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COMPARISON THEOREMS OF SOME NOVEL S,T-ISOMERS*

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ABSTRACT. In [12], we defined a type of topologically related S and T isomers of benzenoid systems, and proved that for $n = 3$, the number of Kekulé structures in an S isomer is not less than that in the related T isomer. As an immediate consequence, the π-electron energy and resonance energy of an S isomer are not lower than those of the related T isomer. In this paper, we prove that the same conclusion holds for $n = 4$ and 5. We conjecture that this is true for all $n \geq 3$.

I. Introduction.

Isomers, which may be constructed from several subunits $A, B, C, \cdots$ by linking them in a different manner, are called topologically related, usually, they are denoted by S and T, respectively. There are several ways in which pairs of topologically related isomers may be constructed, each one is called a topological model or type. Many types of S and T isomers were introduced by Polansky, see [3]. Polansky and Zander [1, 13] discussed the topological effect on the molecular orbitals (TEMO) of topologically related isomers. The comparison of the characteristic polynomials of S and T isomers will indicate that the TEMO has or does not have inversions. In this paper, we will consider the comparison of the numbers of Kekulé structures of a new type of S and T isomers. From [7] and the references therein, we know that the π-electron energy (E) of a hydrocarbon C_nH_s has the following approximate relation

$$E = [0.201n - 0.049s + 0.043K(0.795)^{n-s}] \cdot E(benzene)$$

and the Dewar resonance energy (RE) can be well reproduced by

$$RE = 114.3 \; lnK \qquad [\; kJmol^{-1} \;],$$

where K is the number of Kekulé structures. Thus, our comparison also pertains to the π-electron energy and the Dewar resonance energy.

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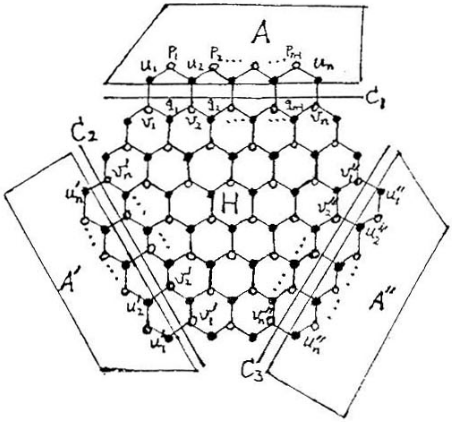
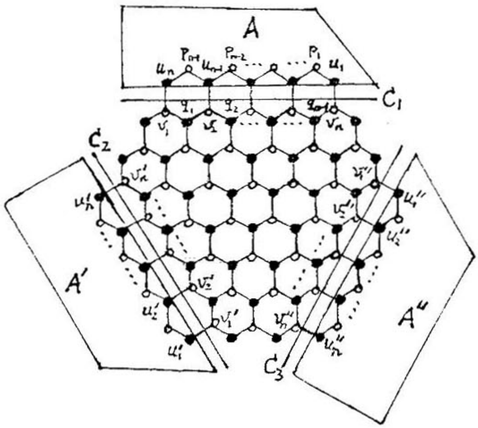
S:



T:



A = A' = A''

(Figure 1)

Our new type of S and T isomers of benzenoid systems is shown in *Figure* 1.

In [12], we proved that for $n = 3$, the number of Kekulé structures in an S isomer is not less than that in the related T isomer. For $n = 4$, we gave the difference, but we could not see if it is always non-negative. In Sections 3 and 4 of this paper, we will show that it is really so.

For terminology and notation not defined here, we refer to [1] and [12].

II. Preliminaries.

Our results mainly rest on the following two lemmas.

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. From [12] we have the first lemma.

LEMMA 2.1. *For any Kekulé structure M of the S or T isomer, we have $M(C_1) = M(C_2) = M(C_3) = 1$, where C_1, C_2 and C_3 are the cut segments shown in Figure 1.*

Denote by $a_{i,j,k}$ the number of Kekulé structures of $H \setminus \{v_i, v'_j, v''_k\}$, where H is given in Figure 1. From the same reference, we have the second lemma.

LEMMA 2.2.

$$(i) \quad a_{i,j,k} = a_{j,k,i};$$
$$(ii) \quad a_{i,j,k} = a_{k,i,j};$$
$$(iii) \quad a_{i,j,k} = a_{n-i+1,n-k+1,n-j+1};$$
$$(iv) \quad a_{i,1,n} = a_{1,n,i} = a_{n,i,1} = 0;$$
$$(v) \quad a_{i,1,n-1} = a_{i,2,n}.$$

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 $K(A \setminus \{u\})$, where u is a vertex of A.

Since $A = A' = A''$ in S and T, by Lemma 2.1, we know

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

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=4.

