

SOME TOPOLOGICAL PROPERTIES OF GENERALIZED
S,T-ISOMERS

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Abstract

Generalized S,T-isomers of benzenoid hydrocarbons are introduced and some of their topological properties established. It is proved that a generalized T-isomer neither has more aromatic π -sextets nor has more Kekulé structures than its S-isomer. This is an extension of the results of [1].

The concept of S,T-isomers was introduced in [2]. In the case when the S,T-isomers were benzenoid, the authors of [2] observed that "where the number of π aromatic sextets is different in the T and S isomer, the latter always possesses the higher number of π sextets". Recently in [1], this hypothesis has been proved, and it has also been shown that the number of Kekulé structures of a T isomer never exceeds that of an S isomer.

In the present paper we shall consider a more general situation, namely when the S,T-isomer pair is obtained by joining two identical fragments by more than two bonds. It will be shown that the results of [1] can be extended also to these generalized S,T-isomers.

The symbolism and terminology used in the present work is the same as in [2] and [3]. Details on the topological theory of benzenoid hydrocarbons as well as an exhaustive bibliography can be found in the review [3].

Recall that benzenoid molecular graphs can be obtained as follows. Let C_B be a cycle of the hexagonal lattice. Then the vertices and the edges which lie on C_B and in the interior of C_B form a benzenoid graph B. It is well known that any benzenoid graph B is bipartite and its vertices can be colored by two colors, so that the vertices of the same color are never adjacent. The Clar formula is obtained by drawing circles in some of the hexagons of B. These circles represent the so called "aromatic sextets". The rules for constructing Clar formulas are the following:

- (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.
- (c) A Clar formula contains the maximal number of circles, which can be drawn in accordance with the rules (a) and (b).

If only the rules (a) and (b) are obeyed, we speak about generalized Clar formulas [3].

Now we define the generalized S,T-isomers of benzenoid hydrocarbons. Let S be a benzenoid molecular graph with an axis of symmetry ℓ which only intersects some of the parallel lines of S. The set of all these parallel lines intersecting ℓ is denoted by P. Obviously, S-P consists of two components A and A' which are isomorphic to each other. For convenience, we shall always assume that the ℓ -axis is in the horizontal position. Specifying members of P in the order from left to right, we can write $P = \{a_0 a'_0, a_1 a'_1, \dots, a_p a'_p\}$, where $a_i \in A$ and $a'_i \in A'$ for $i = 0, 1, \dots, p$. Now we can obtain some new graphs by changing S as follows (see Fig. 1):

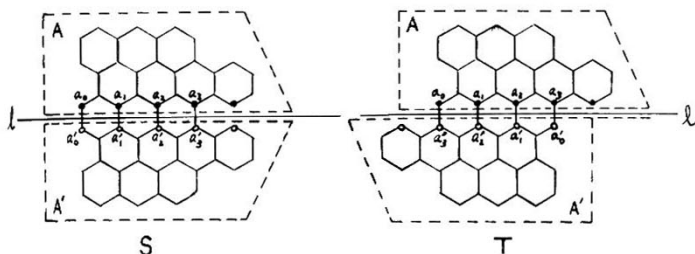


Fig. 1

Rotating the fragment A' of S, we can get a new benzenoid graph T in which a_i is adjacent with a'_{p-i} for $i = 0, 1, \dots, p$. It is evident that T has a center of symmetry.

Similarly, rotating A of S, we get T'; rotating A of T, we get S'. It is easy to see that T' is isomorphic to T and S' is isomorphic to S.

Thus we obtain only two distinct benzenoid systems, which we shall call generalized S,T-isomers. The special case when $p=1$ is just the object examined in [1] and [2].

The hexagons formed by joining the fragments A and A' will be called the central ring chain (of S or T).

Let $\sigma(B)$ denote the number of aromatic π sextets (in a Clar formula) of a benzenoid graph (or a subgraph of a benzenoid graph) B.

Theorem 1. For any pair of generalized S,T-isomers, $\sigma(S) \geq \sigma(T)$. Furthermore, the strict inequality holds only if $0 < \alpha \leq p+1$, where p is the number of hexagons in the central ring chain of S and $\alpha = v_1 - v_2$ where v_1 is the number of the vertices in A which have the same color as a_0 , and v_2 is the number of the other vertices in A.

