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TOPOLOGICAL PROPERTIES OF SOME NOVEL S, T-ISOMERS II *

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Abstract

In this paper, we introduce a new type of topologically related S and T isomers of benzenoid systems and prove that when $n = 3$, the number of Kekulé structures in an S isomer is not less than that in the related T isomer and the number of π aromatic sextets in an S isomer is also not less than that in the related T isomer. When $n \geqslant 4$, there is no such a relationship in general. This enriches the context of S and T isomers, which was first studied by POLANSKY and ZANDER.

I. INTRODUCTION

The concept of S and T isomers was first introduced by POLANSKY and ZANDER [1]. From then on, many types of S and T isomers have appeared, see [2 – 6]. Most of the known results were based on the comparisons of the numbers of Kekulé structures and the numbers of π aromatic sextets in S and T isomers. These comparisons coincide with the comparisons of HÜCKEL total π-electron energy E and reference energy E^R, see

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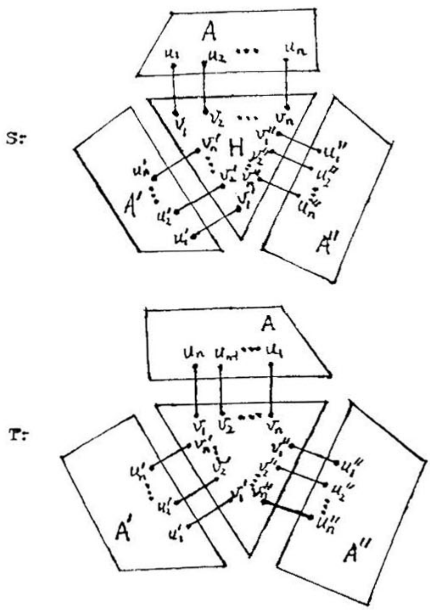
[11]. In this paper we introduce a new type of S and T isomers and give several comparison theorems.

The general structure of the new type of S and T isomer model is schematically depicted below (Figure 1).



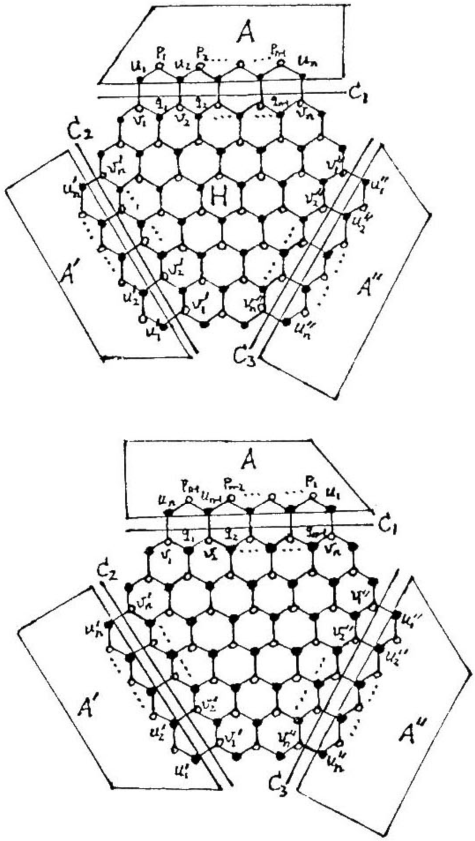
$A = A' = A''$

(Figure 1)

In the following we will confine ourselves on considering an example of this model consisting of only hexagonal cells, i.e., benzenoid systems, which is shown as follows (Figure 2).

S:

T:



$A = A' = A''$

(Figure 2)

For terminology and notation not defined here, we refer to [7].

II. PRELIMINARIES

Let B be a benzenoid system, C be a cut segment and M be a Kekulé structure of B. Denote by M(C) the number of M-double bonds intersected by C.

THEOREM 2.1 [8]. For any two Kekulé structures M and M' of B, we have $M(C) = M'(C)$.

LEMMA 2.1. Let M be a Kekulé structure of the S or T isomer, and the three cut segments C_1, C_2 and C_3 be as shown in Figure 2. Then we have $M(C_1) = M(C_2) = M(C_3)$.

PROOF. By the symmetry of S or T and Theorem 2.1, this lemma follows immediately.

THEOREM 2.2 [7]. Let B be a benzenoid system with a Kekulé structure M and B' be a sub-system of B. Let d be the difference of the number of peaks and the number of valleys of B'. For a normal color of B with black and white, denote by r the difference of the number of black vertices and the number of white vertices of all the M-double bonds, each having precisely one vertex in B". Then we have $d = r$.

LEMMA 2.2. For any Kekulé structure M of the S or T isomer, we have $M(C_1) = M(C_2) = M(C_3)$, where C_1, C_2 and C_3 are the cut segments shown in Figure 2.

