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TOPOLOGICAL PROPERTIES OF SOME NOVEL S,T-ISOMERS (I)

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ABSTRACT: In this paper a type of S,T-isomers is examined, namely S_5,T_5-isomers. They are benzenoid systems formed from three identical subunits, A,A and A', and another one, B. It is proved that an S_5-isomer does not have more aromatic π sextets than its corresponding T_5-isomer. It is also shown that the number of Kekulé structures of an S_5-isomer never exceeds that of its corresponding T_5-isomer.

The concept of S,T-isomers was first introduced by Polansky and Zander [1]. Since then, the concept has been extended in several ways and many properties of such isomers have been studied, see [1]---[7]. In the present paper, we define a new

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type of S,T-isomer pair. They are benzenoid systems. We will consider the Clar formula and the number of Kekulé structures of this pair of isomers.

In [7], some models of topologically related isomers S and T, which are formed from three or four subunits, were given and some of their properties were studied. Motivated by the models in [7], we define a new model of S,T-isomers.

The model is formed from four subunits: three identical terminal ones, A,A and A', and a central one, B. The terminal moieties are linked to the central one by two edges, and each pair of terminal moieties is linked by one edge. (See Fig.1.)

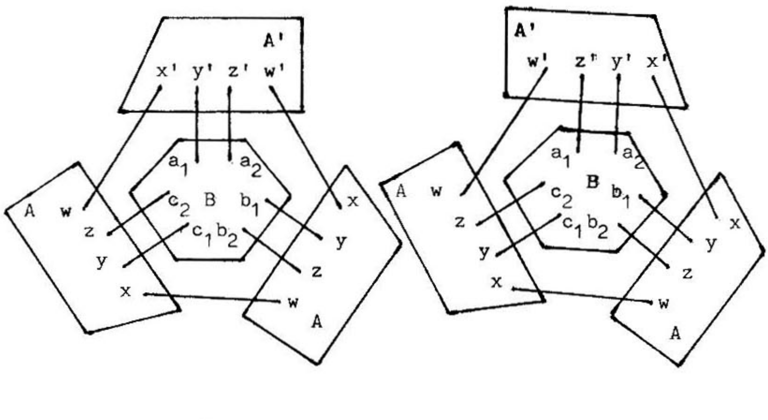
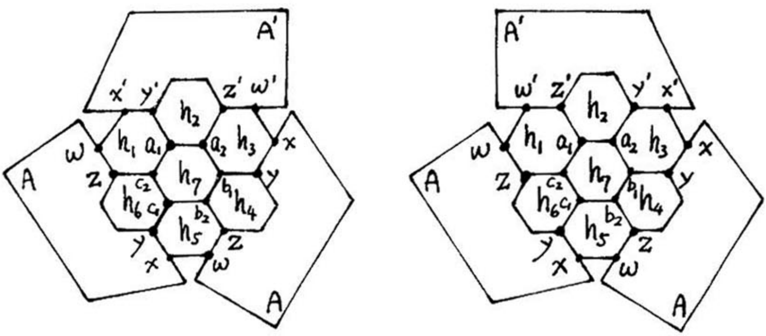


Fig.1

Now we give the definition of the S_5, T_5-isomers. We restrict ourselves to the case of benzenoid system.

We call the S,T-isomers shown in Fig.1 model 1. In model 1, let B be the central subunit consisting of six vertices a_1, a_2, b_1, b_2, c_1, c_2. Let x,y,z,w be four vertices of A and x',y', z',w' four vertices of A' corresponding to the x,y,z,w separately. Conjugated system $S_5(T_5)$ is obtained from the S(T), in model 1, by joining a_1 to a_2, c_2; b_1 to a_2, b_2 and c_1 to b_2, c_2, respectively. (See Fig.2.) These two conjugated systems are called S_5, T_5-isomers.