Proof. Let S and T be an arbitrary pair of the above described isomers. Let λ denote one of the generalized Clar formulas of T. Assume that in λ there are m sextets located in the central ring chain ($m \geq 0$). Let, in addition, the number of double bonds in P is n ($n \geq 0$). This is illustrated in Fig. 2.

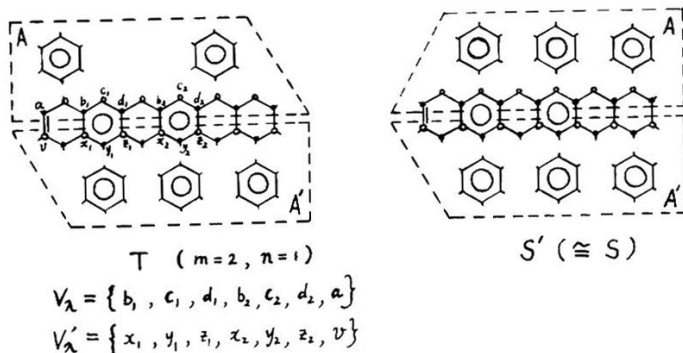


Fig. 2

Denote the vertex set of these sextets and double bonds by

\bar{W}_λ , and denote the vertex set of A (resp. A') by U (resp. U').

$$\text{Let } V_\lambda = \bar{W}_\lambda \cap U, \quad V'_\lambda = \bar{W}_\lambda \cap U',$$

then $\sigma(T) = \max_{\lambda} \{ \sigma(A-V_\lambda) + \sigma(A'-V'_\lambda) + m \}$ where λ runs over all the generalized Clar formulas of T.

Obviously, there must be a certain generalized Clar formula λ , such that

$$\sigma(T) = \sigma(A-V_\lambda) + \sigma(A'-V'_\lambda) + m.$$

We will distinguish two cases: either

$$\sigma(A-V_\lambda) < \sigma(A'-V'_\lambda) \quad \text{or} \quad \sigma(A-V_\lambda) \geq \sigma(A'-V'_\lambda).$$

Case 1. Let $\sigma(A-V_\lambda) < \sigma(A'-V'_\lambda)$. Then we construct a Clar formula μ of S' as follows (see Fig. 2).

- (a) The m sextets in the central ring chain and the n double bonds in P are identical with those in λ of T;
- (b) The sextets and double bonds of μ which belong to $A'-V'_\mu$ are identical with those of λ which belong to $A'-V'_\lambda$;
- (c) The sextets and double bonds of μ which belong to $A-V_\mu$ are 1-axially symmetric with that of μ which belong to $A'-V'_\mu$.

Notice that S is isomorphic to S'. Therefore we have

$$\sigma(S) = \sigma(S') \geq \sigma(A-V_\mu) + \sigma(A'-V'_\mu) + m = 2 \sigma(A'-V'_\mu) + m > \sigma(T).$$

Case 2. If $\sigma(A-V_\lambda) \geq \sigma(A'-V'_\lambda)$ then we proceed in an analogous manner. It is not difficult to see that

$$\sigma(S) \geq 2 \sigma(A - V_{\mu}) + m \geq \sigma(T).$$

Thus the first part of Theorem 1 has been proved.

We prove now its second part. Since the vertices a_0, a_1, \dots, a_p of A must be of the same color (see Fig. 1), if $\alpha=0$ then all the lines of P must be single bonds in all Clar formulas of S . It follows that

$$\sigma(S) = \sigma(S-P) = 2 \sigma(A).$$

Similarly,, $\sigma(T) = \sigma(T-P) = 2 \sigma(A)$, hence $\sigma(S) = \sigma(T)$.

If $\alpha > 0$, notice that from the definition of generalized Clar formulas any formula can correspond to at least one Kekulé structure. Furthermore in the Kekulé structure corresponding to any Clar formula of S or T there must be α vertices of $\{a_0, a_1, \dots, a_p\}$ joined by double bonds to the vertices of A' , we see immediately that no formula exists in S or T when $\alpha > p+1$.

