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SOME TOPOLOGICAL PROPERTIES OF TWO TYPES OF S,T-ISOMERS

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ABSTRACT

In this paper two types of S,T-isomers are considered. Both of T_1, S_1, T_2, S_2-isomers are benzenoid system. It is shown that the $S_1(S_2)$ isomer do not have more aromatic π sextets than its corresponding $T_1(T_2)$ isomer. Furthermore we derive precise conditions under which the $S_1(S_2)$, $T_1(T_2)$ isomers have equal number of sextet. Analogous results of the number of Kekulé structures are also obtained.

After introducing the concept of S,T-isomers, many interesting properties have been studied and the concept of S,T-isomers have been extented in several ways. [1]—[4] The isomer pairs which we deal with are introduced in [3] scheme 5. [3] considers the HMO total π-electron energy of the S and T-isomers.

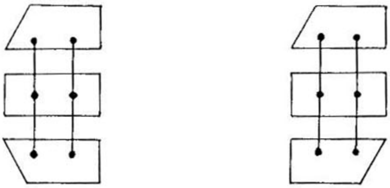


Fig.1

When we restrict ourself to the cases of benzenoid system, obviously only the following two pairs of S,T-isomers are possible.

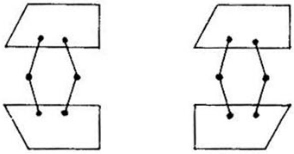


Fig.2

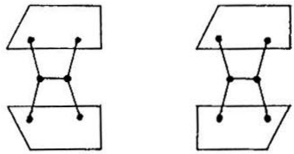


Fig.3

This paper considers the Clar formula and number of Kekulé structure of these two pairs of isomers.

Now we give precise definition. Let A be a conjugated fragment and u,v be two vertices of A. Let A' be another conjugated fragment isomorphic to A and let u',v' be the two vertices of A' corresponding to u,v separately. The conjugated system $S_1(T_1)$ is obtained by joining u and u'(v') with a new vertex x and simultaneously joining v and v'(u') with another new vertex y. (see Fig. 2). There two conjugated systems are called S_1,T_1-isomers.

Furthermore, $S_2(T_2)$isomer is obtained from $S_1(T_1)$isomer by joining x and y with a new edge. (See Fig.3)

Let $K(S_i)$ denote the number of Kekulé structures of S_i, and let $\sigma(S_i)$ denote the number of aromatic π sextets (in a Clar formula) of S_i when the isomer is benzenoid. Similarly, we can define $K(T_i)$ and $\sigma(T_i)$. The symbolism and terminology not defined in this paper is the same as in [1] and the review [5] In the following we shall compare $K(S_i)$ with $K(T_i)$, and $\sigma(S_i)$ with $\sigma(T_i)$. For convenience, we shall use the following symbols.

A^u denotes a graph obtained from A by deleting its vertex u.

$A^{u,v}$ denotes a graph obtained from A by deleting its vertices u and v.

Now we establish the following.

<u>Theorem 1.</u> For any pair of benzenoid S_1, T_1-isomers, $\sigma(S_1) \leq \sigma(T_1)$. Furthermore, the equality holds if and only if $|V(A)|$ is even or $\sigma(A^u) = \sigma(A^v)$ when $|V(A)|$ is odd.

<u>Proof.</u> (i) When $|V(A)|$ is even, let λ denote one of the Clar formulas of S_1 or T_1. If λ has a sextet in the central hexagon, then the number of sextets is

$$\sigma(S_1) = \sigma(T_1) = \sigma(A^{u,v}) + \sigma(A'^{u',v'}) + 1 = 2\sigma(A^{u,v}) + 1. \quad \text{(See Fig.4)}$$

Otherwise, the vertices x and y must match the vertices both in A or both in A', then the number of sextets is

$$\sigma(S_1) = \sigma(T_1) = \max\{\sigma(A^{u,v}) + \sigma(A'), \ \sigma(A'^{u',v'}) + \sigma(A)\}$$
$$= \sigma(A^{u,v}) + \sigma(A). \quad \text{(See Fig.5)}$$

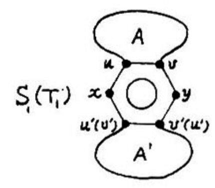


Fig.4

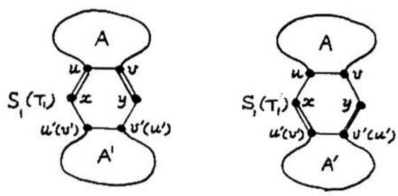


Fig.5

Thus we have

$$\sigma(S_1)=\sigma(T_1)=\max\{\,2\sigma(A^{u,v})+1,\ \sigma(A^{u,v})+\sigma(A)\,\}.$$

