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BENZENOID CHAINS WITH THE UNIQUE CLAR FORMULA

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ABSTRACT

A characterization is given for a benzenoid chain to be a Clar chain, i.e. the benzenoid chain with the unique Clar formula. The number of non-isoarithmic Clar chains with h hexagons is determined.

INTRODUCTION

This paper investigates some problems of benzenoid chemistry, a subject which plays a role in astrophysics, cancer research, etc. Graph-theoretical aspects of benzenoid chemistry have recently been reviewed by El-Basil [1]. For general introductory material see the review and references therein.

According to the Clar aromatic sextet theory, a benzenoid hydrocarbon is represented by a Clar formula which is obtained by drawing circles in some of the hexagons of the corresponding benzenoid graph. These circles represent the so-called "aromatic sextets". The rules for constructing a Clar formula are [2,3]: (a) it is not allowed to draw circles in adjacent hexagons; (b) circles can be drawn in hexagons if the rest of the conjugated system has at least one Kekulé structure; and (c) a Clar formula contains the maximum number of circles which can be drawn in accordance with rules (a) and (b).

We shall denote the number of circles in a Clar formula as $S(\mathrm{B})$.

Hosoya and Yamaguchi [4] were the first to define Clar-type formulae, i.e. formulae with less than $S(\mathrm{B})$ circles, constructed by taking into account rules (a) and (b), but not requirement (c).

A one-to-one correspondence exists between Kekulé structures and Clar-type formulae. However [5], in the case of the unique Clar formula, the Clar aromatic sextet theory leads to the same quantitive predictions as the "resonance theory" model of Herndon and Ellzey [6].

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In this paper we characterize benzenoid chains by the unique Clar formula (Clar chains) and determine the number of non-isoarithmic Clar chains with h hexagons.

A CHARACTERISATION OF CLAR CHAINS

We represent a benzenoid chain with h hexagons by the corresponding LA sequence [7], i.e. by an ordered h-typle of the symbols L and A. The ith symbol is A if the ith hexagon is a kink (A-mode hexagon), otherwise the ith symbol is L (for an L-mode hexagon). For instance, the LA sequence of the benzenoid chain shown in Fig. 1 is LLALAALLL, or, in abbreviated form, $L^2ALA^2L^3$.

Let B be a benzenoid chain given by the LA sequence

$$L^{m'_0} A^{m_1} L^{m'_1} A^{m_2} L^{m'_2} \ldots L^{m'_{k-1}} A^{m_k} L^{m'_k} \qquad (1)$$

where: $m'_0 \geq 1$; $m'_k \geq 1$; $m'_i \geq 0$ for $i=1, \ldots, k-1$; and $m_k \geq 1$, for $i=1,2, \ldots, k$.

The part of this chain between the two successive appearances of the A-mode hexagon are said to be an open segment of B. The first m'_0 L-mode hexagons and m'_k last L-mode hexagons also constitute the segments (end segments) of the lengths m'_0 and m'_k, respectively. An inner open segment may be without any hexagon, a "no hexagon" segment.

A closed segment is obtained by adding to an open segment two A-mode hexagons which bound it (if it is an inner segment), and one A-mode hexagon

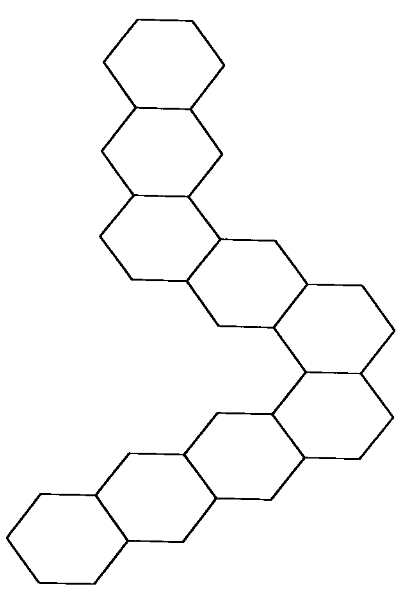

Fig. 1. The LA sequence of the benzenoid chain.

which bounds it (if it is an end segment). Two adjoint closed segments always have exactly one common A-mode hexagon.

According to the rules (a)-(c), the following two observations can be stated. (i) Between any two circles in a Clar-type formula of a benzenoid chain there must be at least one A-mode hexagon (kink) of that chain. (ii) Each closed segment of a benzenoid chain contains exactly one circle in any Clar formula of that chain.

We now prove two statements.

Theorem 1. Let B be a Clar chain and let H be an A-mode hexagon of B adjacent to at least one L-mode hexagon of B. Then H is without circle in any Clar formula of B.

Proof. Consider a closed segment of B with at least one L-mode hexagon. If either of the two A-mode hexagons of that segment has an inscribed circle of the Clar formula of B, then that circle can be replaced by a circle in any of the L-mode hexagon of that segment, producing another Clar formula of B. It is in contradiction with the fact that B is a Clar chain.

