\,b'\,a]\}=K\{[a\,b'\,a\,R(t)]\}$, $0=K\{[a\,b\,a'\,t]\}=K\{R([a\,b\,a'\,t]\}=K\{[a'\,b\,a\,R(t)]\}$, and $0=K\{[a'\,b\,a\,t]\}=K\{R([a'\,b\,a\,t]\}=K\{[a\,b\,a'\,R(t)]\}$. We can find five null cycles on the polyhex lattice as part of the "eight concealed non-

Kekuléan benzenoids [4]"; they are expressed in our notation as

$[b\,a\,b\,a\,a\,a\,b\,a\,b\,a\,a\,a\,b\,a\,b\,r]$,
$[b\,a\,a\,a\,b\,a\,b\,a\,b\,a\,a\,a\,b\,a\,a\,a\,b\,b\,b\,r]$,
$[b\,a\,b\,a\,b\,a\,a\,a\,b\,a\,a\,a\,b\,b\,b\,a\,a\,a\,b\,r]$,

and as the reflection of the last two (Fig. 2, below). The simplest cycle $[a\,b'\,a\,t]$ with $K>0$ on the polyhex lattice is given by the path $(t)=(a\,a'\,a\,b\,a\,a\,a)$; this cycle is formed from two hexagons.

3. The discussion similar to *Lemma 7* mentioned above leads to the second case, where (s) is chosen as $(b\,b)$. Note that

$K\{[a\,b\,b\,a\,t]\}$
$=K\{[a'\,b'\,b'\,a'\,t]\}+K\{[a-b\,b'\,a'\,t]\}+K\{[a\,b'\,b'\,a\,t]\}$
$+K\{[a'\,b'\,b-a\,t]\}+K\{[a-b-b-a\,t]\}$,
$K\{[a\,b\,b\,a'\,t]\}$
$=K\{[a\,b'\,b'\,a'\,t]\}+K\{[a-b-b\,a'\,t]\}$
$+K\{[a'\,b'\,b\,a'\,t]\}$, $K\{[a'\,b\,b\,a\,t]\}$
$=K\{[a'\,b'\,b'\,a\,t]\}+K\{[a'\,b-b\,a\,t]\}+K\{[a'\,b\,b'\,a'\,t]\}$,
$K\{[a'\,b\,b\,a'\,t]\}$
$=K\{[a'\,b'\,b'\,a'\,t]\}+K\{[a'\,b-b\,a'\,t]\}$, $K\{[a\,b'\,b\,a\,t]\}$
$=K\{[a\,b'\,b'\,a'\,t]\}+K\{[a\,b'\,b-a\,t]\}$, and
$K\{[a\,b\,b'\,a\,t]\}=K\{[a'\,b'\,b'\,a\,t]\}+K\{[a-b\,b'\,a\,t]\}$.

Thus the cycle $[b\,t\,b\,r]$ is decomposed into 32 factor cycles, and is reduced to null cycles in the following.

Lemma 8: Two cycles, $[b\,t\,b\,b\,b]$ and $[b\,b\,b\,b\,r]$, connected with each other by sharing the path $(b\,b\,b\,b)$, are given. (i) Either if $K\{[a\,b'\,b\,a'\,t]\}=w_1>0$ or if $K\{[a'\,b\,b'\,a\,t]\}=w_2>0$, and if $K\{[a\,b\,b\,a\,t]\}=K\{[a'\,b\,b\,a'\,t]\}=0$, then $K\{[b\,t\,b\,r]\}=w_1\,K\{[a\,a'\,a\,a'\,r]\}+w_2\,K\{[a'\,a\,a'\,a\,r]\}$, and vice versa. (ii) Either if $K\{[a\,b\,b'\,a\,t]\}=w_1>0$ or if $K\{[a\,b'\,b\,a\,t]\}=w_2>0$, and if $K\{[a'\,b\,b\,a\,t]\}=K\{[a\,b\,b\,a'\,t]\}=0$, then $K\{[b\,t\,b\,r]\}=w_1\,K\{[a'\,a\,a'\,a'\,r]\}+w_2\,K\{[a'\,a'\,a\,a'\,r]\}$, and vice versa.

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