

ISOMERIZATION OF ALTERNANT HYDROCARBONS

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Abstract

Within the framework of the Hückel molecular orbital theory four theorems are deduced, related to the isomerization of alternant hydrocarbons.

1. Introduction

Isomerism is an interesting subject of chemistry. From the point of view of organic chemistry, the isomeric substances are classified into different categories, such as geometrical, structural, positional, optical, topological and even rotational isomers [1]. The topological investigations of isomeric structures allow one to speak of topomers, namely of isomeric structures possessing different constitutions, but having isomorphic topological subspaces [2]. The pronounced differences in the chemical properties of isomers obviously arise from various realizations of a given topology. Indeed, the topological effect on molecular orbitals [3] (TEMO) provides solid evidence that topology plays a very important role. Topomers have attracted the attention of various investigators [4-13]. In what follows, isomeric alternant hydrocarbons are studied in terms of molecular orbital energies.

2. Theory

In the present treatment of alternant hydrocarbons, rules governing the structural isomerization are considered, in which the number of atoms and carbon-carbon bonds remain constant throughout the isomerization process.

Suppose A and B are two isomeric even alternant hydrocarbons both having $2n$ carbon atoms and e carbon-carbon bonds. Let $X_1 \geq X_2 \geq \dots \geq X_n > 0$ and $X'_1 \geq X'_2 \geq \dots \geq X'_n > 0$ stand for the occupied molecular orbital energies of A and B, respectively.

Here and later the energies are expressed in the units of the HMO carbon-carbon resonance integral β [2]. Consequently, the numbers X_i and X'_j correspond to the eigenvalues of the molecular graphs of A and B, respectively [2]. It is further assumed that neither A nor B have non-bonding molecular orbitals; this restriction is irrelevant for the subsequent considerations, except in the case of Theorem 4.

According to a well-known relation in graph spectral theory [2],

$$\sum_{i=1}^n (X_i)^2 = \sum_{i=1}^n (X'_i)^2 = e \quad (1)$$

3. The Main Results

Theorem 1.

$$0 < \sum_{i=1}^n X_i X'_i \leq e$$

Proof. Define the vectors C and D in the n -dimensional Euclidean space [14] as $C = (X_1, X_2, \dots, X_n)$ and $D = (X'_1, X'_2, \dots, X'_n)$. The scalar product of these vectors is given by either (2) or (3):

$$C \cdot D = \sum_{i=1}^n X_i X'_i \quad (2)$$

and

$$C \circ D = \left[\sum_{i=1}^n (X_i)^2 \right]^{1/2} \left[\sum_{i=1}^n (X'_i)^2 \right]^{1/2} \cos \phi \quad (3)$$

where ϕ is the angle between the vectors C and D. Bearing in mind relation (1), we transform Eq. (3) into

$$\sum_{i=1}^n X_i X'_i = e \cos \phi \quad (4)$$

The angle ϕ occurring in Eq. (4) will be called the *angle of isomerization* [15]. Note that this angle is zero in the case of identity ($A = B$) or if the molecular graphs of A and B are isospectral [18-20]. The angle of isomerization cannot be equal to $\pi/2$ because both X_i and X'_i are occupied molecular orbitals, and thus $X_i X'_i > 0$. Even if non-bonding MOs are permitted, the former condition will be fulfilled, at least, for $i = 1$. Then, obviously, $\sum_{i=1}^n X_i X'_i > 0$. Since $\cos \phi \leq 1$, Theorem 1 follows. \square

Define the quantities ΔX_i , $i = 1, 2, \dots, n$, via $X'_i = X_i + \Delta X_i$.

Theorem 2.

$$\sum_{i=1}^n \Delta X_i (X_i + X'_i) = 0 \quad .$$

Proof.

$$\begin{aligned} \sum_{i=1}^n \Delta X_i (X_i + X'_i) &= \sum_{i=1}^n (X'_i - X_i)(X_i + X'_i) = \sum_{i=1}^n \left[(X_i)^2 - (X'_i)^2 \right] \\ &= \sum_{i=1}^n (X_i)^2 - \sum_{i=1}^n (X'_i)^2 \quad . \end{aligned}$$

The above is equal to zero because of Eq. (1). \square

Theorem 3.

$$\sum_{i=1}^n (\Delta X_i)^2 < 2e \quad .$$

Proof.

$$\sum_{i=1}^n (\Delta X_1)^2 = \sum_{i=1}^n (X'_1 - X_1)^2 = \sum_{i=1}^n (X_1)^2 + \sum_{i=1}^n (X'_1)^2 - 2 \sum_{i=1}^n X_1 X'_1 .$$

Because of Theorem 1,

$$\sum_{i=1}^n (\Delta X_1)^2 < \sum_{i=1}^n (X_1)^2 + \sum_{i=1}^n (X'_1)^2$$

and now Theorem 3 follows from Eq. (1). \square

Theorem 4. Let the characteristic polynomial of the molecular graph of A be written in the form $x^{2n} + a_1 x^{2n-2} + \dots + a_{n-1} x^2 + a_n$. Then

$$\sum_{i=1}^n (\Delta X_1 / X_1) \leq (e a_{n-1} / a_n)^{1/2} - n .$$

Proof. Since $\Delta X_1 / X_1 = (X'_1 - X_1) / X_1 = (X'_1 / X_1) - 1$,

$$\sum_{i=1}^n (\Delta X_1 / X_1) = \sum_{i=1}^n (X'_1 / X_1) - n . \quad (5)$$

On the other hand, if we introduce the n-dimensional vector E as

$E = (1/X_1, 1/X_2, \dots, 1/X_n)$, then

$$\sum_{i=1}^n (X'_1 / X_1) = \sum_{i=1}^n X'_1 (1/X_1) = D \cdot E = \left[\sum_{i=1}^n (X'_1)^2 \right]^{1/2} \left[\sum_{i=1}^n (1/X_1^2) \right]^{1/2} \cos \beta \quad (6)$$

where β is the angle between D and E. The relation

$$\sum_{i=1}^n (1/X_1^2) = a_{n-1} / a_n \quad (7)$$

was deduced elsewhere [21]. Substituting (6) and (7) back into formula (5),

we readily obtain

$$\sum_{i=1}^n (\Delta X_1 / X_1) = (e a_{n-1} / a_n)^{1/2} \cos \beta - n$$

from which Theorem 4 follows immediately. \square

3. Conclusion

The above theorems, proved here for isomeric even alternant hydrocarbons are also true for odd alternants. The reason for this is obvious: for an odd alternant hydrocarbon with $2n+1$ carbon atoms the $(n+1)$ -th molecular orbital is necessarily non-bonding [2], i.e. $X_{n+1} = 0$. We can simply disregard this energy level and treat the odd system as an even system with $2n$ carbon atoms, whose bonding energy levels are X_1, X_2, \dots, X_n . As already mentioned, if additional non-bonding MOs exist, then one must be cautious in the case of Theorem 4, whereas the validity of the Theorems 1-3 is not affected.

On the other hand, the theorems presented above are true for all sorts of structural isomers of alternant hydrocarbons, irrespective of any difference in their gross or fine topologies.

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