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SOME TOPOLOGICAL PROPERTIES OF ISOMERIC BENZENOID HYDROCARBONS

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Abstract

In the present paper benzenoid *S* and *T* isomers are examined and some of their topological properties established. The previous observation that a *T* isomer does not have more aromatic π sextets than its *S* isomer is demonstrated to be generally valid. It has also been shown that the number of Kekulé structures of a *T* isomer never exceeds that of an *S* isomer.

INTRODUCTION

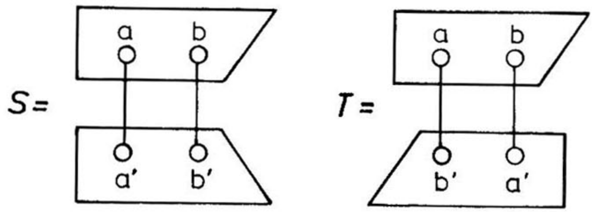
Recently the concept of *S*,*T* isomers was introduced [1]. It has been demonstrated [1,2] that some very interesting regularities, termed "topological effect on MO energies" (TEMO), exist in the electronic structure of these isomers. TEMO was further elaborated and analysed in a series of publications [2].

In the case when the S,T isomers were benzenoid, the authors of [1] 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". The chemical consequences of this finding were also discussed in ref. [1]. In the present paper we continue examinations along these lines and conclude that the above hypothesis is true. We shall derive precise conditions under which the S,T isomers have equal (respectively unequal) number of π sextets. We shall also offer some related results concerning the number of Kekulé structures of the S,T isomers.

The symbolism and terminology used in this paper is fully identical with the S,T formalism introduced in ref. [1]. Details on the topological theory of benzenoid hydrocarbons as well as an exhaustive bibliography can be found in the review [3].

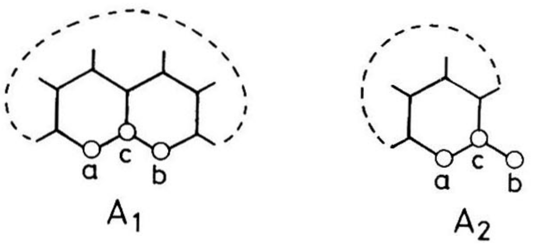
Let A be an arbitrary conjugated fragment and a and b two of its centers (of residual valency) [1]. Let A' be fully identical with A, except that the above mentioned centers are now labelled by a' and b'.

The two conjugated systems S and T, obtained by joining a and b with a' and b' in two different ways, represent two distinct isomers whenever a and b are inequivalent.



The number of carbon atoms in the conjugated fragment A is denoted by n_A. Consequently, both S and T consist of $2n_A$ carbon atoms.

From the above construction one immediately concluds that S and T will be benzenoid hydrocarbons only if the fragment A has one of the following structures: A_1 or A_2.



The dashed line in A_1 and A_2 symbolizes a benzenoid system (i.e. a system being composed exclusively of condensed hexagons [3]).

The isomeric pairs obtained by joining fragments of type A_1 will be said to belong to class C_1 of (benzenoid) S,T isomers;

those pairs which are obtained from fragments of type A_2 belong to class C_2. In Figs. 1 and 2 examples are given of S,T isomers from C_1 and C_2, respectively.