(ii) When $|V(A)|$ is odd, it is easily seen that in any Clar formula of S_1 or T_1 the vertices x and y must match the vertices in different A and A' respectively and that there is no sextet of Clar formula in the central hexagon. Thus we have

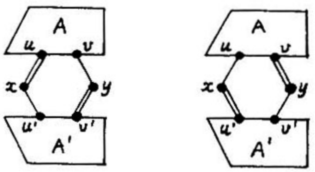
$$\sigma(S_1)=\max\{\sigma(A^{u})+\sigma(A'^{v'}),\ \sigma(A'^{u'})+\sigma(A^{v})\}$$
$$=\sigma(A^{u})+\sigma(A^{v}),\qquad \text{(See Fig.6)}$$

and

$$\sigma(T_1)=\max\{\sigma(A^{u})+\sigma(A'^{u'}),\ \sigma(A'^{v'})+\sigma(A^{v})\}$$
$$=2\max\{\sigma(A^{u}),\sigma(A^{v})\},\qquad \text{(See Fig.7)}$$

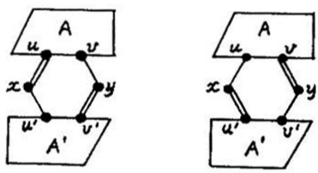
therefore $\sigma(S_1)\le\sigma(T_1)$, where the equality holds if and only if $\sigma(A^{u})=\sigma(A^{v})$.

Theorem 1 is thus proved.



S_1 S_1

Fig.6



T_1 T_1

Fig.7

<u>Theorem 2.</u> For any pair of benzenoid S_2,T_2-isomers, $\sigma(T_2)\geq\sigma(S_2)$. Furthermore, the equality holds iff $|V(A)|$ is even or $\sigma(A^u)=\sigma(A^v)$ when $|V(A)|$ is odd.

<u>Proof.</u> (i) When $|V(A)|$ is even, only the following cases are possible

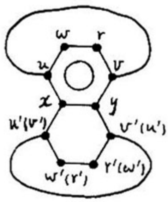
(a) When one of the Clar formulas λ has a sextet in one of central hexagons, then the number of sextets is

$$\sigma(S_2)=\sigma(T_2)=\max\{\sigma(A)+\sigma(A'^{u',v',w',r'})+1,\ \sigma(A')+\sigma(A^{u,v,w,r})+1\}$$

$$=\sigma(A)+\sigma(A^{u,v,w,r})+1 \qquad \text{(See Fig.8)}$$

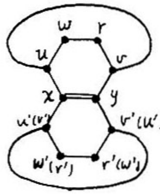
(b) When x match y, then the number of sextets is

$$\sigma(S_2)=\sigma(T_2)=\sigma(A)+\sigma(A') \qquad \text{(See Fig.9)}$$



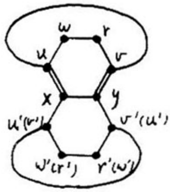
$S_2(T_2)$

Fig.8



$S_2(T_2)$

Fig.9



$S_2(T_2)$

Fig.10

(c) When the vertices x and y match the vertices both in A or both in A', then the number of sextets is

$$\sigma(S_2)=\sigma(T_2)=\max\{\sigma(A^{u,v})+\sigma(A'),\ \sigma(A)+\ (A'^{u',v'})$$

$$=\sigma(A)+\sigma(A^{u,v}) \qquad \text{(See Fig.10)}$$

Thus we have

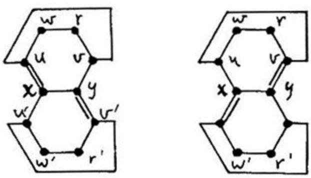
$$\sigma(S_2)=\sigma(T_2)=\max\{\sigma(A)+\sigma(A^{u,v,w,r})+1,\ \sigma(A)+\sigma(A^{u,v}),\ \sigma(A')+\sigma(A)\}.$$

(ii) When $|V(A)|$ is odd, it is easily seen that there is no sextet of any Clar formula in central hexagon and x and y must match the vertices in different A and A', respectively. Thus we have

$$\sigma(S_2)=\max\{\sigma(A^u)+\sigma(A'^{v'}),\ \sigma(A'^{u'})+\sigma(A^v)\}$$
$$=\sigma(A^u)+\sigma(A^v), \qquad \text{(See Fig.11)}$$