This completes our proof.

In the following we shall consider the number of Kekulé structures. Recall that a Kekulé structure coincides with what in graph theory is known under the name "perfect matching". It is obvious that perfect matchings can exist only if the numbers of two kinds of colored vertices in the colored graph are equal. This simple fact will be useful in the proof of the next theorem. The number of Kekulé structures of a graph B will be denoted by $K(B)$.

Theorem 2. For any pair of generalized S,T-isomers, $K(S) \geq K(T)$.

Proof. Let M be an arbitrary matching of P. Let $K_M(S)$ be the number of all perfect matchings of S which are extended from M. $K_M(T)$ is defined similarly. It is easy to see that $K(S) = \sum_M K_M(S)$, where M runs over all possible matchings of P. (Note that the empty set is also regarded as a matching.)

Let V_M (resp. V'_M) denote the vertices of A (resp. A') which are vertices of lines of M. Then $K_M(S) = K(A-V_M) \cdot K(A'-V'_M) = K(A-V_M)^2$ hence $K(S) = \sum_M K(A-V_M)^2$. Similarly, we can define U_M, U'_M for T.

$$K(T) = \sum_M K(A-U_M) \cdot K(A'-U'_M)$$

Notice that the matchings (M) of P can be divided into two classes satisfying one of the following two conditions respectively.

- (1) $A-U_M$ is isomorphic to $A'-U'_M$;
- (2) $A-U_M$ is not isomorphic to $A'-U'_M$.

Any matching M of the first class contributes by $K(A-V_M)^2$ to $K(S)$ and by $K(A-U_M)^2$ to $K(T)$.

Since $A-V_M$ and $A-U_M$ are isomorphic, we immediately see that M has equal contributions to both $K(S)$ and $K(T)$. For any matching M of the second class, there is just one matching M' of the same class such that $A-U_M$ is isomorphic to $A'-U'_M$. Hence the matchings of the second class can be divided into some pairs. Any pair (M, M') contributes by $K(A-V_M)^2 + K(A-V_{M'})^2$ to $K(S)$, and by

$K(A-U_M) \cdot K(A'-U_M') + K(A-U_{M'}) \cdot K(A'-U_{M'})$ to $K(T)$. Since $V_M = U_M$, $V_M' = U_M'$, and M satisfies the condition (2), we have

$$\begin{aligned} & K(A-U_M) \cdot K(A'-U_M') + K(A-U_{M'}) \cdot K(A'-U_{M'}) \\ = & K(A-U_M) \cdot K(A-U_{M'}) + K(A-U_{M'}) \cdot K(A-U_M) \\ = & 2K(A-U_M) \cdot K(A-U_{M'}) \\ = & 2K(A-V_M) \cdot K(A-V_{M'}) \leq K(A-V_M)^2 + K(A-V_{M'})^2. \end{aligned}$$

Therefore, taking the sum of all these contributions (when M runs over all possible matchings of P) it follows that $K(S) \geq K(T)$.

This completes the proof.

Remark 1. In the proof of Theorem 2 we have not used the fact that S and T are benzenoid systems. Hence Theorem 2 holds for all (both benzenoid and non-benzenoid) S, T -isomers.

Remark 2. We wish to point at a minor error in [1]. Proposition 1 of [1] says that "if the S, T -isomers belong to class C_1 and n_A is even, then $\sigma(S) = \sigma(T) = 2\sigma(A)$ ". S, T -isomers of class C_1 are obtained by joining fragments of type A_1 (see Fig. 3) and n_A is the number of vertices of the fragment A .

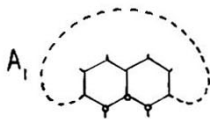


Fig. 3

Proposition 1 is not correct. In fact, the following case exists:

$\sigma(A) = 0$, but $\sigma(S) = \sigma(T) \neq 0$.

An example of this kind is given in Fig. 4.

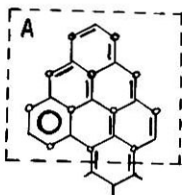


Fig. 4

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