THEOREM 3.1. *When $n = 4$, the number of Kekulé structures in S is not less than that in the related T, i.e., $K(S) \geq K(T)$.*

Proof. From the calculation in Section 4 of [12], we know

$$\begin{aligned} D =& K(S) - K(T) \\ =& 20(A^{u_1} - A^{u_4})^2(A^{u_1} + A^{u_4}) + 5(A^{u_2} - A^{u_3})^2(A^{u_2} + A^{u_3}) \\ &+ (40A^{u_1} + 10A^{u_2} - 10A^{u_3} - 40A^{u_4})(A^{u_1}A^{u_2} - A^{u_3}A^{u_4}) \\ &+ 15(A^{u_1} - A^{u_4})(A^{u_2} - A^{u_3})(A^{u_2} + A^{u_3}). \end{aligned}$$

Using the linear transformation

$$\begin{cases} x_1 = A^{u_1} - A^{u_4} \\ x_2 = A^{u_2} - A^{u_3} \\ x_3 = A^{u_2} + A^{u_3} \\ x_4 = A^{u_1} + A^{u_4}, \end{cases}$$

namely,

$$\begin{cases} A^{u_1} = \dfrac{x_1 + x_4}{2} \\ A^{u_2} = \dfrac{x_2 + x_3}{2} \\ A^{u_3} = \dfrac{x_3 - x_2}{2} \\ A^{u_4} = \dfrac{x_4 - x_1}{2}, \end{cases}$$

we get

$$\begin{aligned} D = D(x_1, x_2, x_3, x_4) =& 20x_1^2x_4 + 5x_2^2x_3 + 15x_1x_2x_3 \\ &+ (40x_1 + 10x_2)\frac{x_1x_3 + x_2x_4}{2} \\ =& 5x_2^2(x_3 + x_4) + 20x_1^2(x_3 + x_4) + 20x_1x_2(x_3 + x_4) \\ =& 5(x_3 + x_4)(2x_1 + x_2)^2. \end{aligned}$$

Since $x_3 = A^{u_2} + A^{u_3} \geq 0$ and $x_4 = A^{u_1} + A^{u_4} \geq 0$, it follows immediately $D \geq 0$. ∎

IV. The Case n=5.

THEOREM 4.1. *When $n = 5$, the number of Kekulé structures in S is not less than that in the related T, i.e., $K(S) \geq K(T)$.*

Proof. Since $n = 5$, there are $5^3 = 125$ possible $a_{i,j,k}$'s in all. By Lemma 2.2, we can group them into 21 groups in each of which the elements are equal numbers. See the following

$$
\begin{aligned}
Group\ 1 &: a_{1,1,1}, a_{5,5,5};\\
Group\ 2 &: a_{1,1,2}, a_{1,2,1}, a_{2,1,1}, a_{5,4,5}, a_{4,5,5}, a_{5,5,4};\\
Group\ 3 &: a_{1,1,3}, a_{1,3,1}, a_{3,1,1}, a_{5,3,5}, a_{3,5,5}, a_{5,5,3};\\
Group\ 4 &: a_{1,1,4}, a_{1,4,1}, a_{4,1,1}, a_{5,2,5}, a_{2,5,5}, a_{5,5,2},\\
&\quad a_{1,2,5}, a_{2,5,1}, a_{5,1,2}, a_{5,1,4}, a_{1,4,5}, a_{4,5,1};\\
Group\ 5 &: a_{1,2,2}, a_{2,2,1}, a_{2,1,2}, a_{5,4,4}, a_{4,4,5}, a_{4,5,4};\\
Group\ 6 &: a_{1,2,3}, a_{2,3,1}, a_{3,1,2}, a_{5,3,4}, a_{3,4,5}, a_{4,5,3};\\
Group\ 7 &: a_{1,2,4}, a_{2,4,1}, a_{4,1,2}, a_{5,2,4}, a_{2,4,5}, a_{4,5,2};\\
Group\ 8 &: a_{1,3,2}, a_{3,2,1}, a_{2,1,3}, a_{5,4,3}, a_{4,3,5}, a_{3,5,4};\\
Group\ 9 &: a_{1,3,3}, a_{3,3,1}, a_{3,1,3}, a_{5,3,3}, a_{3,3,5}, a_{3,5,3};\\
Group\ 10 &: a_{1,3,4}, a_{3,4,1}, a_{4,1,3}, a_{5,2,3}, a_{2,3,5}, a_{3,5,2};\\
Group\ 11 &: a_{1,3,5}, a_{3,5,1}, a_{5,1,3};\\
Group\ 12 &: a_{1,4,2}, a_{4,2,1}, a_{2,1,4}, a_{5,4,2}, a_{4,2,5}, a_{2,5,4},\\
&\quad a_{4,1,4}, a_{1,4,4}, a_{4,4,1}, a_{2,2,5}, a_{2,5,2}, a_{5,2,2};\\
Group\ 13 &: a_{1,4,3}, a_{4,3,1}, a_{3,1,4}, a_{5,3,2}, a_{3,2,5}, a_{2,5,3};\\
Group\ 14 &: a_{2,2,2}, a_{4,4,4};\\
Group\ 15 &: a_{2,2,3}, a_{2,3,2}, a_{3,2,2}, a_{4,3,4}, a_{3,4,4}, a_{4,4,3};\\
Group\ 16 &: a_{2,2,4}, a_{2,4,2}, a_{4,2,2}, a_{4,2,4}, a_{2,4,4}, a_{4,4,2};\\
Group\ 17 &: a_{2,3,3}, a_{3,3,2}, a_{3,2,3}, a_{4,3,3}, a_{3,3,4}, a_{3,4,3};\\
Group\ 18 &: a_{2,3,4}, a_{3,4,2}, a_{4,2,3};\\
Group\ 19 &: a_{2,4,3}, a_{4,3,2}, a_{3,2,4};\\
Group\ 20 &: a_{3,3,3};\\
Group\ 21 &: a_{1,1,5}, a_{2,1,5}, a_{3,1,5}, a_{4,1,5}, a_{5,1,5}, a_{1,5,1},\\
&\quad a_{1,5,2}, a_{1,5,3}, a_{1,5,4}, a_{1,5,5}, a_{5,1,1}, a_{5,2,1},\\
&\quad a_{5,3,1}, a_{5,4,1}, a_{5,5,1}.
\end{aligned}
$$