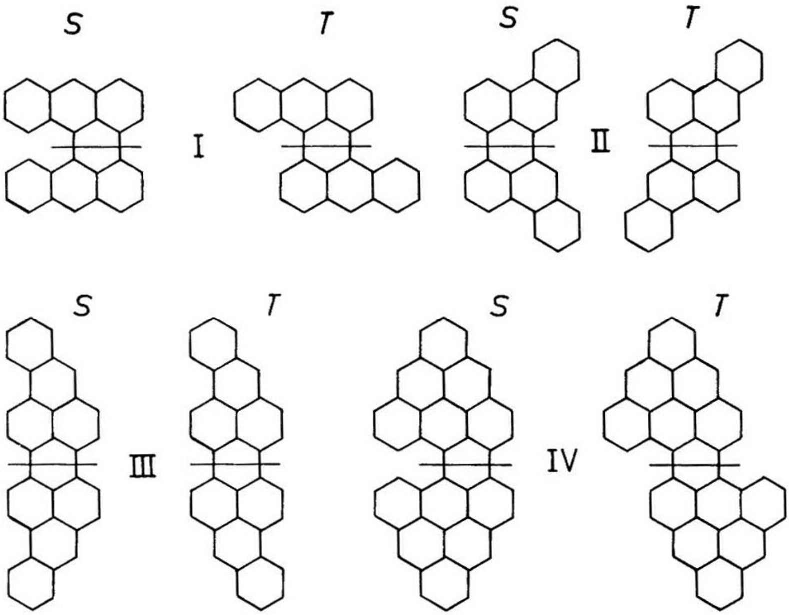


Fig. 1. Pairs of benzenoid isomers belonging to class C_1

Any fragment of the type A_1 is a benzenoid system itself. The fragments of the type A_2 are, however, not pure benzenoid, since they possess a pendent vertex, namely b. By deletion of this vertex one obtains a benzenoid system. Hence A_2-b is

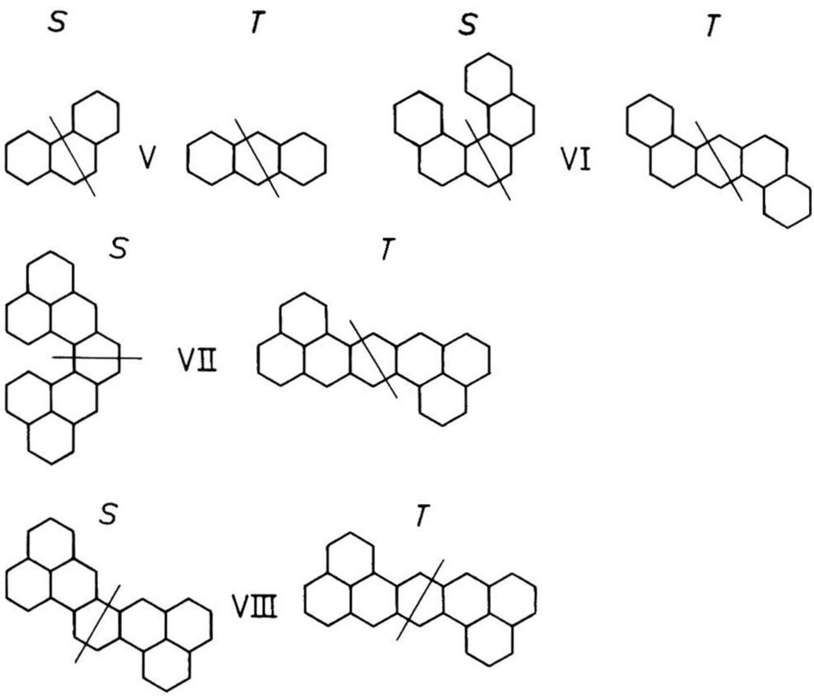


Fig. 2. Pairs of benzenoid isomers belonging to class C_2

benzenoid. In both A_1 and A_2 the distance between the vertices a and b is two. The unique vertex lying between a and b will be labelled by c. The hexagon of A_2 (and also of A_2-b), containing the vertex a will be denoted by H_a.

The hexagon formed by joining the fragments A and A' will be called the central ring (of S or T). Hence the central ring of S consists of the vertices $\underline{a},\underline{c},\underline{b},\underline{b}',\underline{c}',\underline{a}'$ (in that order); the central ring of T embraces the vertices $\underline{a},\underline{c},\underline{b},\underline{a}',\underline{c}',\underline{b}'$ (in that order).

Note finally that the number of vertices of A (denoted by n_A) may be either even (e.g. I,II,IV,VII,VIII) or odd (e.g. III,V,VI). Hydrocarbons from class C_1 must be peri-condensed, whereas hydrocarbons from the class C_2 need not (e.g. V,VI).

BENZENOID S,T ISOMERS AND THEIR AROMATIC SEXTETS

In this section we determine the relations between the number of aromatic π sextets of the isomers S and T. Let $\sigma(B)$ denote the number of aromatic π sextets (in a Clar formula) of a benzenoid molecule B.

PROPOSITION 1. If the S,T isomers belong to class C_1 and n_A is even, then

$$\sigma(S) = \sigma(T) = 2\sigma(A). \quad (1)$$

PROOF of this proposition is elementary. Namely, the central ring of both S and T is empty (in the sense of Clar's theory [4]) and therefore both S and T can be considered as being composed of two independent and non-interacting parts A and A'. Hence $\sigma(S) = \sigma(T) = \sigma(A) + \sigma(A')$ and, of course, $\sigma(A) = \sigma(A')$.

