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

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Z. Naturforsch. 49a, 719–722 (1994); received March 15, 1994

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{P} of conjugated patterns of P. By use of the first algorithm Lemma 1 in [1] stated that: If K{P} > 0, then v(P) + n(P) is even. Here v(P) is the number of vertices of P, and n(P) is the number of prime marks on P. The odd-even parity for v(P) + n(P) coincides with that for {v(P) − n(P)}, because v(P) + n(P) = {v(P) − n(P)} + 2n(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') path, composed of (a), (a'), (b) and (b'), on a cycle of P
r abbreviation for the rest,
v_i definite integer, in calculation,
i 1, 2, ...
K{P} number of conjugated patterns of P
K{[...]} number of conjugated patterns of a polygonal skeleton having a cycle [...]
v(1) number of vertices for (1)
v(P) number of prime marks on the vertices of P,
n(P) number of prime marks on the vertices of P, m_{1,3}(P, S) number of classes a^1 and a^3 on a route from P to S,
P(n) polygonal skeleton with n prime marks.

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Existence Theorem on Conjugated Patterns

It is impossible to complete the conjugated structure of P if the cycle [a' a a'a'] occurs in the route of contraction and elimination of (A). Note that K{[a' a a'a']_2} = K{[a' a a'a']}. Such a cycle is called “null” hereafter. Three cycles, [b' a a'a'], [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'd'a'], and the tetragons, [a' a a'd'] and [a'd' a'], are all null polygons (cf., (28), (28'), (28'')) and (28''), and (28'').
(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 \( K\{P\} > 0 \), and vice versa. (Contraposition) If \( K\{P\} = 0 \), then either the number of conjugated vertices is odd, or \( P \) involves null cycles, and vice versa.

Radical Sites on Polygonal Skeletons

\( P^{(n)} \) may be called an \( n \)-radical (conjugated) if \( K\{P^{(n)}\} > 0 \) \((n > 0)\) 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 \( P^{(n)} \). Practical construction of \( P^{(n + k)} \) is done as follows.

(i) If \( K\{P^{(n)}\} > 0 \), then every reduction rule in [1] can be read as an algorithm for forming \( P^{(n + k)} \). In the \( a^2 \) class \((8)\) of [1], for example,

\[
K\{baabr\} + K\{baabb\} = K\{b'a'br\} + K\{b'aab\} \quad \text{or} \quad K\{baabr\} = K\{b'a'br\} + K\{b'aab\}.
\]

(ii) The classes \( a^3 \) and \( a^1 \) change the odd-even parity for \( P \).

\[
K\{phenalene\} = K\{baabaabaaaba\} = 0, \quad \text{but} \quad K\{baabaabaaaba\} > 0; \quad \text{i.e.,} \quad [baaabaabaa] \quad \text{is a monoradical.}
\]

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

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 \((i)\) may or may not contain \((b)\)'s and \((b)'\)s. Then \([b t b r]\) is separated into 8 factor cycles (Fig. 1 above):

\[
K\{b t b r\} = K\{b t b\} \times K\{b b r\}
\]

\[
= K\{a' a' l\} \times K\{a a' r\} + K\{a a' l\} \times K\{a' a' r\}
\]

\[
+ K\{a a' l\} \times K\{a' a' r\} + K\{a' a' l\} \times K\{a' a' r\}.
\]

This equation gives two equalities:

\[
K\{b t b r\} = K\{a' a' l\} \times K\{a a' r\} + K\{a a' l\} \times K\{a' a' r\}
\]

\[
+ K\{a a' l\} \times K\{a' a' r\} + K\{a' a' l\} \times K\{a' a' r\}.
\]

The first equality is rewritten as \( K\{b t b r\} = K\{a a' l\} \times K\{a a' r\} + K\{a a' l\} \times K\{a' a' r\} \times K\{a' a' l\} \)

\[
\text{for either} \quad K\{a a' l\} > 0 \quad \text{or} \quad K\{a a' r\} > 0;
\]

\[
K\{b t b r\} = K\{a a' l\} \times K\{a a' r\} + K\{a a' l\} \times K\{a' a' r\} \times K\{a' a' l\}
\]

\[
\text{for either} \quad K\{a a' l\} > 0 \quad \text{or} \quad K\{a a' r\} > 0.
\]

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, 
\[ K\{[bR(t)br]\} = K\{[btbr]\}, \]
only if 
\[ K\{[a^'a't]\} = K\{[a'ta']\} = 0. \]
We combine the first and the second equality. Then the cycle \([btbbubr]\) of \(P\) becomes null as follows (Fig. 1, left below).

**Lemma 6:** Four cycles in \(P, [btbbubr]\), (its decomposition factors) \([aa't], [aat]\) and \([aau]\), are given.

(i) If \( K\{[a^'a't]\} = w_1 > 0, K\{[aat]\} = 0, K\{[aau]\} = 0, \)
and \( K\{[btbbubr]\} = w_1 w_2 K\{[a^'a'a'dar]\}, \)
and vice versa.