The numbers in Group 21 are equal to 0. By the recurrence relation $K(B) = K(B-e) + K(B-u-v)$ and some known Kekulé structure counting formulas, see [7], we obtain that

$$
\begin{aligned}
&a_{1,1,1} = 980, a_{1,1,2} = 1470, a_{1,1,3} = 1176, a_{1,1,4} = 490,\\
&a_{1,2,2} = 2450, a_{1,2,3} = 2352, a_{1,2,4} = 1470, a_{1,3,2} = 2156,\\
&a_{1,3,3} = 2352, a_{1,3,4} = 1764, a_{1,3,5} = 784, a_{1,4,2} = 980,\\
&a_{1,4,3} = 1176, a_{2,2,2} = 4410, a_{2,2,3} = 4508, a_{2,2,4} = 2940,\\
&a_{2,3,3} = 5096, a_{2,3,4} = 3920, a_{2,4,3} = 3528, a_{3,3,3} = 6272.
\end{aligned}
$$

We omit the detailed calculations, and get

$$
\begin{aligned}
D = K(S) - K(T) = &980(A^{u_1} + A^{u_5})[(A^{u_1} - A^{u_5})^2 + (A^{u_1} - A^{u_5})(A^{u_2} - A^{u_4})]\\
&+ 2450(A^{u_1}A^{u_2} - A^{u_4}A^{u_5})[(A^{u_1} - A^{u_5}) + (A^{u_2} - A^{u_4})] +\\
&1470(A^{u_2} + A^{u_4})[(A^{u_1} - A^{u_5})(A^{u_2} - A^{u_4}) + (A^{u_2} - A^{u_4})^2]\\
&+ 1568A^{u_3}(A^{u_1} - A^{u_5})[(A^{u_1} - A^{u_5}) + (A^{u_2} - A^{u_4})]\\
&+ 490(A^{u_1}A^{u_4} - A^{u_2}A^{u_5})[(A^{u_1} - A^{u_5}) + (A^{u_2} - A^{u_4})]\\
&+ 1568A^{u_2}(A^{u_2} - A^{u_4})[(A^{u_1} - A^{u_5}) + (A^{u_2} - A^{u_4})].
\end{aligned}
$$

Using the similar linear transformation as above,

$$
\begin{cases}
x_1 = A^{u_1} - A^{u_5}\\
x_2 = A^{u_2} - A^{u_4}\\
x_3 = A^{u_3}\\
x_4 = A^{u_2} + A^{u_4}\\
x_5 = A^{u_1} + A^{u_5},
\end{cases}
$$

namely,

$$
\begin{cases}
A^{u_1} = \dfrac{x_1 + x_5}{2}\\
A^{u_2} = \dfrac{x_2 + x_4}{2}\\
A^{u_3} = x_3\\
A^{u_4} = \dfrac{x_4 - x_2}{2}\\
A^{u_5} = \dfrac{x_5 - x_1}{2},
\end{cases}
$$

we can obtain

$$\begin{aligned}D =&D(x_1,x_2,x_3,x_4,x_5)\\ =&980x_1x_5(x_1+x_2)+1225(x_1+x_2)(x_2x_5+x_1x_4)+1470x_2x_4(x_1+x_2)\\ &+1568x_3(x_1+x_2)^2+245(x_1+x_2)(x_1x_4-x_2x_5)\\ =&x_5[980x_1(x_1+x_2)+1225x_2(x_1+x_2)-245x_2(x_1+x_2)]\\ &+x_4[1225(x_1+x_2)+1470x_2(x_1+x_2)+245x_1(x_1+x_2)]\\ &+1568x_3(x_1+x_2)^2\\ =&(980x_5+1470x_4+1568x_3)(x_1+x_2)^2.\end{aligned}$$

Since

$$x_5 = A^{u_1}+A^{u_5}\geq 0,\ x_4 = A^{u_2}+A^{u_4}\geq 0,\ x_3 = A^{u_3}\geq 0,$$

it follows that $D \geq 0$.■

V. Conjecture.

we have proved that $K(S) \geq K(T)$ for $n = 3, 4$ and 5. This supports us to conjecture that $K(S) \geq K(T)$ for all $n \geq 3$.

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