PROOF. By Lemma 2.1, we can assume that

$$M(C_1) = M(C_2) = M(C_3) = k.$$

Since 3 is the difference of the number of peaks and the number of valleys of H, from the color given in Figure 2 and Theorem 2.2 we obtain $3k = 3$. Thus, $k = 1$ and the proof is complete.

Denote by $a_{i,j,k}$ the number of Kekulé structures of $H - \{v_i, v'_j, v''_k\}$, where H is given in Figure 2. Then by the symmetry property of H, we obtain the following lemma.

LEMMA 2.3. (i) $a_{i,j,k} = a_{j,k,i}$;

(ii) $a_{i,j,k} = a_{k,i,j}$;

(iii) $a_{i,j,k} = a_{n-i+1,n-k+1,n-j+1}$;

(iv) $a_{i,1,n} = a_{1,n,i} = a_{n,i,1} = 0$;

(v) $a_{i,1,n-1} = a_{i,2,n}$.

PROOF. The first two equalities can be obtained by turning H respectively in a clockwise and counter-clockwise manner. The third one can be obtained by reflecting H with respect to the vertical line that bisects H. The remaining two equalities can be obtained by successive matching of the vertices of valence one.

The number of Kekulé structures of a benzenoid system B will be denoted by $K(B)$, as usual. For simplicity, we will use A^u to denote $K(A-u)$, where u is a vertex of A.

Since $A = A' = A''$ in S and T, by Lemma 2.2 we know that

$$K(S) = \sum a_{i,j,k} A^{u_i} A^{u_j} A^{u_k}$$

$$\text{and } K(T) = \sum a_{i,j,k} A^{u_{n-i+1}} A^{u_j} A^{u_k} .$$

Denote by D the difference of K(S) and K(T). Then we have

$$D = \sum (a_{i,j,k} - a_{n-i+1,j,k}) A^{u_i} A^{u_j} A^{u_k} .$$

III. THE CASE $n = 3$

THEOREM 3.1. When $n = 3$, the number of Kekulé structures in S is not smaller than the number of Kekulé structures in T, i.e., $K(S) \geqslant K(T)$.

PROOF. From Lemma 2.3 and careful calculation, we obtain

$$D = K(S) - K(T) =$$

$$a_{1,1,1} A^{u_1} A^{u_1} A^{u_1} + a_{1,2,1} A^{u_1} A^{u_2} A^{u_1} + a_{3,3,2} A^{u_3} A^{u_3} A^{u_2} +$$

$$+ a_{3,3,3} A^{u_3} A^{u_3} A^{u_3} - a_{1,1,1} A^{u_3} A^{u_1} A^{u_1} - a_{1,2,1} A^{u_3} A^{u_2} A^{u_1} -$$

$$- a_{3,3,2} A^{u_1} A^{u_3} A^{u_2} - a_{3,3,3} A^{u_1} A^{u_3} A^{u_3} =$$

$$= (a_{1,1,1} A^{u_1} + a_{1,2,1} A^{u_2} + a_{1,1,1} A^{u_3})(A^{u_1} - A^{u_3})^2 \geqslant 0$$

The proof is complete.

The Clar's covering polynomial of a benzenoid system B is defined as follows (see [9]):

$$P(B,x) = \sum_{i=0}^{\sigma(B)} c_i x^i ,$$

$$\text{where } c_i = \sum_{\{s_1, s_2, \ldots, s_i\}} K(B - \{s_1, s_2, \ldots, s_i\})$$

for all possible i independent hexagonal cells $s_1, s_2, \ldots, s_i$ of B.

It is easily seen that c_0 is the number of Kekulé structures of B and $\sigma(B)$ is the number of aromatic sextets in a Clar's formula of B. For details on this polynomial we refer to [9]. The point for introducing the Clar's covering polynomial is that to get the two pairs of comparisons: K(S) and K(T), σ(S) and σ(T), we only need to do one pair of comparison of P(S,x) and P(T,x).

From a result of [9] and the fact A = A' = A" in S and T, we can get

$$P(S,x) = \sum a_{i,j,k}(x)\ x^b\ A^{U_i}(x)\ A^{U_j}(x)\ A^{U_k}(x), \qquad (*)$$

where $U_i = \{u_i\}$ or $\{u_i,p_i,u_{i+1}\}$ for $i = 1,2,\ldots,n-1$ and

$U_n = \{u_n\}$;

b = the number of sets with cardinality 3 among U_i, U_j and U_k;

$a_{i,j,k}(x) = P(H-(V_i \cup V_j \cup V_k),x)$, where $V_i = \{v_i\}$ or $\{v_i,q_i,v_{i+1}\}$ for $i = 1,2,\ldots,n-1$ and $V_n = \{v_n\}$ with the property that $|V_i| = |U_i|$;

$A^X(x) = P(A-X,\ x)$, where X is a subset of the vertex set of A.