PROPOSITION 2. If the S,T isomers belong to class C_1 and n_A is odd, then

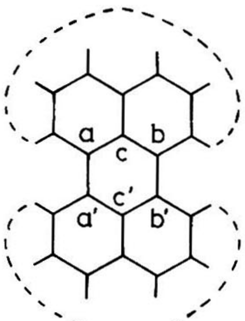
$$\sigma(S) = \max\{2\sigma(A-\underline{a}-\underline{b}-\underline{c})+1\ ,\quad 2\sigma(A-\underline{a}),2\sigma(A-\underline{b})\} \qquad (2)$$

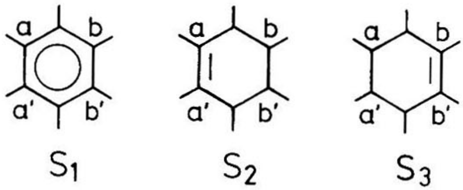
$$\sigma(T) = \max\{2\sigma(A-\underline{a}-\underline{b}-\underline{c})+1\ ,\quad \sigma(A-\underline{a})+\sigma(A-\underline{b})\}. \qquad (3)$$

Consequently, either $\sigma(S) = \sigma(T)$ or

$$\sigma(S)-\sigma(T) = |\sigma(A-\underline{a})-\sigma(A-\underline{b})|. \qquad (4)$$

PROOF. Consider an S isomer from the class C_1. Consider one of its Clar π sextet formulas. In this formula there is either a sextet in the central ring (case S_1) or a double bond between $\underline{a}$ and $\underline{a}'$ and a single bond between $\underline{b}$ and $\underline{b}'$ (case S_2) or a single bond between $\underline{a}$ and $\underline{a}'$ and a double bond between $\underline{b}$ and $\underline{b}'$ (case S_3). The number of π sextets of S is then





in the case S_1: $1 + \sigma(S-\underline{a}-\underline{c}-\underline{b}-\underline{b}'-\underline{c}'-\underline{a}')$

in the case S_2: $\sigma(S-\underline{a}-\underline{a}')$

in the case S_3: $\sigma(S-\underline{b}-\underline{b}')$.

Clearly,

$$\sigma(S\text{-}\underline{a}\text{-}\underline{c}\text{-}\underline{b}\text{-}\underline{b}'\text{-}\underline{c}'\text{-}\underline{a}') = \sigma(A\text{-}\underline{a}\text{-}\underline{b}\text{-}\underline{c}) + \sigma(\underline{A}'\text{-}\underline{a}'\text{-}\underline{b}'\text{-}\underline{c}') = $$

$$= 2\sigma(A\text{-}\underline{a}\text{-}\underline{b}\text{-}\underline{c}) \qquad (5)$$

$$\sigma(S\text{-}\underline{a}\text{-}\underline{a}') = \sigma(A\text{-}\underline{a}) + \sigma(A\text{-}\underline{a}') = 2\sigma(A\text{-}\underline{a}) \qquad (6)$$

$$\sigma(S\text{-}\underline{b}\text{-}\underline{b}') = \sigma(A\text{-}\underline{b}) + \sigma(A\text{-}\underline{b}') = 2\sigma(A\text{-}\underline{b}). \qquad (7)$$

Relation (2) follows.

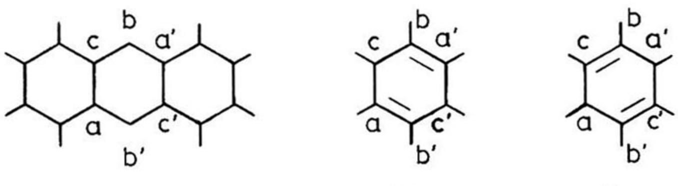
The relation (3) can be deduced in a completely analogous manner. This completes the proof. In addition we mention that it can be verified that the right-hand side of eq. (4) is either zero or unity.

It remains now to examine the S,T isomers of the class C_2.