(ii) If \( K\{[aat]\} = w_1 > 0, K\{[a^'a't]\} = 0, K\{[aau]\} = 0, \)
and \( K\{[btbbubr]\} = w_1 w_2 K\{[a^'a'a'dar]\}, \)
and vice versa.

(iii) If \( K\{[a^'a't]\} = w_1 > 0, K\{[aat]\} = 0, K\{[aau]\} = w_2 > 0, \)
and \( K\{[btbbubr]\} = w_1 w_2 K\{[a^'a'a'dar]\}, \)
and vice versa.

(iv) If \( K\{[a^'a't]\} = w_1 > 0, K\{[aat]\} = 0, K\{[a^'a'u]\} = w_2 > 0, \)
and \( K\{[btbbubr]\} = w_1 w_2 K\{[a^'a'a'dar]\}, \)
and vice versa.

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

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

\[ K\{[btbb]\} = K\{[bbbr]\} \]
\[ = K\{[-a-b(-)-a-t] \times K\{[aaar]\} \]
\[ + K\{[-a-b(-)-a-t] \times K\{[aard]\} \]
\[ + K\{[-a-b(=)-a-t] \times K\{[aarr]\} \]
\[ + K\{[-a-b(=)-a-t] \times K\{[aard]\} \]
\[ + K\{[-a-b(=)-a-t] \times K\{[aaar]\} \]
\[ + K\{[-a-b(=)-a-t] \times K\{[aaar]\} \]
\[ = K\{[a^'a'dar]\} \times K\{[aaar]\} \]
\[ + K\{[a^'a'dar]\} \times K\{[aaar]\} \]
\[ + K\{[a^'a'dar]\} \times K\{[aard]\} \]
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Notice that if \( K\{[ab'a't]\} > 0 \) (the coefficient of \( K\{[a^'a'a'dar]\} \)), then \( K\{[ab'a't]\} = K\{[a^'a'a'dar]\} = 0 \) (Lemma 2 of [1]), and that \( K\{[abat]\} = K\{[a^'b'a't]\} + K\{[aa'a't]\} + K\{[ab'a't]\}, \)
\( K\{[a^'b'a't]\} = K\{[ab't]\} + K\{[ab'a't]\}, \)
and \( K\{[abat]\} = K\{[a^'b'a't]\} + K\{[ab't]\}. \)
Thus we obtain

**Lemma 7:** A cycle \([btbr]\) in \(P\), composed of \([bbbr]\) and \([btbb]\), is given; they are connected with each other by sharing the path \((bbb)\). If \( K\{[ab'a't]\} = w > 0 \) and \( K\{[ab'a't]\} = w K\{[a^'b'a't]\} \)
\( = K\{[ab'a't]\} = 0 \) (Lemma 2 of [1]), and \( K\{[btbr]\} = w K\{[a^'b'a't]\}, \)
that is, \([btbr]\) is null, and vice versa.

If \([btbr]\) is null, then \( K\{[bR(t)br]\}\) is also null, because
\( 0 < K\{[ab'a't]\} = K\{[R(a^'b'a't)]\} = K\{[R(t)a'b'a]\} = K\{[a^'b'a\{R(t)\}]\}, \)
\( K\{[ab'a't]\} = K\{[a^'b'a\{R(t)\}]\}, \)
\( 0 = K\{[a^'b'a\{R(t)\}]\} = 0 = K\{[ab'a't]\} = K\{[a^'b'a\{R(t)\}]\} = K\{[a^'b'a\{R(t)\}]\}. \)
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

\[
[bababaaababababr],
[babababababaaabbr],
[bababababababbabr],
\]
and as the reflection of the last two (Fig. 2, below).
The simplest cycle \([ab' a t]\) with \(K > 0\) on the polyhex lattice is given by the path \((t) = (a'd'abaad)\); 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 \((bb)\). Note that

\[
K[[abbat]]
= K[[a'b' b' a't]] + K[[a'b' b' a't]] + K[[a'b' a't]],
+ K[[a'b' b' a't]],
K[[abbat]]
= K[[a'b' b' a't]] + K[[a'b' b' a't]]
+ K[[a'b' b' a't]],
K[[abbat]]
\]

Thus the cycle \([btbr]\) is decomposed into 32 factor cycles, and is reduced to null cycles in the following.

**Lemma 8**: Two cycles, \([b b b b]\) 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 \(K[[a'b' b' a't]] = w_1 \) \(K[[a'a'd' a'r]] + w_2 K[[a'a'd' a'r]]\), 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 \(K[[a'b' b' a't]] = w_1 \) \(K[[a'b' b' a't]] = 0\), then \(K[[b t b r]] = w_1 K[[a'a'd' a'r]] + w_2 K[[a'a'd' a'r]]\), and vice versa.