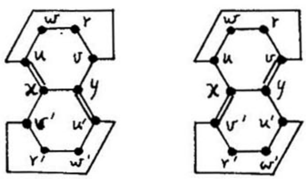
and

$$\sigma(T_2)=\max\{\sigma(A^u)+\sigma(A'^{u'}),\ \sigma(A'^{v'})+\sigma(A^v)\}$$
$$=2\max\{\sigma(A^u),\ \sigma(A^v)\} \qquad \text{(See Fig.12)}$$



S_2 S_2

Fig.11



T_2 T_2

Fig.12

Therefore $\sigma(S_2)\le\sigma(T_2)$, where equality holds iff $\sigma(A^u)=\sigma(A^v)$.

The proof is thus completed.

Theorem 3. For any pair of S_1,T_1-isomers, $K(S_1)\le K(T_1)$. Furthermore, the equality holds iff $|V(A)|$ is even or $K(A^u)=K(A^v)$ when $|V(A)|$ is odd.

Proof. (i) When $|V(A)|$ is even, it is easy to see that in any perfect matching of S_1 or T_1 the vertices x and y must match the vertices both in A or both in A'. Thus we immediately have

$$K(S_1)= K(T_1)= K(A^{u,v})\cdot K(A')+ K(A)\cdot K(A'^{u',v'})=2K(A)K(A^{u,v}).$$

(ii) When $|V(A)|$ is odd, we can see that in any perfect matching of S_1 or T_1 the vertices x and y must match the vertices in different A and A', respectively. Thus we have (See Fig.6)

$$K(S_1)=K(A^u)\cdot K(A'^{v'})+ K(A^v)\cdot K(A'^{u'})= 2K(A^u)\cdot K(A^v),$$

and (See Fig.7)

$$K(T_1)=K(A^u)\cdot K(A'^{u'})+ K(A^v)\cdot K(A'^{v'})= [K(A^u)]^2+ [K(A^v)]^2.$$

Therefore, $K(S_1)\leq K(T_1)$, where the equality holds iff $K(A^u)= K(A^v)$.

Theorem 3 is thus proved.

Theorem 4. For any pair of S_2,T_2-isomers, $K(T_2)\geq K(S_2)$. Furthermore, the equality holds if and only if $|V(A)|$ is even or $K(A^u)= K(A^v)$ when $|V(A)|$ is odd.

Proof. It is analogous the proof of theorem 3.

(i) When $|V(A)|$ is even, then (See Fig.9 and Fig.10)

$$K(S_2)= K(T_2)= 2K(A)\cdot K(A^{u,v})+ [K(A)]^2.$$

(ii) $|V(A)|$ is odd, then (See Fig.11 and Fig.12)

$$K(S_2)= 2K(A^u)\cdot K(A^v),$$

$$K(T_2)= K(A^u)^2+ K(A^v)^2.$$

Hence we have $K(T_2)\geq K(S_2)$ and the equality holds if and only if $|V(A)|$ is even or $|V(A)|$ is odd and $K(A^u)= K(A^v)$.

The proof is thus completed.

Finally, let us turn to the relation between S,T-isomers and S_1,T_1-isomers for benzenoid hydrocarbons. Usually, a T_1-isomer can be considered as a T-isomer because of its central symmetry. (See the two examples in Fig.13).

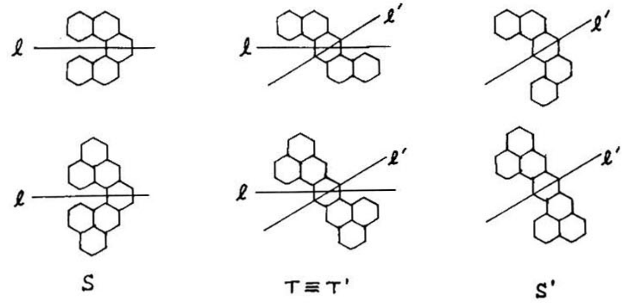


Fig.13

Therefore, combining the results of [2] and the above theorem 1,3, we obtain the following

Theorem 5. For the isomers S, T≡T', S', we have

$$K(S) \geq K(T) \geq K(S_1) \quad \text{and} \quad \sigma(S) \geq \sigma(T) \geq \sigma(S_1).$$

REMARK

From (10) and (17)of [3] we can see that the following inequalities hold for Hückel total π-electron energy and reference energy.

$$E(T_i) \geq E(S_i), \qquad E^R(T_i) \geq E^R(S_i), \qquad i=1,2.$$

These results are agree with theorem 1-4 of this paper.

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