PROPOSITION 3. If the S,T isomers belong to class C_2 and n_A is even, then

$$\sigma(S) = \sigma(T) = 2\max\{\sigma(A\text{-}\underline{a}\text{-}\underline{b}), \sigma(A\text{-}\underline{b}\text{-}\underline{c})\}. \qquad (8)$$

PROOF. Consider a T isomer from the class C_2. Consider one of its Clar π sextet formulas. Since n_A is assumed to be even, there cannot be a π sextet in the central ring of T. The double bonds in the Clar formula considered are arranged either in



T $\quad$ S_1 $\quad$ S_2

mode S_1 or in mode S_2. The number of π sextets of T is then

in the case S_1: $\sigma(T-\underline{a}-\underline{b}-\underline{a}'-\underline{b}')$

in the case S_2: $\sigma(T-\underline{b}-\underline{c}-\underline{b}'-\underline{c}')$

From the obvious identities

$$\sigma(T-\underline{a}-\underline{b}-\underline{a}'-\underline{b}') = 2\sigma(A-\underline{a}-\underline{b}) \tag{9}$$

$$\sigma(T-\underline{b}-\underline{c}-\underline{b}'-\underline{c}') = 2\sigma(A-\underline{b}-\underline{c}) \tag{10}$$

we immediately gain (8) for the isomer T.

In a fully analogous manner one can verify eq. (8) also for the S isomer.

The following proposition may be proved using an equivalent way of reasoning.

<u>PROPOSITION 4</u>. If the S,T isomers belong to class C_2 and n_A is odd, then

$$\sigma(S) = \max\{2\sigma(A-\underline{a}-\underline{b}-\underline{c})+1,\ 2\sigma(A-\underline{b})\} \tag{11}$$

$$\sigma(T) = \max\{2\sigma(A-\underline{a}-\underline{b}-\underline{c})+1,\ \sigma(A-\underline{a}-\underline{b}-\underline{c})+\sigma(A-\underline{b})\} \tag{12}$$

It can be also demonstrated that either

$\sigma(A-\underline{a}-\underline{b}-\underline{c}) = \sigma(A-\underline{b})$ or $\sigma(A-\underline{a}-\underline{b}-\underline{c}) = \sigma(A-\underline{b})-1$.

In the former case, of course, S and T have equal number of π sextets. In the latter case,

$$\sigma(S) = \sigma(T) + 1 \tag{13}$$

The case (13) occurs only when the benzenoid system $A_2-\underline{b}$ possesses a fixed π sextet in its hexagon H_a (see before).

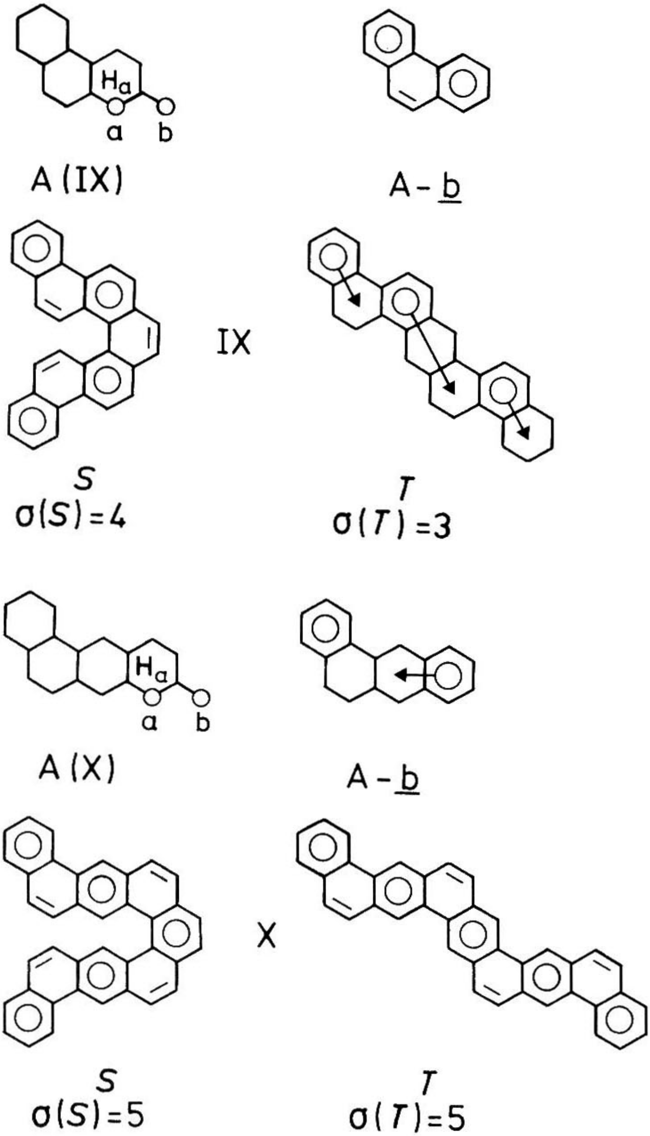


Fig. 3. Illustrations of eq. (13)