Theorem 2. Let B be a Clar chain. Then B does not contain two adjacent L-mode hexagons.

Proof. Consider a closed segment of B with at least two L-mode hexagons. According to Theorem 1, neither of the end hexagons of that segment is circled in the Clar formula of B. According to observations (i) and (ii), exactly one L-mode hexagon of that segment is circled. However, it is clear that each of two L-mode hexagons can be chosen to be circled. So, the existence of two adjacent L-mode hexagons implies that the Clar formula of B is not unique, i.e. B is not a Clar chain.

It is clear that the chain with exactly one hexagon ($h=1$) is a Clar chain. In what follows we consider the non-trivial chains, with $h>1$ hexagons.

From Theorems 1 and 2, the following consequences can be easily derived.

Corollary 1. Let B be a Clar chain with h hexagons ($h>1$). Then the LA sequence of B has the form

$$\mathrm{L\,A}^{m_1}\,\mathrm{L\,A}^{m_2}\,\mathrm{L}\,...\,\mathrm{L\,A}^{m_k}\,\mathrm{L} \qquad (2)$$

where $k\geq 1$; $m_i\geq 1$, for $i=1,2, ..., k$.

Corollary 2. Each L mode hexagon of a Clar chain is circled in the Clar formula of that chain.

A benzenoid chain with h hexagons in which all hexagons except the first and the last are A-mode hexagons is called a zig-zag chain and is denoted by A(h) [8].

Theorem 3. A zig-zag chain A(h) with h hexagons is a Clar chain if, and only if, h is an odd number.

Proof. According to rule (a) of the definition of a Clar formula, a chain with h hexagons cannot have more than $\lceil h/2 \rceil$ circles in its Clar formula. However, if $h=2k+1$ is odd, then the choice of $\lceil h/2 \rceil = k+1$ nonadjacent hexagons of

A(*h*) is unique and obviously it determines the unique Clar formula of A(*h*) ($\lceil x \rceil$ means the least integer $\geq x$).

Consider now an A(*h*) with *h* even. The number of circles in that Clar formula is not greater than $h/2$. However, by removing an L-mode hexagon of A(*h*), we obtain the zig-zag chain A($h-1$) with an odd number of hexagons, which has Clar formula with $h/2$ circles. This Clar formula of A($h-1$) is, at the same time, a Clar formula of the considered A(*h*) without a circle in an L-mode hexagon. According to Corollary 2, A(*h*) is not a Clar chain.

Theorem 4. A benzenoid chain B is a Clar chain if, and only if, it has an LA sequence of the form

$$LA^{m_1}\,L\,A^{m_2}\,L\,...\,L\,A^{m_k}\,L$$

where all the numbers m_1, m_2, ..., m_k are odd.

Proof. If B is a zig-zag chain, the statement is true according to Theorem 3.

Consider the case when B is not a zig-zag chain. In that case B has at least three L-mode hexagons.

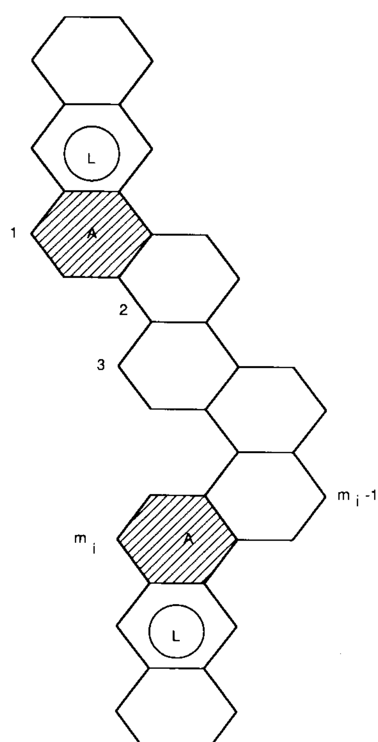

Fig. 2. The part of the benzenoid chain corresponding to the subword A^{m_i}.

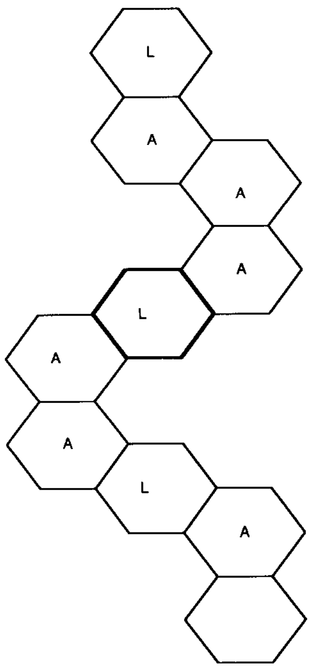

Fig. 3. The last L-mode hexagon of B_1 and the first L-mode hexagon of B_2 of a benzenoid chain.