S_5 T_5

Fig.2

For convenience, the hexagon B together with the hexagons which have an edge in common with B are labelled by h_i, i = 1, 2,...,7.(See Fig.2.) The subgraph consisting of these seven hexagons will be denoted by H. Recall that H is the molecular graph of coronene. Let P denote the set $\{a_1, a_2, b_1, b_2, c_1, c_2\}$ and n(G) the number of vertices of graph G. Since n(P) is even, if $S_5(T_5)$ has a Kekulé structure, n(A) must be even. Therefore, in what follows we always assume that n(A) is even. Denote the number of Kekulé structures of $S_5(T_5)$ by $K(S_5)(K(T_5))$ and the number of aromatic π sextets of $S_5(T_5)$ by $\sigma(S_5)(\sigma(T_5))$, respectively. Vertices removed from a graph will be denoted by superscripts; e.g. $A - \{x,y\}$ will be denoted by A^{xy}. For terminology not defined here, one can find them in [8] and [9]. If m is a matching of H that saturates the vertices of P, then the number of Kekulé structures of $S_5(T_5)$ in which the vertices of P are saturated by way of m will be denoted by $K_m(S_5)(K_m(T_5))$. Clearly, $K(S_5) = \sum K_m(S_5)$, $K(T_5) = \sum K_m(T_5)$, where the summation is over those matchings which saturate the vertices of P.

Theorem 1. For any pair of S_5,T_5-isomers, $K(S_5) \leq K(T_5)$. (1)

Proof. Because n(A) is even, the graph obtained by removing odd number of vertices from A does not have Kekulé structures. For this reason, we only need to consider those matchings of H which saturate even number of vertices of A. Furthermore, if m is a matching of H, which saturates the vertices y',z' of hexagon h_2, then it is easy to see that $K_m(S_5) = K_m(T_5)$. From the symmetry of h_1,h_2,h_3, in the case that m saturates the vertices x',w' or x',y',z',w' of h_1,h_2,h_3, or m does not saturate any of the vertices x', y', z', w', it is clear that $K_m(S_5) = K_m(T_5)$.

From the above observation, it suffices to consider those m such that $K_m(S_5) \neq K_m(T_5)$. There are 33 possible matchings of H which saturate even number of vertices of A, we denote them by $m_i (i = 1,2,\ldots,33)$. For $i = 13,14,\ldots,33$, the equality $K_{m_i}(S_5) = K_{m_i}(T_5)$ holds, so we only consider the matchings m_i, $i = 1,2,\ldots,12$, as shown in Fig.3. For simplicity, we only draw the subgraph H of $S_5(T_5)$.