Let us illustrate the above statement by two examples depicted on Fig. 3. In the example IX, A_2-$\underline{b}$ possesses a fixed π sextet in the hexagon H_a and consequently the number of π sextets in S exceeds that of T. In the example X, a π sextet is not necessarily located in H_a and S and T have equal number of π sextets.

We should like to conclude this section by summarizing the Propositions 1-4.

<u>THEOREM</u>. If S and T are benzenoid hydrocarbons, then the number of π sextets in the isomer S is equal to, or greater by one than the number of π sextets in the isomer T. The number of π sextets in S exceed that of T only if the isomers S and T have 4k+2 carbon atoms (k = integer).

The conditions under which $\sigma(S)$ is greater than $\sigma(T)$ as well as the dependence of $\sigma(S)$ and $\sigma(T)$ on the structure of the fragment A are specified in Propositions 1-4.

ON THE NUMBER OF KEKULÉ STRUCTURES OF BENZENOID S,T ISOMERS

It has been shown [1] that for arbitrary S,T isomers

$$\mu(T)-\mu(S) = [\mu(A-\underline{a})-\mu(A-\underline{b})]^2 \qquad (14)$$

where $\mu(G) = \mu(G,x,t)$ denotes the μ-polynomial [5] of the graph G. Choosing $t = 1$ and $t = 0$ we obtain the following two special cases of (14) [5]:

$$\phi(T)-\phi(S) = [\phi(A-\underline{a})-\phi(A-\underline{b})]^2 \qquad (15)$$

$$\alpha(T)-\alpha(S) = [\alpha(A-\underline{a})-\alpha(A-\underline{b})]^2 \qquad (16)$$

where $\phi(G) = \phi(G,x)$ and $\alpha(G) = \alpha(G,x)$ are the characteristic and the matching polynomial, respectively, of the graph G.

It is well known [6] that for the molecular graphs of benzenoid hydrocarbons (and also for their subgraphs [7]) the following relations are valid:

$$\phi(B,0) = (-1)^{n/2}K(B)^2 \tag{17}$$

$$\alpha(B,0) = (-1)^{n/2}K(B). \tag{18}$$

Here B symbolizes a benzenoid graph with n vertices and K(B) is the number of Kekulé structures of the corresponding hydrocarbon.

Setting x = 0 in eqs. (15) and (16) and applying (17) and (18) we arrive to the identities

$$K(T)^2-K(S)^2 = (-1)^{n_A}[K(A-\underline{a})^2-K(A-\underline{b})^2]^2 \tag{19}$$

$$K(T)-K(S) = (-1)^{n_A}[K(A-\underline{a})-K(A-\underline{b})]^2. \tag{20}$$

PROPOSITION 5. If the S,T isomers are benzenoid and n_A is even, then

$$K(S) = K(T) = K(A)^2 + K(A-\underline{a}-\underline{b})^2. \tag{21}$$

PROOF. The left-hand equality in (21) follows immediately from either (19) or (20) if one has in mind that for n_A being even, $A-\underline{a}$ and $A-\underline{b}$ possess odd number of vertices and thus cannot have Kekulé structures.

The right-hand equality in (21) is a consequence of the fact that in the Kekulé structural formulas of S and T, the two bonds connecting A with A' are either both double or both single.

PROPOSITION 6. If the S,T isomers are benzenoid and n_A is odd, then

$$K(S) = K(A-\underline{a})^2 + K(A-\underline{b})^2 \quad (22)$$

$$K(T) = 2K(A-\underline{a})K(A-\underline{b}). \quad (23)$$

Therefore, $K(S)$ is not smaller than $K(T)$. Furthermore, $K(S)$ is greater than $K(T)$ if and only if $K(A-\underline{a}) \neq K(A-\underline{b})$.

PROOF. Eqs. (22) and (23) follow from (19) and (20) by simple algebraic transformations.

One can also demonstrate that if n_A is odd, then the difference between $K(S)$ and $K(T)$ can be arbitrarily large.

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