First, by the same arguments as in the proof of Lemma 2.3 we can show that all the five equalities for $a_{i,j,k}$ in Lemma 2.3 still hold for $a_{i,j,k}(x)$. Then, by similar calculation as in the proof of Theorem 3.1 we can deduce the following result.

THEOREM 3.2. When n = 3, we have that for $x \geq 0$,

$$P(S,x) \geq P(T,x).$$

PROOF. First, we divide the sum in (*) into four partial sums according to $b = 0, 1, 2, 3$. By a similar method as in the proof of Theorem 3.1, for each partial sum we can get a similar inequality. The details are omitted here.

COROLLARY 3.3. (i) $K(S) \geqslant K(T)$;

(ii) $\sigma(S) \geqslant \sigma(T)$.

PROOF. By setting $x = 0$ in Theorem 3.2 we obtain the first ineqality. By setting x to become arbitrarily large we get the second one.

IV. THE CASE $n \geqslant 4$

At first thought, we conjectured that $K(S) \geqslant K(T)$ is also true for $n > 3$, as proved in [4-5] for other pairs of S,T-isomers. Unfortunately, after some concrete calculations for the case $n = 4$ we give up that conjecture.

Since $m = 4$, there are $4^3 = 64$ possible $a_{i,j,k}$'s in all. By Lemma 2.3, we can group them into 9 groups in each of which the elements are equal numbers. See the following.

Group 1: $a_{1,1,1}$, $a_{4,4,4}$;

Group 2: $a_{1,1,2}$, $a_{1,2,1}$, $a_{2,1,1}$, $a_{4,3,4}$, $a_{4,4,3}$, $a_{3,4,4}$;

Group 3: $a_{1,1,3}$, $a_{1,3,1}$, $a_{3,1,1}$, $a_{4,2,4}$, $a_{4,4,2}$, $a_{2,4,4}$,
$a_{1,2,4}$, $a_{2,4,1}$, $a_{4,1,2}$, $a_{4,1,3}$, $a_{3,4,1}$, $a_{1,3,4}$;

Group 4: $a_{1,2,2}$, $a_{2,2,1}$, $a_{2,1,2}$, $a_{4,3,3}$, $a_{3,4,3}$, $a_{3,3,4}$;

Group 5: $a_{1,2,3}$, $a_{2,3,1}$, $a_{3,1,2}$, $a_{4,2,3}$, $a_{3,4,2}$, $a_{2,3,4}$;

Group 6: $a_{1,3,2}$, $a_{3,2,1}$, $a_{2,1,3}$, $a_{4,3,2}$, $a_{2,4,3}$, $a_{3,2,4}$,
$a_{1,3,3}$, $a_{3,3,1}$, $a_{3,1,3}$, $a_{4,2,2}$, $a_{2,4,2}$, $a_{2,2,4}$;

Group 7: $a_{2,2,2}$, $a_{3,3,3}$;

Group 8: $a_{2,2,3}$, $a_{2,3,2}$, $a_{3,2,2}$, $a_{3,2,3}$, $a_{3,3,2}$, $a_{2,3,3}$;

Group 9: $a_{1,1,4}$, $a_{1,4,1}$, $a_{1,4,2}$, $a_{1,4,3}$, $a_{1,4,4}$, $a_{2,1,4}$, $a_{3,1,4}$, $a_{4,1,1}$, $a_{4,1,4}$, $a_{4,2,1}$, $a_{4,3,2}$, $a_{4,4,1}$.

The numbers in Group 9 are equal to 0. By the recurrence relation $K(B) = K(B-e) + K(B-u-v)$, we can obtain that $a_{1,1,1} = 20$, $a_{1,1,2} = 20$, $a_{1,1,3} = 10$, $a_{1,2,2} = 25$, $a_{1,2,3} = 20$, $a_{1,3,2} = 15$, $a_{2,2,2} = 35$, $a_{2,2,3} = 30$. We omit the detailed calculations. From these we get $D = K(S) - K(T) =$

$$20(A^{u_1}-A^{u_4})^2(A^{u_1}+A^{u_4}) + 5(A^{u_2}-A^{u_3})^2(A^{u_2}+A^{u_3}) +$$
$$+ (40A^{u_1}+10A^{u_2}-10A^{u_3}-40A^{u_4})(A^{u_1}A^{u_2}-A^{u_3}A^{u_4}) +$$
$$+ 15(A^{u_1}-A^{u_4})(A^{u_2}-A^{u_3})(A^{u_2}+A^{u_3}).$$

This cannot tell us, of $K(S)$ and $K(T)$, which is greater. We have not find examples to show that for some concrete A $K(S)$ is greater than $K(T)$ and for the others $K(S)$ is smaller than $K(T)$. For $n \geq 5$, things would become more involved. Anyway, the above difference **gives** us the idea that the two possibilities that $K(S) > K(T)$ and $K(S) < K(T)$ all may happen.

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