(a) Necessity. Suppose that B is a Clar chain and for some i, $1 \leq i \leq k$, m_i is even. Consider the part of B corresponding to the subword A^{m_i} (Fig. 2), which is a zig-zag chain $A(m_i)$. Two L-mode hexagons which bound this zig-zag chain in B have circles in the unique Clar formula of B (Corollary 2).

It follows that the first and the last hexagons of $A(m_i)$ (numbered by 1 and m_i in Fig. 2) are without circles in that formula. The remaining part of $A(m_i)$ is a zig-zag chain $A(m_i-2)$ with an even number of hexagons and it is independent of the rest of B with respect to the distribution of circles in the Clar formula of B. So, $A(m_i-2)$ itself must be a Clar chain. This is in contradiction to Theorem 3; it means that m_i cannot be even.

Before proceeding with the proof of the sufficiency part of Theorem 4, we shall formulate a direct consequence of the necessity part of the theorem.

Corollary 3. Let B be a Clar chain with h hexagons. Then h is an odd number.

Proof. The number of hexagons of B is $h = m_1 + m_2 + \ldots + m_k + (k+1)$, where all the members $m_1, m_2, \ldots, m_k$, are odd numbers; so h must be odd.

(b) Proof of sufficiency of Theorem 4. Let B be a benzenoid chain with the LA sequence (2), where all the numbers $m_1, m_2, \ldots, m_k$ are odd, and $k > 1$. According to Corollary 3, the number of hexagons, h, of B is also odd.

Consider B as obtained from two chains B_1 and B_2 with LA sequences of

$LA^{m_1}\,LA^{m_2}\,L\,...\,LA^{m_{k-1}}\,L$

and

$LA^{m_k}\,L$

respectively, by identifying the last L-mode hexagon of B_1 and the first L-mode hexagon of B_2 (Fig. 3).

By induction hypothesis both B_1 and B_2 are Clar chains. The common L-mode hexagon of B_1 and B_2 has a circle in both Clar formulae, i.e. for both B_1 and B_2 (Corollary 2). Hence follows the statement.

Theorem 5. Let B be a Clar chain with h hexagons. Then the number of circles in the unique Clar formula of B is $S(B) = (h+1)/2$.

Proof. It is easy to see that the statement holds if B is a zig-zag chain (see the proof of Theorem 3). Otherwise, consider B as obtained from the chains B_1 and B_2 as in the proof of Theorem 4 (b).

The number of circles in B_1 and B_2 are, by induction hypothesis, $S(B_1) = (m_1+m_2+...+m_{k-1}+k+1)/2$ and $S(B_2) = (m_k+3)/2$, respectively. Taking into account that one circle is common to both formulae, the number of circles in the Clar formula of B is $S(B) = S(B_1) + S(B_2) - 1 = (m_1 + ... + m_k + k + 2)/2 = (h+1)/2$.

THE NUMBER OF NON-ISOARITHMIC CLAR CHAINS

Two benzenoid chains with the same number of hexagons h are isoarithmic if they have equivalent LA sequences. We say that two LA sequences are equivalent if they coincide or can be obtained from each other by reversal. So, the number of non-isoarithmic chains with h hexagons is equal to the number of nonequivalent LA sequences of length h.

The number of nonisoarithmic benzenoid chains with h hexagons is determined in Ref. 9. Here, we shall determine the number of non-isoarithmic chains with h hexagons and with a unique Clar formula. We denote this number by $N(h)$. According to Corollary 3, $N(h) = 0$ if h is an even number, and $N(1) = 1$.

Theorem 6. Let h be an odd positive integer, $h > 1$. Then

$$N(h) = 2^{(h-5)/2} + 2^{\lfloor (h-1)/4 \rfloor - 1}$$

where $\lfloor x \rfloor$ indicates the highest integer $\leqslant x$.

Proof. From Theorem 4 it follows that $N(h)$ is equal to the number of LA sequences of form (2), such that $m_1 + m_2 + ... + m_k = h - k - 1$, $k \geq 1$, and all the numbers $m_1, m_2, ..., m_k$ are odd. However, the number of such LA sequences is equal to the number of partitions of $h-1$ into even positive integers, i.e. to the number of partitions of $n = (h-1)/2$ into positive integers. This last number is equal to $2^{n-1} = 2^{(h-3)/2}$. Among these partitions there are $2^{\lfloor n/2 \rfloor} = 2^{\lfloor (h-1)/4 \rfloor}$

which are symmetric, i.e. which correspond to symmetric (self-reversible) LA sequences. So, the number of nonequivalent LA sequences in question is

$$(2^{(h-3)/2}-2^{\lfloor (h-1)/4\rfloor})/2+2^{\lfloor (h-1)/4\rfloor}=2^{(h-5)/2}+2^{\lfloor (h-1)/4\rfloor-1}$$

which is also the number of non-isoarithmic Clar chains. Among them, $2^{[(h-1)/4]}$ chains are self-isoarithmic.

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