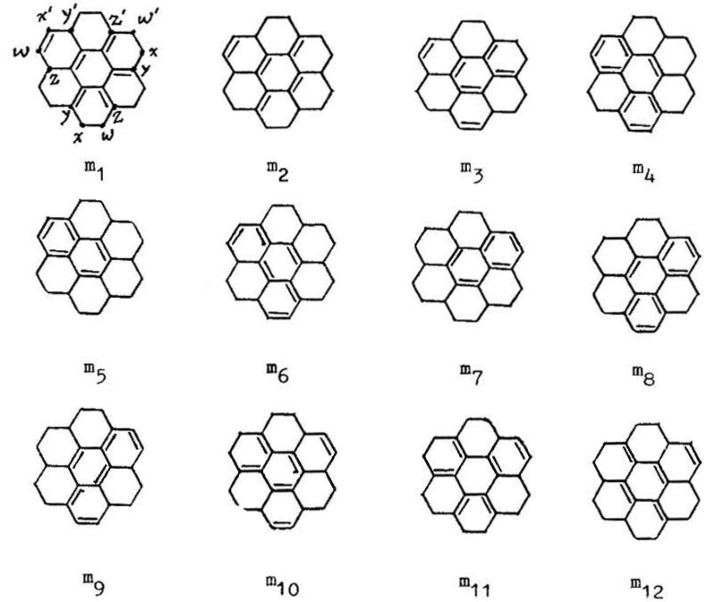


Fig.3

After some simple calculation, we can get

$$K(T_5) - K(S_5) = \sum_{i=1}^{33}(K_{m_i}(T_5) - K_{m_i}(S_5)) =$$
$$= \sum_{i=1}^{12}(K_{m_i}(T_5) - K_{m_i}(S_5)) = K(A^{yw})^2 \cdot K(A^{yz}) + K(A^{yw})^2 \cdot K(A) +$$
$$+ K(A^{yw})^2 \cdot K(A^{xw}) + K(A^{zw})^2 \cdot K(A^{xyzw}) + K(A^{zw})^2 \cdot K(A) + K(A^{zw})^2 \cdot$$
$$\cdot K(A^{xw}) + K(A^{xy})^2 \cdot K(A) + K(A^{xy})^2 \cdot K(A^{xyzw}) + K(A^{xy})^2 \cdot K(A^{xw}) +$$
$$+ K(A^{xz})^2 \cdot K(A^{xw}) + K(A^{xz})^2 \cdot K(A^{yz}) + K(A^{xz})^2 \cdot K(A) - 2K(A^{xy}) \cdot$$
$$\cdot K(A^{xyzw}) \cdot K(A^{zw}) - 2K(A^{xz}) \cdot K(A^{yz}) \cdot K(A^{yw}) - 2K(A^{yw}) \cdot K(A^{xw}) \cdot K(A^{xz})$$
$$- 2K(A^{xy}) \cdot K(A^{zw}) \cdot K(A) - 2K(A^{xz}) \cdot K(A^{yw}) \cdot K(A) - 2K(A^{xy}) \cdot K(A^{xw}) \cdot$$
$$\cdot K(A^{zw}) = (K(A^{xy}) - K(A^{zw}))^2 \cdot (K(A^{xyzw}) + K(A^{xw}) + K(A)) +$$
$$+ (K(A^{yw}) - K(A^{xz}))^2 \cdot (K(A^{xw}) + K(A^{yz}) + K(A)) \geqslant 0.$$

Therefore, the inequality (1) holds.

Now we turn to discussing the number of Clar formula of S_5, T_5-isomers. Let $\sigma(A^{xy})$ denote the maximum number of circles which can be drawn in A^{xy}. (Note that A^{xy} need not be a benzenoid system.) Let m_i be a matching of H(see Fig.3), then the maximum number of circles which can be drawn in $S_5 - P$ $(T_5 - P)$ will be denoted by $\sigma_{m_i}(S_5)(\sigma_{m_i}(T_5))$ when the vertices of H are saturated by way of m_i.

Theorem 2. For any pair of S_5, T_5-isomers, $\sigma(S_5) \leq \sigma(T_5)$. (2)

Proof. We will distinguish four cases.

Case 1. There is a Clar formula of S_5 which has no sextets in H. Clearly, $\sigma(S_5) = \max \sigma_{m_i}(S_5)$. If $\sigma(S_5) = \sigma_{m_i}(S_5)$,

$i = 13, 14, \ldots, 33$, then from $\sigma_{m_i}(S_5) = \sigma_{m_i}(T_5)$, it follows that $\sigma(T_5) \geqslant \sigma_{m_i}(T_5) = \sigma_{m_i}(S_5) = \sigma(S_5)$.

Suppose that $\sigma(S_5) = \sigma_{m_1}(S_5)$, namely, $\sigma(S_5) = \sigma_{m_1}(S_5) = \sigma(A^{xz}) + \sigma(A^{yz}) + \sigma(A^{yw})$. If $\sigma(A^{yw}) \geqslant \sigma(A^{xz})$ then $\sigma(T_5) \geqslant \sigma_{m_1}(T_5) = \sigma(A^{yw}) + \sigma(A^{yz}) + \sigma(A^{yw}) \geqslant \sigma_{m_1}(S_5) = \sigma(S_5)$. If $\sigma(A^{yw}) < \sigma(A^{xz})$ then $\sigma(T_5) \geqslant \sigma_{m_{11}}(T_5) = \sigma(A^{xz}) + \sigma(A^{xz}) + \sigma(A^{yz}) > \sigma_{m_1}(S_5) = \sigma(S_5)$. Thus, when $\sigma(S_5) = \sigma_{m_1}(S_5)$, the inequality (2) holds.

If $\sigma(S_5) = \sigma_{m_i}(S_5)$, $i = 2, 3, \ldots, 12$, then in the same way as for the case $\sigma(S_5) = \sigma_{m_1}(S_5)$, one can get the inequality (2).

Case 2. There exists a Clar formula of S_5 which has precisely one sextet in H. Obviously, if the sextet is in one of the hexagons h_2, h_4, h_5, h_6 and h_7, then the inequality (2) holds. We consider two subcases as follows.

Subcase 2.1. The sextet is in h_1, see Fig.4(a).

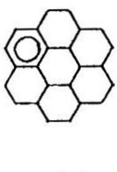


Fig.4(a)

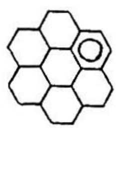


Fig.4(b)

We consider a Clar formula of T_5 which has exactly one sextet in H, see Fig.4(b). It is not difficult to see that the number of sextets of T_5, in this Clar formula, is equal to $\sigma(S_5)$, therefore, $\sigma(S_5) \leq \sigma(T_5)$.

Subcase 2.2. The sextet is in h_3. This case is completely equivalent to subcase 2.1.

Case 3. There is a Clar formula of S_5 which has precisely two sextets in H. Obviously, if these two sextets are in $\{h_1,h_3\}\cup\{h_2,h_4\}\cup\{h_2,h_5\}\cup\{h_2,h_6\}\cup\{h_4,h_6\}$, then the inequality (2) holds.

Now let us consider two subcases.

Subcase 3.1. The sextets are in h_1 and h_5, or in h_3 and h_5. Without loss of generality, we may assume that the sextets are in h_1 and h_5, see Fig.5(a).

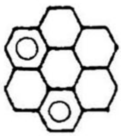


Fig.5(a)

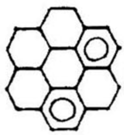
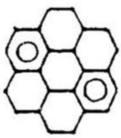


Fig.5(b)

We consider a Clar formula of T_5 which has precisely two circles drawn in H, see Fig.5(b). It is easy to see that the number of sextets of T_5, in this Clar formula, is equal to $\sigma(S_5)$, thus, $\sigma(S_5) \leq \sigma(T_5)$.

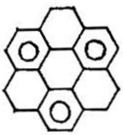
Subcase 3.2. The sextets are in h_1 and h_4, or in h_3 and h_6 as shown in the following graphs:



or

In a fully analogous manner as for subcase 3.1, one can get the result (2).

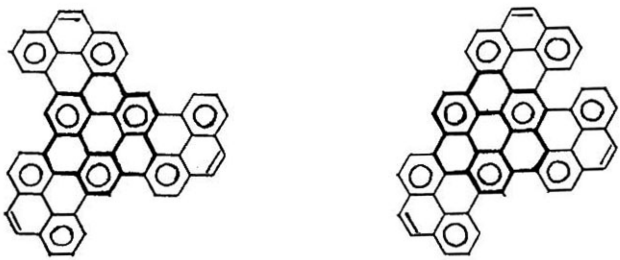
Case 4. There exists a Clar formula of S_5 which has three sextets in H as shown in the following:



or

It is clear that $\sigma(S_5) = \sigma(T_5)$. Hence, the inequality (2) holds. The proof is completed.

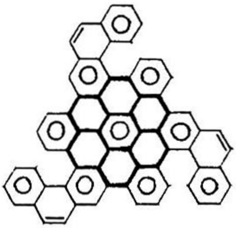
We conclude this paper by giving two examples of S_5,T_5-isomers (see Fig.6 and Fig.7).



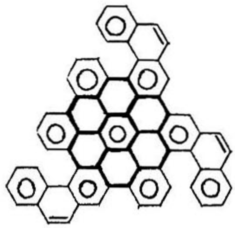
S_5 T_5

$$K(T_5) - K(S_5) = 14, \quad \sigma(T_5) - \sigma(S_5) = 0.$$

Fig.6



S_5



T_5

$$K(T_5) - K(S_5) = 12, \quad \sigma(T_5) - \sigma(S_5) = 0.$$

Fig.7

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